Simultaneous imaging of temperature and concentration of ethanol–water mixtures in microchannel using near-infrared dual-wavelength absorption technique

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2016 Meas. Sci. Technol. 27 115401
(http://iopscience.iop.org/0957-0233/27/11/115401)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 54.191.40.80
This content was downloaded on 31/08/2017 at 06:23

Please note that terms and conditions apply.

You may also be interested in:

MIR-ATR sensor for process monitoring
Daniel Geörg, Robert Schalk, Frank-Jürgen Methner et al.

Two-wavelength Raman imaging for non-intrusive monitoring of transient temperature in microfluidic devices
Reiko Kuriyama and Yohei Sato

Sandwich-format 3D printed microfluidic mixers: a flexible platform for multi-probe analysis
Drew P Kise, Michael J Reddish and R Brian Dyer

Micro-Raman thermometry for the microchannel of PCR chip
Soo Ho Kim, Jermim Noh, Min Ku Jeon et al.

Water vapour concentration near phase boundaries with evaporation
Bernd Schirmer, Adrian Melling and Günter Brenn

Visualization of convective mixing in microchannel by fluorescence imaging
Yohei Sato, Gentaro Irisawa, Masanori Ishizuka et al.

Understanding the mixing process in 3D microfluidic nozzle/diffuser systems: simulations and experiments
Abdeljalil Sayah and Martin A M Gijs

A calibrated dual-wavelength IR thermometry approach with non-greybody compensation
A Hijazi, S Sachidanandan, R Singh et al.

Techniques for nonlinear optical characterization of materials: a review
Cid B de Araújo, Anderson S L Gomes and Georges Boudebs
Simultaneous imaging of temperature and concentration of ethanol–water mixtures in microchannel using near-infrared dual-wavelength absorption technique

Naoto Kakuta1, Hiroki Yamashita1, Daisuke Kawashima1, Katsuya Kondo2, Hidenobu Arimoto3 and Yukio Yamada4

1 Department of Mechanical Engineering, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan
2 Department of Electrical and Electronic Engineering, Tottori University, 4-101 Koyama-Minami, Tottori 680-8552, Japan
3 Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, AIST Central 5, Tsukuba, Ibaraki 305-8565, Japan
4 Brain Science Inspired Life Support Research Center, The University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

E-mail: kakuta-n@tmu.ac.jp

Received 11 March 2016, revised 7 August 2016
Accepted for publication 19 August 2016
Published 23 September 2016

Abstract
This paper presents a simultaneous imaging method of temperature and ethanol concentration of ethanol–water mixtures in microfluidic channels. The principle is based on the facts that the absorbance at a wavelength of 1905 nm is dependent on the temperature of water and that the absorbance at 1935 nm is independent of the temperature but strongly dependent on the molar concentration of water, which is reciprocal to the molar concentration of ethanol in the mixture. The absorbance images at the two wavelengths were acquired alternately, each at 50 frames per second, by an alternate irradiation system and near-infrared (NIR) camera, and then converted to the temperature and concentration images by a linear regression model. The imaging method was applied to a dilute ethanol–water mixture with an ethanol concentration of 0.43 M and water flowing side by side in a temperature-controlled Y-channel. The concentration images clearly showed differences between the mixture and water streams, and that the transverse concentration gradient between the two streams decreased downstream by mutual diffusion. It was also confirmed that the mutual diffusion coefficient increased as the temperature increased. The temperature images showed that uniform distributions were immediately formed due to heat transfer between the fluid and channel materials.

Keywords: simultaneous imaging, water, ethanol, near-infrared absorption, temperature, concentration, microfluidic channel

(Some figures may appear in colour only in the online journal)

1. Introduction
Quantitative understanding of mass transfer and chemical reactions occurring between different fluids is a very important topic for fundamental chemical physics and applied microtechnology such as lab-on-a-chip synthesis [1–3] and fuel cells [4, 5]. In these researches, microfluidic devices are effectively used because they can produce the observable interfaces between two liquid fluids, where mass transfer and chemical reactions take place intensely. To analyze the
diffusion and reaction processes at the interfaces, one needs to measure the concentrations of target molecules/ions. Various optical techniques using fluorescence, infrared and Raman spectroscopy have thus been extensively studied [6–10]. As well as concentration, temperature also plays an important role because the diffusivity and reaction rate are dependent on temperature and because the temperature gradient is a driving force for mass transfer by Marangoni effect and Soret effect [11]. Temperature monitoring is useful for analyzing exo/endothermic reactions [12–14], and, in some microfluidic applications, e.g. on-chip polymerase chain reaction, local temperature control is needed for each process in the chip [15, 16]. It is thus necessary and useful for many microfluidic applications to measure not only concentration but also temperature simultaneously.

To achieve the simultaneous measurement of temperature and concentration by an optical technique, at least two different wavelengths need to be used, i.e. one for temperature and the other for concentration. Fluorescence-based techniques often employ ratiometric measurement using relative intensity between two wavelengths from single kind of fluorescent molecules; however, the image constructed from the relative intensity is of either concentration [6, 8, 17] or temperature [18–24]. Raman imaging [9], a developing label-free imaging technique, has also never been used for the simultaneous measurement. Regarding mid-infrared (MIR) imaging, a method combining wavelength-scanning imaging and MIR thermography was proposed recently [25, 26]. MIR thermography is a convenient and high-speed imaging technique, but, in the case of microfluidic chips, it is almost impossible to selectively detect MIR thermal radiation from liquids inside the chips because MIR thermal radiation from the outer surface of chip materials is dominant.

This study uses a near-infrared (NIR) absorption imaging technique for the simultaneous imaging. NIR absorption spectroscopy/imaging has been widely used in chemistry, food science, and biomedicine [27–29] because of its practical advantages: label-free, convenience, safety, and low cost. In addition, since glass, polydimethylsiloxane (PDMS) and silicon, of which microfluidic chips are made, are almost transparent to radiation in the NIR region, the absorption information of liquid in the channel can be selectively obtained. Nevertheless, NIR-based methods may be recognized to be less useful for concentration imaging in microfluidic applications because of the following two reasons. First, NIR absorption bands are so broad, compared to MIR and Raman bands, that it is hard to identify and quantify target molecules. Second, in the case of aqueous solutions, the absorption bands of water are so strong that they obscure the absorption bands of solute molecules. In particular, the $\nu_2 + \nu_3$ absorption band of water at around a wavelength of 1935 nm ($\sim$5168 cm$^{-1}$), which is the strongest among the absorption bands of water from 800 nm to 2200 nm, has been often excluded in spectral measurements. Here, $\nu_2 + \nu_3$ represents the combination of the bending vibrational mode ($\nu_2$) and the antisymmetric OH stretching vibrational modes ($\nu_3$) of water molecules [27, 30–34]. From the other point of view, however, this strong absorption means that the $\nu_2 + \nu_3$ band of water is highly sensitive to a variation in the mole fraction of water, and that a variation in the mole fraction of solute, which is reciprocal to that of water, can be measured more precisely than by using any absorption band of the solute itself. Another interesting (or unfavorable for some cases) feature of the $\nu_2 + \nu_3$ band of water is that it is isotropic with the temperature [27, 31–34]. In this variation, two characteristic wavelengths are found. One is 1905 nm, which is the most sensitive to the temperature in the band. The wavelength of 1905 nm was indeed used for the temperature imaging of water flowing through a microfluidic channel in our previous work [31]. The other is 1935 nm, which is independent of temperature, called isosbestic point [32–34]. This study thus utilizes the different characteristics in absorption between the two wavelengths, i.e. the absorbance at 1905 nm is sensitive to both concentration and temperature while the absorbance at 1935 nm is sensitive to concentration only.

To acquire the absorbance images at 1905 nm and 1935 nm, we developed an imaging system consisting of two narrow bandpass filters (NBPFs) for wavelength selection, a rotating optical chopper disk for alternate irradiation of the two wavelengths, and an NIR camera. The absorbance images were converted to the temperature and concentration images by a linear model which was derived in this study. In this paper, the temperature and concentration images of a dilute ethanol–water mixture and water flowing side by side in a Y-shaped microchannel are shown and discussed. Alcohol–water mixtures have been of great interest because they are widely used in biochemistry, medicine, and food science, and because their hydration structure and thermodynamic properties vary anomallyistically [35–42]. Fluorescence-based techniques [8, 17], third harmonic microscopy [43], coherent anti-Stokes Raman scattering microscopy [44], surface plasmon resonance reflectance imaging [45], and terahertz time-domain spectroscopy [46] have been used to measure/image alcohol concentrations in water. However, none of these techniques has been applied to simultaneous imaging of temperature and concentration, as mentioned above. Also, the minimum concentration measurable by these techniques was more than a few tens of mol%. On the other hand, this study used a dilute mixture with an ethanol concentration of 0.79 mol%, 0.43 M (mol l$^{-1}$), to demonstrate the high sensitivity of the proposed method.

In the following section 2, the theory of simultaneous measurement of concentration and temperature is explained. Then in section 3, the experimental setup and procedure are described. In section 4, the results are shown and discussion is made. In particular, variations in the ethanol concentration by diffusion and the temperature dependence of the diffusion coefficient are discussed. Finally in section 5, the conclusions are drawn.

2. Theory

2.1. NIR absorption spectra of ethanol–water mixtures

Figure 1(a) shows the absorption spectra of water at four temperatures of 16.0, 24.0, 32.0 and 40.0 °C. The arrows indicate the direction of temperature increase. The inset shows the
Temperature is 16.0 °C. The optical path length is 0.094 mm. The arrows indicate the direction of temperature increase.

Absorbance spectra of water at 16.0, 24.0, 32.0 and 40.0 °C. Here, the absorbance, $A$, is defined as $A = -\log_{10}(I/I_0)$, where $I_0$ and $I$ are the intensities of the incident and transmitted light, respectively. The absorbance difference, $\Delta A$, is calculated by $\Delta A = A - A_i = -\log_{10}(I/I_0)$, where the subscript $r$ represents the reference. The spectra were acquired by a Fourier transform infrared spectrometer (IRPrestige-21, Shimadzu, Japan) with a Peltier temperature control unit (110-6015, PIKE Technology, USA). In figures 1(a) and (b), the optical path length of the liquid in a quartz cell was 0.094 mm, which was determined from the interference pattern in the spectra. For ethanol in figure 1(c), a quartz cell with a nominal optical path length of 1.0 mm was used. For making the mixtures, 99.5% grade liquid ethanol (Amakasu Chemical Industries, Japan) was used. The intensity of the light transmitted through the empty quartz cell was taken as $I_0$ so that the spectra of $A$ included no absorbance of quartz glass.

In figures 1(a) and (b), two distinct absorption bands of water are seen: the $\nu_1 + \nu_3$ band at $\lambda \sim 1440$ nm and the $\nu_2 + \nu_3$ band at $\lambda \sim 1935$ nm, where $\nu_1$ represents the symmetric OH stretching mode, $\nu_2$ the bending mode, and $\nu_3$ the antisymmetric OH stretching mode of water molecules, and $\lambda$ is the wavelength [27, 30]. In figure 1(c), three major absorption bands of ethanol are seen in the wavelength ranges of 1400–1650 nm, 1670–1800 nm, and 2000–2150 nm, corresponding mainly to the first overtone of OH stretching mode, the first overtone of CH stretching mode, and the combination of CH stretching and COH bending modes of ethanol molecules, respectively [30, 47]. It is noted that, between 1900 nm and 2000 nm, where the $\nu_2 + \nu_3$ band of water exists, there is no significant band of ethanol. At $\lambda = 1935$ nm, the peak wavelength of the $\nu_2 + \nu_3$ band, $A$ of water is about fifty times as large as $A$ of ethanol. It can thus be assumed that $A$ of the mixtures at 1935 nm depend only on the weight fraction of water. At the same time, however, since the fraction of ethanol is reciprocal to that of water, $A$ at 1935 nm can be used for measuring a variation in the fraction of ethanol.

The spectrum of the $\nu_2 + \nu_3$ band varies with the temperature, as shown in figure 1(a). This temperature dependence is explained in terms of the state of hydrogen bonds (H-bonds) between water molecules [27, 32–34]. In the spectra of $\Delta A$, the most temperature-sensitive wavelength at 1905 nm and the temperature-independent wavelength at 1935 nm are seen. The latter is often called isosbestic point (but it moves slightly with temperature [33, 34]).

For the simultaneous measurement of temperature and concentration, this study used the differences in the absorption characteristics between $\lambda = 1905$ nm and 1935 nm, i.e. $A$ at 1905 nm is sensitive to both concentration and temperature, but $A$ at 1935 nm is sensitive to concentration only. Also, this principle can be easily applied to other aqueous solutions such as alcohols, ketones, and aldehydes because they have similar absorption characteristics at 1905 nm and 1935 nm to ethanol [30]. Hereafter, the wavelengths of 1905 nm and 1935 nm will be represented by $\lambda_1$ and $\lambda_2$, respectively, and variables with subscripts 1 and 2 will represent those at $\lambda_1$ and $\lambda_2$, respectively.
2.2. Absorbance as a function of temperature and concentration

The absorbance, $A$, of an ethanol–water mixture is given by

$$A(\lambda, T, c_e) = \mu(\lambda, T, c_e) l \cdot \log_{10} e,$$  

(1)

$$\mu(\lambda, T, c_e) = \varepsilon_w(\lambda, T, c_e) c_w + \varepsilon_E(\lambda, T, c_e) c_E,$$  

(2)

where $\lambda$ is wavelength in nm, $T$ is temperature in K or °C, $\mu$ is the absorption coefficient in $\text{mm}^{-1}$, $\varepsilon$ is the partial molar absorptivity (or extinction coefficient) in $\text{mm}^{-1} \cdot \text{M}^{-1}$, $c$ is the molar concentration in M, $l$ is the light path length in mm, and the subscripts $w$ and $e$ represent water and ethanol, respectively. Since the structures of inter-association and self-association of ethanol and water molecules depend on $c_e$, with influencing their intramolecular vibration [35–40], $\varepsilon_w$ and $\varepsilon_E$ are the functions of $c_e$. For such non-ideal mixtures, the excess absorption is often introduced [48–51], and equation (2) is rewritten as

$$\mu = (\varepsilon_w^o + \varepsilon_E^o) c_w + (\varepsilon_w^e + \varepsilon_E^e) c_E,$$  

(3)

where the superscripts $o$ and $E$ represent the pure substance and the excess absorption, respectively. Here, the dependencies of $\varepsilon_w$ and $\varepsilon_E$ on $\lambda$, $T$, and $c_e$ are omitted for simplicity, but note that $\varepsilon_w^o$ and $\varepsilon_E^o$ are the intrinsic properties being dependent on $T$ but independent of $c_e$. Moreover, by defining the total excess molar absorptivity, $\varepsilon^E = (\varepsilon_E^E c_w/c_E + \varepsilon_w^E)$, $\mu$ is given by

$$\mu = \varepsilon_w^o c_w + \varepsilon_E^o c_E + \varepsilon_w^e c_w + \varepsilon_E^e c_E.$$  

(4)

When $T$ and $c_e$ change infinitesimally, the total differential of $\mu$ is defined as

$$d\mu = \left( \frac{\partial \mu}{\partial T} \right)_{c_e} dT + \left( \frac{\partial \mu}{\partial c_e} \right)_T dc_e.$$  

(5)

By using equation (4), the coefficient of $dT$ in equation (5) is given by

$$\left( \frac{\partial \mu}{\partial T} \right)_{c_e} = \left( \frac{\partial \varepsilon_w^o}{\partial T} \right) c_w + \left( \frac{\partial \varepsilon_E^o}{\partial T} \right) c_E + \left( \frac{\partial \varepsilon_w^e}{\partial T} \right) c_w + \left( \frac{\partial \varepsilon_E^e}{\partial T} \right) c_E.$$  

(6)

It can be assumed that $|\partial \varepsilon_w^o/\partial T| \ll |\partial \varepsilon_w^e/\partial T|$ and $|\partial \varepsilon_E^o/\partial T| \ll |\partial \varepsilon_E^e/\partial T|$ at $\lambda_1$ and $\lambda_2$, from the arguments in the previous subsection. Hence, the first term on the right hand side of equation (6) is dominant over other two terms as long as $c_w$ is not so small. At $\lambda_1$, since $\partial \varepsilon_w^o/\partial T$ is fairly constant around room temperature [31, 33, 34], $\partial \varepsilon_w^o/\partial T$ is assumed to be proportional to $c_w$. In the simultaneous measurement, $\partial \mu/\partial T$ should thus be updated according to $c_w$ or it is assumed constant in practical cases with a small variation in $c_w$. The value of $\partial \mu/\partial T$ of water is $5.0 \times 10^{-2} \text{mm}^{-1} \cdot \text{K}^{-1}$ from 16.0 to 44.0 °C by our experimental data [31], and this value was used for the calculation in this study. It is noted that the very accurate measurement of $\mu_1$ and $\partial \mu_1/\partial T$ is difficult because there are uncertainties in the reflectance of cuvette, light path length, temperature, and other parameters. Also, to be exact, the refractive index and thickness of cuvette glass vary slightly with temperature, leading to slight changes in the reflectance and in the light path length, respectively.

Kou et al [52] showed that $\partial \mu_1/\partial T$ of water at $\lambda = 1908 \text{nm}$ is $7.5 \times 10^{-2} \text{mm}^{-1} \cdot \text{K}^{-1}$ (our calculation using their original data at $T = 22 \text{ °C}$ and $-8 \text{ °C}$). Rüttgers et al [53] provided that $\partial \mu_2/\partial T = 5.28 \times 10^{-2} \text{mm}^{-1} \cdot \text{K}^{-1}$ (s.d. $= 0.5 \times 10^{-4} \text{mm}^{-1} \cdot \text{K}^{-1}$) for water from 15.0 to 60.0 °C. At $\lambda_2$, on the other hand, $\partial \mu_2/\partial T$ is almost zero because of the isosbestic point with regard to temperature.

The coefficient of $dc_e$ in equation (5) is given by

$$\left( \frac{\partial \mu}{\partial c_e} \right)_T = \varepsilon_w^o \left( \frac{\partial c_w}{\partial c_e} \right) + \varepsilon_E^o + \left( \frac{\partial (\varepsilon_E c_E)}{\partial c_E} \right).$$  

(7)

The black squares in figures 2(a) and (b) are the measured data of the absorption coefficient differences, $\Delta \mu_1$ and $\Delta \mu_2$, respectively, of the ethanol–water mixture as functions of $c_e$ from 0 to 8.0 M at 24 °C (here, 8.0 M is equivalent to ~40 wt% of ethanol and ~0.207 mol e/mole $c_e$), where the references for $\Delta \mu_1$ and $\Delta \mu_2$ are $\mu_1$ and $\mu_2$ of pure water ($c_e = 0$), respectively. For comparison, the absorption coefficients of ideal mixtures (i.e. $\varepsilon^E = 0$ in equation (4)) are also shown by red dashed lines, calculated by using $\mu_1 = 10.8 \text{mm}^{-1}$ and $\mu_2 = 13.5 \text{mm}^{-1}$ for water from [52], and $\mu_1 = 0.2 \text{mm}^{-1}$ and $\mu_2 = 0.2 \text{mm}^{-1}$ for ethanol from our data.

In figure 2(a), the measured data of $\Delta \mu_1$ are considerably smaller than the ideal ones because of $\varepsilon^E$, and show the slightly concave curve, i.e. $|\partial \mu_1/\partial c_e|$ decreases with the increase in $c_e$. This nonlinearity is caused by the third term on the right hand side in equation (7) because $\varepsilon^E$ of alcohol–water mixtures depends on the alcohol concentration [35, 48, 49]. In the first term, $\partial c_w/\partial c_e$ is also not constant because the partial molar volumes of water and ethanol vary with composition [35, 36]; however, the contribution of $\partial c_w/\partial c_e$ to the nonlinearity is even smaller than that of $\varepsilon^E$. The concave curve is explained partly by the self-aggregation of alcohol molecules occurring beyond its threshold concentration (~2.1 M), where the CH stretching frequency decreases but little affects the hydrogen bonding state between water and alcohol molecules [49]. Thereby, to the data of $\Delta \mu_1$ for $0 \leq c_e \leq 2.1 \text{M}$, a linear regression line was fitted, and we obtained $\partial \mu_1/\partial c_e = -1.02 \text{mm}^{-1} \cdot \text{M}^{-1}$ with the coefficient of determination of ~0.99. In the region of $c_e > 2.1 \text{M}$, another appropriate linear function or a polynomial may be applied. Particular for $c_e > 8 \text{M}$ (not shown here), it should be noted that the nonlinearity becomes more significant because the structure formation drastically changes at an alcohol mole fraction of 0.15–0.20 (~6.4–7.9 M), as reported by NIR spectroscopy [48], Raman spectroscopy [38, 54], fluorescence spectroscopy [37], x-ray Compton scattering [40], nuclear magnetic resonance (NMR) techniques [55, 56], and terahertz spectroscopy with pulsed field gradient NMR [57].

In figure 2(b), the measured $\Delta \mu_2$ show a good linearity to $c_e$ and a good agreement with the line of the ideal mixture, meaning that $\varepsilon^E$ is relatively very small at $\lambda_2$. The smallness of $\varepsilon^E$ at $\lambda_2$ has been suggested by some works; Onori [48] showed that, in the $\nu_1 + \nu_1$ band of water, the dependence of $\varepsilon^E$ on $c_e$ is similar to that of $\varepsilon^o_w$ on $T$, i.e. $\varepsilon^E$ decreases the most at $\lambda = 1412 \text{nm}$ as $c_e$ increases, whereas $\varepsilon^E$ at $\lambda \sim 1440 \text{nm}$
remains at zero like an isosbestic point. Di Michele et al. [49] showed a similar trend regarding a tert-butyl alcohol–water mixture in the $\nu_2 + \nu_3$ band of water, i.e. a peak of variation in $\varepsilon_e$ exists at $\lambda_1$ and an invariant point exists at $\lambda_2$. Therefore, a linear approximation can be reasonably applied to the relationship between $\mu_2$ and $\varepsilon_e$ in the entire region of $\varepsilon_e$. The fitted line in figure 2(b) gives the coefficient of determination of $-0.99$ and $\partial \mu_2/\partial \varepsilon_e = -0.87 \text{ mm}^{-1} \cdot \text{ M}^{-1}$.

Hence, the relationships among the changes in the absorbances at $\lambda_1$ and $\lambda_2$, temperature and concentration, $\Delta \varepsilon_1$, $\Delta \varepsilon_2$, $\Delta T$ and $\Delta \varepsilon_e$, are expressed as follows,

$$\frac{\Delta \varepsilon_1}{l \cdot \log_{10} e} = \left( \frac{\partial \mu_1}{\partial T} \right)_{\varepsilon_e} \Delta T + \left( \frac{\partial \mu_1}{\partial \varepsilon_e} \right)_{T} \Delta \varepsilon_e, \quad (8)$$

By solving equations (8) and (9) for $\Delta T$ and $\Delta \varepsilon_e$, the following equations are obtained,

$$\Delta \varepsilon_e = \ln \frac{10}{l} \left( \frac{\partial \mu_2}{\partial \varepsilon_e} \right)_{T} \Delta A_2 = a_c \Delta A_2, \quad (10)$$

$$\Delta T = \ln \frac{10}{l} \left( \frac{\partial \mu_1}{\partial \varepsilon_e} \right)_{T}^{-1} \Delta A_1 - \left( \frac{\partial \mu_1}{\partial \varepsilon_e} \right)_{T}^{-1} \Delta \varepsilon_e + b_T \Delta \varepsilon_e, \quad (11)$$

where

$$a_c = \ln \frac{10}{l} \left( \frac{\partial \mu_2}{\partial \varepsilon_e} \right)_{T}^{-1}, \quad a_T = \ln \frac{10}{l} \left( \frac{\partial \mu_1}{\partial \varepsilon_e} \right)_{T}^{-1}, \quad b_T = - \left( \frac{\partial \mu_1}{\partial \varepsilon_e} \right)_{T}^{-1}. \quad (12)$$

Using the regression coefficients on $\Delta \mu_1$ and $\Delta \mu_2$ determined above, we obtained $a_c = -2.65 \text{ M} \cdot \text{ mm}$, $a_T = 46.1 \text{ mm} \cdot \text{ K}$ and $b_T = 20.4 \text{ M}^{-1} \cdot \text{ K}$ for $0 \leq \varepsilon_e \leq 2.1 \text{ M}$. Then $\Delta T$ and $\Delta \varepsilon_e$ are obtained by substituting the measured $\Delta A_1$ and $\Delta A_2$ into equations (10)–(12). Note that the values of $a_c$, $a_T$ and $b_T$ are monochromatic and intrinsic coefficients, but when a bandpass filter is used, they must be recalculated by considering the transmission spectrum of the filter [31], as described below.

3. Experiment

3.1. Imaging system

Figure 3(a) shows a schematic of the imaging system. Light emitted from each of two halogen lamps was condensed and vertically hit a chopper disk with a diameter of 200 mm and with three 60° apertures equiangularly. This configuration between the light beams and the disk ensured that when one light beam passed through an aperture of the rotating chopper disk, the other was blocked by the disk blade. A NBPF with the transmission peak wavelength of 1905 nm ($\lambda_1$) was placed in one light path and another NBPF with 1935 nm ($\lambda_2$) was in the other light path. The full width at half maximum of both NBPFs was 10 nm. Between the halogen lamps and the NBPFs, bandpass filters (BPFs) with the transmission wavelength range from 1600 nm to 2200 nm were placed to prevent the NBPFs from thermal damage. As a result, a microfluidic chip on an IR microscope stage was irradiated with the light at $\lambda_1$ and $\lambda_2$ alternately. The light transmitted through the chip was detected by an NIR camera (CV-N800, Sumitomo Electronics, Japan) with a 320 (H) × 256 (V), 30 μm-pitch indium gallium arsenide (InGaAs) array detector. The camera provides 16-bit digital images and its response wavelength range is from 1000 nm to 2350 nm. The maximum of the acquisition speed is 320 frames s$^{-1}$ (fps). The image acquisition
A microfluidic chip was irradiated with two light beams at the wavelengths of 1905 nm and 1935 nm alternately by using NBPFs and a rotating chopper disk. The transmitted images are acquired by a NIR camera, synchronized with the timing of irradiation. Other bandpass filters (BPFs) were installed to prevent the NBPFs from transmission bandwidth is larger than that of the NBPF, especially for an NIR region. However, the authors expect that the development of spectral devices and cameras will improve the proposed imaging method in terms of frame rate, sensitivity, and usability.

3.2. Microfluidic chip and experimental procedure

A microfluidic chip consisted of a PDMS plate with a Y-channel etched on its surface and a glass plate covering the channel (A1-1, Fluidware Technologies Inc., Japan) [31], as shown in figure 3(b). Thicknesses of the glass and PDMS plates were 1 mm and 2 mm, respectively. The cross-sectional dimensions of the channel were 45 ± 1 μm in depth and 200 μm in width, and the length of the main channel was 32 mm. The depth, or the light path length, was determined from spectral interference patterns and confocal scanning laser microscopy images. Water was flowed from one branch channel named Branch A (see figure 3(b)) and an ethanol–water mixture with a concentration of 0.43 M (2.0 wt%) or water, switched by a three-way solenoid valve, was flowed from Branch B into the main channel by a syringe pump in a withdrawal mode. The flow rates in the two branches were equal and set to be 0.25 or 1.0 μl min⁻¹. Initially, water was flowed in the entire channel, and the acquired images of the light intensity at λ₁ and λ₂ were defined as the reference images for calculating the images of ΔAf₁ and ΔAf₂. Next, the ethanol–water mixture was flowed from Branch B, and then, the time origin, t = 0 s, was defined at the time when the mixture reached the observation area, which was judged by observing the images. After that, an interface between the mixture and water streams was formed along the center line of the main channel.

An electrical tape heater and electrical film heater (20mm × 20 mm × 0.3 mm) was used to raise the temperature of water in Branch A, as shown in figure 3(b). Thus, T was changed in Branch A, while cₑ was changed in Branch B to evaluate each contribution of ΔT and Δcₑ to ΔAf₁ and ΔAf₂. To control the temperature of the whole chip, a disk heater with a diameter of 100 mm was installed in the microscope stage. Two thin thermocouples monitored the temperatures at the top surface of the PDMS plate and at the bottom surface of the glass plate, near the merging point of the Y-channel. By using these two temperatures with a 1D thermal conduction model, the temperature at the boundary between the glass and PDMS plates was determined, which was referred to as the channel temperature in the observation area. The x-y coordinates of the chip, near the merging point. The inset shows the x-y coordinates of the channel.

was synchronized with the time when each light beam passed through the apertures. In this study, the images at each wavelength were sequentially acquired at 50 fps, meaning 100 fps for the camera.

Due to the band width of the NBPFs, the absorbance differences and the coefficients, a₁, a_T and b_T, in our measurement system were slightly different from those in the ideal monochromatic measurement. The absorbance differences measured with the NBPFs at λ₁ and λ₂ were hereafter referred to as ΔAf₁ and ΔAf₂, respectively. The symbols and values of a₁, a_T and b_T were modified to a₁ = 2.69 M⁻¹·mm, a_T = 51.8 M⁻¹·mm and b_T = 21.7 M⁻¹·mm, which were calculated by using the transmittance spectra of the NBPFs and the absorption spectra of the mixtures and water. The deviations of ΔAf from a₁, a_T and b_T are 1.5%, 12.4% and 6.4%, respectively.

Filter exchange systems [58, 59], including ours, seem to be more appropriate for staring imaging of rapid transient phenomena than other systems, at present. The frame rates of filter exchange systems are, in principle, higher than those of linescan hyperspectral imaging systems [25, 28, 29]. Acousto-optic tunable filter (AOTF) is a solid-state device for spectral imaging [60–62] but its active aperture is too small for staring imaging. Of liquid crystal tunable filter (LCTF) [63–66], the frame rate is lower than that of filter exchange systems, and its transmission bandwidth is larger than that of the NBPF, especially for an NIR region. However, the authors expect that the development of spectral devices and cameras will improve the proposed imaging method in terms of frame rate, sensitivity, and usability.
smoothed with an 11-point, 5th-order Savitzky–Goaly filter [31]. Subsequently, the sequential image frames were sorted into odd and even frames, corresponding to the images at $\lambda_1$ and $\lambda_2$, respectively. Between two temporally adjacent frames in each sequence, the average frame was newly inserted to construct (pseudo-) simultaneous frames for $\lambda_1$ and $\lambda_2$.

4. Results and discussion

4.1. Absorbance, temperature and concentration images in a transient state

Figure 4(a) show the images of $\Delta \lambda_{\beta}$ and $\Delta \lambda_{\gamma}$, and the images of $\Delta c_\varepsilon$ and $\Delta T$ obtained from $\Delta \lambda_{\alpha}$ and $\Delta \lambda_{\beta}$ by equations (10)-(12) at $t = 1.02$, 1.80 and 6.22 s in the case that water and ethanol–water mixture with $c_e = 0.43$ M flowed from Branch A and Branch B, respectively. The heating of water by the tape and film heaters started at $t = -40$ s to observe the onset of the increase in $\lambda_{\beta}$ by temperature at $t = 0$. The disk heater was off, and the initial temperature of the chip was the room temperature of 18 °C. The flow rates of both the mixture and water were 1.0 $\mu$1 min$^{-1}$, corresponding to the average flow velocity of 3.7 mm s$^{-1}$. The magnification of an IR objective lens was five times. Figure 4(b) show the line profiles of $\Delta \lambda_{\beta}$, $\Delta \lambda_{\gamma}$, $\Delta c_\varepsilon$ and $\Delta T$ in the $x$-direction across the channel at the positions of $y = 220$ $\mu$m indicated by white dotted lines in the images of figure 4(a).

The images of $\Delta \lambda_{\beta}$ and $\Delta \lambda_{\gamma}$ at $t = 1.02$ s show that both $\Delta \lambda_{\beta}$ and $\Delta \lambda_{\gamma}$ remained unchanged in the left side ($x < 0$), where the water continued to flow. Regarding $\Delta \lambda_{\gamma}$, which depends only on $\Delta c_\varepsilon$, the difference between the two streams at $t = 1.80$ s was seen more clearly than that at $t = 1.02$ s, and remained unchanged to $t = 6.22$ s, meaning that the right side of the main channel was filled with the mixture with $c_e = 0.43$ M at or before $t = 1.80$ s. However, since $\Delta \lambda_{\beta}$ depends not only on $\Delta c_\varepsilon$ but also on $\Delta T$, the images of $\Delta \lambda_{\beta}$ at $t = 1.80$ s and $t = 6.22$ s were different from those of $\Delta \lambda_{\gamma}$.

The images of $\Delta T$ showed that, at $t = 1.80$ s, $\Delta T$ of the water in Branch A was slightly larger than $\Delta T$ of the mixture in Branch B by the local heating. However, at $t = 6.22$ s, $\Delta T$ increased significantly in the whole region, and the difference in $\Delta T$ was no longer observed. This was mainly due to heat transfer between the fluid and the chip materials. Since the local heating in this case was made at the outside of the chip and tube, the temperatures around Branch B and the main channel also increased by thermal conduction in the chip. It is also thought that the temperatures of the fluids became very close to those of the surroundings until arriving at the observation area because the thermal time constant of the fluids was less than 10 ms. In addition to the effect of the chip temperatures, thermal conduction within the fluid itself was expected to contribute to the uniformity of $\Delta T$ because the thermal diffusivity of water is $1.44 \times 10^{-7}$ m$^2$ s$^{-1}$ at 25 °C, which is larger than the mutual diffusion coefficient of ethanol in ethanol–water mixture of $1.22 \times 10^{-9}$ m$^2$ s$^{-1}$ at 25 °C [67]. It was thus hard to produce and preserve a temperature difference between the two fluids.

Some discussions can be made on the line profiles of $\Delta c_e$ and $\Delta T$ in figure 4(b). The average of $\Delta c_e$ over the region of $x = 0$–100 $\mu$m at $t = 6.22$ s was 0.37 M. This value was slightly smaller than the ethanol concentration of the original mixture of 0.43 M. However, this difference is small enough to be acceptable in many cases, especially for the purpose of observing spatiotemporal variations in $\Delta c_e$. Also, it is found that $\Delta c_e$ decreased from $x = 0$ to 100 $\mu$m and, in particular, $\Delta c_e$ at $t = 1.02$ s near $x = 100$ $\mu$m was very small. One of the reasons may be that the flow velocity near the sidewall was smaller than that at the channel center. Resultantly, water existing initially near the sidewall was not completely replaced with the mixture with $c_e = 0.43$ M from Branch B. At $x > 0$ $\mu$m, small peak-like increases in $\Delta c_e$ were seen at $t = 1.80$ s and 6.22 s. These local increases were mainly caused by a difference in the refractive indices between the two liquids. This unavoidable effect can be neglected for dilute solutions as used in this study, but, for non-dilute solutions with a large difference in concentration, it would need to be carefully evaluated. Regarding $\Delta T$, the average over the observation area at $t = 6.22$ s was 3.9 K (s.d. 1.2 K) while the increase in the channel temperature given by the thermocouples was 2 K. Thus, the measured values of $\Delta T$ were confirmed to be consistent with the channel temperatures.

4.2. Observation of diffusion at different constant temperatures

In order to investigate the mass diffusion in the $x$-direction (transverse to the flow direction), stable parallel flows of water and an ethanol–water mixture with a concentration of 0.43 M were produced in the same manner as in the previous experiment. The temperature of the whole microfluidic chip was adjusted at 16 °C or 27 °C by the disk heater. The tape and film heaters attached to Branch A were off. The flow rate in the main channel was 0.5 $\mu$m min$^{-1}$ (0.25 $\mu$m min$^{-1}$ for each liquid from the two branches). The magnification of an IR objective lens was two times.

Figure 5(a) shows the images of $c_e$ and $T$ at 16 °C and 27 °C. Here, $c_e = c_{e,ref} + \Delta c_e$ and $T = T_r + \Delta T$, where $c_{e,ref}$ is the reference concentration of ethanol, given as the initial value of 0 M, and $T_r$ is the reference temperature, given as the initial chip temperature of 16 °C. Each image of $c_e$ indicates that the difference in $c_e$ between the two streams gradually decreased along the flow in the $y$-direction by the mutual diffusion of ethanol and water molecules. The decrease in the difference in $c_e$ is a typical phenomenon observed in microfluidics, and is indeed similar to the results in some previous works using alcohol–water mixtures, although the concentrations used in these works ranged from a few tens to a hundred mol% [8, 17, 43, 44], which were much larger than 0.43 M = 0.79 mol% in this study. By comparison of the two images of $c_e$, it is obvious that the diffusive mixing was faster at 27 °C than at 16 °C. Meanwhile, the distributions of $T$ were homogeneous in the
entire channel, and the values of $T$ agreed with the adjusted temperatures of 16 °C and 27 °C; the averages of $T$ over the observation area were 16.9 °C (s.d. 0.5 °C) and 26.8 °C (s.d 0.4 °C). The slight increase in $T$ along the interface between the two flows, especially near the merging point, was caused by a difference in the refractive indices, as described in section 4.1.

Figure 5(b) shows the plots of $c_e$ in the $x$-direction at three positions of the $y$-coordinate ($y = 0.2, 1.2$ and $2.2$ mm), as indicated by white dot lines in figure 5(a). To verify the measured distributions of $c_e$ at the different temperatures qualitatively and quantitatively, we compared them with the calculated distributions of $c_e$, which were the numerical solutions of the steady state convection diffusion equation in two-dimension,

$$D_{ew} \left[ \frac{\partial^2 c_e(x, y)}{\partial x^2} + \frac{\partial^2 c_e(x, y)}{\partial y^2} \right] - v(x) \frac{\partial c_e(x, y)}{\partial y} = 0,$$

where $D_{ew}$ is the mutual diffusion coefficient of ethanol in ethanol–water mixture and $v$ is the flow velocity in the $y$-direction. From the calculated $c_e(x, y)$, three line profiles at the same positions of $y$ as the measured ones are drawn as the smooth dashed curves in figure 5(b). In the calculation, since the flow is laminar with low Reynolds numbers of about 0.07, the velocities in the $x$-direction and $z$-direction (light path direction) were neglected. It was thus assumed that $v(x) = 3v_m (1 - x^2/w^2)/2$, which is the theoretical velocity profile for the fully-developed laminar flow between the two plates with non-slip condition, where $v_m$ is the mean velocity ($v_m = 0.92$ mm s$^{-1}$, Meas. Sci. Technol. 27 (2016) 115401
here) and \( w \) is the width of the channel (\( w = 200 \, \mu\text{m} \)). A finite volume method was used to solve equation (13) numerically under the boundary conditions consistent to the experiment, i.e. \( c_e = 0 \) for \(-100 \, \mu\text{m} < x \leq 0 \, \mu\text{m} \) and \( c_e = 0.43 \, \text{M} \) for \( 0 < x < 100 \, \mu\text{m} \) at the inlet of the main channel (\( y = 0 \)), a free outflow condition at the outlet, and \( \partial c_e / \partial x = 0 \) at the channel sidewalls (\( x = \pm 100 \, \mu\text{m} \)). In this calculation, we gave \( D_{ew} = 9.1 \times 10^{-9} \, \text{m}^2 \text{s}^{-1} \) and \( 1.30 \times 10^{-9} \, \text{m}^2 \text{s}^{-1} \) for 16 \( {\circ} \text{C} \) and 27 \( {\circ} \text{C} \), respectively, obtained by interpolation of the data presented by Easteal and Woolf [67] and Pratt and Wakeham [68] for dilute ethanol–water mixtures. No dependence of \( D_{ew} \) on \( c_e \) was assumed because \( \partial D_{ew} / \partial c_e \) is very small, about \( 0.026 \times 10^{-9} \, \text{m}^2 \text{s}^{-1} \) per 0.21 M for dilute mixtures [68, 69].

The measured data and the calculated curves in figure 5(b) show, on the whole, similar trends and good agreements. The gradient, \( \partial c_e / \partial x \), at \( x = 0 \, \mu\text{m} \) in the case of 27 \( {\circ} \text{C} \) decreased faster than that in the case of 16 \( {\circ} \text{C} \). The measured values of \( \partial c_e / \partial x \) at 16 \( {\circ} \text{C} \) were 1.09, 0.55 and 0.31 \( \times 10^{-2} \, \text{M} \mu\text{m}^{-1} \) at \( y = 0.2, 1.2 \) and 2.2 mm, respectively, while those at 27 \( {\circ} \text{C} \) were 0.70, 0.27 and 0.17 \( \times 10^{-2} \, \text{M} \mu\text{m}^{-1} \). At 16 \( {\circ} \text{C} \), the calculated values of \( \partial c_e / \partial x \) (1.08, 0.52 and 0.29 \( \times 10^{-2} \, \text{M} \mu\text{m}^{-1} \)) agreed well with the measured ones, but, at 27 \( {\circ} \text{C} \), the agreement was moderate; the calculated values were 0.84, 0.35 and 0.25 \( \times 10^{-2} \, \text{M} \mu\text{m}^{-1} \). This moderate agreement at 27 \( {\circ} \text{C} \) may be due to the assumption of \( v(x) \) and the boundary conditions of \( c_e \) at the inlet of \( y = 0 \) because the actual velocity distributions are complicated especially in the merging region and near the wall [10, 70], meaning that the mixing may be more enhanced in the actual situation than in the calculation.
From the good agreement between the measured and calculated concentration profiles as shown in figure 5(b), the NIR-based method proposed in this study is verified. As the future works, applications of the NIR-based method will include obtaining various parameters and properties of the thermal and chemical fields in microfluidic chips [6, 12, 13, 17].

5. Conclusions

This paper proposed a simultaneous imaging method of temperature and concentration of dilute ethanol–water mixtures in microfluidic channels. The principle is based on the facts that the absorbance at a wavelength of 1905 nm is dependent on temperature while the absorbance at 1935 nm is independent of temperature, and that the absorbances at both wavelengths are highly sensitive to the molar concentration of water, which is reciprocal to that of ethanol. The method was applied to an ethanol–water mixture with the ethanol concentration of 0.43 M and water flowing in a microfluidic Y-channel. The concentration images clearly showed that the concentrations were different between the mixture and water streams, and that the transverse concentration gradient across the interface decreased along the flow direction by mutual diffusion. The decreasing rate of the gradient, i.e. diffusion coefficient, increased as the temperature increased, and this result was consistent with the numerical simulation results. The temperature images showed that uniform temperature distributions were rapidly formed in the channel due to heat transfer between the fluid and the surrounding materials. These results indicated the validity and utility of the proposed method for simultaneous imaging of temperature and concentration. This method is expected to be used in a variety of microfluidic applications that need the measurements or imaging of temperature and concentration.

Acknowledgments

This work was supported by the Canon Foundation and the JSPS KAKENHI Number 26289049.

References


[34] Czarnik-Matuszewicz B and Pilorz S 2006 Study of the temperature-dependent near-infrared spectra of water by two-dimensional correlation spectroscopy and principal components analysis Vib. Spectrosc. 40 235–45


[52] Kou L, Labrie D and Chylek P 1993 Refractive indices of water and ice in the 0.65- to 2.5 μm spectral range Appl. Opt. 32 3531–40


[56] Hu N, Wu D, Cross K J and Schaefer D W 2010 Structural basis of the 1H-nuclear magnetic resonance spectra of ethanol–water solutions based on multivariate curve resolution analysis of mid-infrared spectra Appl. Spectrosc. 64 337–42


[64] Latorre-Carmona P, Sánchez-Ortega E, Xiao X, Pta F, Jiménez-Corral M, Navarro H, Saavedra G and Javidi B 2012 Multispectral integral imaging acquisition and
processing using a monochrome camera and a liquid crystal tunable filter *Opt. Express* **20** 25960–9


