Investigation Of Binary Liquid Aqueous Methanol And Ethanol Mixtures Using Meander-Shaped Fibre-Optic Evanescent-Wave Absorption Sensors

Matthias Fabian, Elfred Lewis, Thomas Newe
Optical Fibre Sensors Research Centre (OFSRSC)
Dept. of Electronics and Computer Engineering
University of Limerick
Republic of Ireland
Email: www.ofsrc.ul.ie

Steffen I. Lochmann
Fachbereich Electrotechnik und Informatik
Hochschule Wismar
PF 1210, 23952 Wismar, Germany
Email: www.et.hs-wismar.de

Abstract—A fibre-optic evanescent-wave field absorption sensor based on a meander-shaped sensing probe is described. The influences of the fibre core diameter and the refractive index of the surrounding medium on the sensitivity are evaluated by using binary liquid mixtures, in particular methanol and ethanol solved in distilled water at concentrations from 0 to 10 volume percent (%vol). The resolution was experimentally proved to be about 5·10⁻⁵ refractive index units at a wavelength of 650nm, which corresponds to a resolution of about 0.2%vol methanol and 0.1%vol ethanol concentration. The LED based design as well as the chosen wavelength (POF suitable) result in a low cost sensing application. Finally, an analytical approach for predicting the refractices indices of liquid mixtures (Lorentz-Lorenz equation) was examined for validity with regards to the mentioned aqueous methanol/ethanol solutions.

I. INTRODUCTION

The present investigation is based on previous work by the authors of this article where a meander-shaped sensing probe with an optical fibre of 600µm core diameter was used [1]. The result was an increase of the sensitivity by more than 30 times (in the case of methanol) compared to a single U-bend sensor of the same core diameter. Similar approaches for increasing the sensitivity of straight exposed optical fibres have previously been adopted by deforming the fibre core using techniques such as tapers [2]–[4] and D-fibres [5], [6].

In this paper we examined the influence of the fibre core diameter of the meander-shaped sensing probes on their sensitivity. The measurement hardware used for the investigations described in this article are the same as previously reported [1].

Due to the increasing importance of direct liquid-feed fuel cells (DLFCs), we have chosen methanol and ethanol contents to be determined for testing the sensing elements. Both fluids have to be monitored with high resolution for an optimal fuel cell performance, in particular for the direct methanol and direct ethanol fuel cells. Beside their application as fuels, both alcohols are also used in a large variety of industrial and chemical processes.

To relate the acquired refractive indices of the mixtures to their methanol/ethanol contents we tested a refractive index prediction formula, the Lorentz-Lorenz equation. Its original form as it is shown in equation (1) is actually due to Lorentz only [7], but is generally referred to as the Lorentz-Lorenz equation, although only the equation for a one component system was derived independently by both authors [8], [9]. However, this equation has been widely used for binary, ternary, and quaternary liquid mixtures and has been found to result in reliable predictions for many organic and inorganic compounds, e.g. [10]–[13]. It relates the density of a mixture to its refractive index through a knowledge of the densities and refractive indices of the pure compounds as well as the concentration of each of the compounds.

\[
\frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \phi_1 \frac{(n_1^2 - 1)}{(n_1^2 + 2)} + \phi_2 \frac{(n_2^2 - 1)}{(n_2^2 + 2)}
\]

In equation (1) \( n_{12}, n_1 \) and \( n_2 \) are the refractive indices of the mixture (solution), compound 1 (solvent) and compound 2 (solute), respectively. \( \phi_1 \) and \( \phi_2 \) are the volume fractions of the respective components in the solution which are defined by

\[
\phi_i = \frac{c_i}{\rho_i} = w_i \left( \frac{\rho_{i2}}{\rho_i} \right)
\]

where \( c_i \) is the concentration in g/cm³ or ml/cm³, \( \rho_i \) the density of compound \( i, w_i \) the weight fraction (also referred to as mass fraction) of compound \( i \) and \( \rho_{i2} \) the density of the mixture of the two components. The mass fraction \( w_i \), if unknown, can be calculated as follows:

\[
w_i = \frac{m_i}{m_1 + m_2} = \frac{x_i M_i}{x_1 M_1 + x_2 M_2}
\]

where \( m_i, x_i, \) and \( M_i \) are the mass, the molar fraction, and the molar mass of compound \( i \), respectively. Using equation (2) and (3) a mass fraction can be converted to its respective volume fraction and vice versa. Out of them the mass fraction is commonly used in chemistry because the resulting volume of two fluids does not equal the sum of the compound volumes.
prior to mixing for many fluids but their masses are additive in every case.

In order to directly calculate the refractive index of a binary liquid mixture the following analytical expression can be derived from equation (1):

\[ n_{12} = \sqrt{\frac{1 + 2K}{1 - K}} \]  \hspace{1cm} (4)

where \( K \) is defined by

\[ K = \sum_{i=1}^{2} \phi_i \left( \frac{n_i^2 - 1}{n_i^2 + 2} \right) \]  \hspace{1cm} (5)

with \( \phi_i \) identical to equation (2).

The Lorentz-Lorenz equation is well accepted in science because it was theoretically derived from Maxwell’s electromagnetic theory.

II. EXPERIMENT

A. Sensor fabrication

To fabricate the sensors plastic clad silica (PCS) fibres with core diameters of 200\( \mu \)m, 400\( \mu \)m, and 600\( \mu \)m with a numerical aperture (NA) of 0.4 and a core refractive index of 1.48 were used. The bend radii of the meander-shapes were measured to be 1.1mm.

To form the meander shapes, a sufficiently long part of the fibre coating and cladding was removed from around the central position of the fibre. Afterwards, the exposed fibre core was burned off in an open flame to ensure a complete removal of the cladding for an optimal interaction with the surrounding medium in later use. The uncovered fibre core was then heated with a propane flame and bent slowly until it became u-shaped. Then it was cooled down before forming the next adjacent bend. During the bending processes care was taken to maintain an optimum temperature and bending force to ensure that the fibre core diameter remains the same throughout the bent region.

The limitation of the bending radius in the case of meander-shapes is governed by the flame dimensions because if the heat conus around the flame is too wide an already existing bend will be heated and deformed as well which is difficult to repair in a group of closely adjacent bends. This problem especially arises in the case of the smaller fibre core radius because thinner fibres require less heat to be deformed than thicker ones. An image of the 600\( \mu \)m sensing probe can be seen in fig. 1.

B. Measurement setup

Based on the broadband measurements in our previous work the selected source wavelength was chosen to be 650nm, generated by a low cost LED. The receiver was also identically dimensioned for comparison reasons, consisting a common silicon photodiode, an I-to-V stage, voltage amplification and offset reduction stage and a microcontroller that controls sampling, hardware monitoring, and measurement data transmission tasks. Generally speaking, the hardware setup was designed as simple as possible. A more detailed description of the measurement hardware environment can be found in [1].

III. RESULTS

To evaluate the sensing probes of different core diameters they were exposed to aqueous methanol and ethanol solutions. The alcohol content was increased stepwise by 1\% vol each two minutes. The output voltage of the I-to-V stage was monitored simultaneously since it corresponds to the optical losses due to the evanescent-wave absorption. The resulting curves are shown in fig. 2(a) and 2(b) supplemented by the basic setup of the receiver circuit. The upper x-axis shows the appropriate alcohol concentrations for each time slot at the lower x-axis. For both mixtures we can observe an almost two times higher sensitivity of the 400\( \mu \)m probe compared to the 600\( \mu \)m version while the sensitivity of the 200\( \mu \)m probe just slightly differs from the latter one. It is expected that 200\( \mu \)m probe sensitivity will exceed that of the 400\( \mu \)m diameter probe for bending radii smaller than 1mm as it was shown for single U-bends (200/600\( \mu \)m) by Gupta et al. [14] but smaller bending radii result in difficulties in the bending process as mentioned in the introduction. The output voltage change in case of ethanol is about 2.7 times higher than in the case of methanol due to larger refractive index changes of the solution for each concentration step as it will be shown later. The small peaks at the points of concentration changes are caused by the chemical mixing process which commonly takes a few seconds.

In order to relate the output voltage changes to the refractive index or the density of the mixture and vice versa the respective refractive indices found in literature [15], [16] were compared with those calculated by the Lorentz-Lorenz equation.

Fig. 3 shows that there is an almost linear relationship between the methanol/ethanol content and the corresponding refractive indices of the solutions in the lower concentration range (which turns out to be strongly non linear for the higher concentration range). However, for the small alcohol concentrations used in the liquid feed of fuel cells an elementary linear fitting is possible to determine the refractive indices of concentration values that are not listed in tables.

It is further clear from fig. 3 that the refractive index difference for each integer concentration step is about 0.00023
Fig. 2. Comparison of the sensitivity of the meander-shaped sensing probes for different fibre diameters (NA=0.4, bending radii=1.1mm). The methanol/ethanol concentration (upper x-axis) was changed every two minutes (lower x-axis) by steps of 1% vol. The graphs show the output voltages changes of the I-to-V stage vs. alcohol concentration.

Fig. 3. Interpolated absolute refractive indices of aqueous methanol and ethanol solutions vs. alcohol concentrations from 0% wt to 10% wt at 589nm and 20°C [15], [16].

In fig. 4 the deviations $\delta_i$, with $\delta_i = n_{i,\text{calc}} - n_{i,\text{lit}}$, of the calculated refractive indices compared to the literature values are shown.

To avoid very small numbers on the y-axis it is scaled in terms of $10^5$ refractive index units. The deviations of both mixtures are almost the same up to 8% wt alcohol content which affects the accuracy of methanol solutions more than those of ethanol solutions because of the smaller refractive index changes for each concentration step. However, with these values appropriate correction algorithms could be implemented to accurately relate the concentration of those mixtures to their densities or refractive indices using the analytical approach due to Lorentz.

Table I comprises the discrete values of the refractive indices from literature as well as the deviations caused by the Lorentz-Lorenz equation. Additionally the refractive index difference $\Delta n$ for each concentration step compared to pure water is shown.
With these values known we experimentally proved a resolution of $5 \times 10^{-5}$ refractive index units for the 400μm sensing probe which corresponds to 0.2% methanol and 0.1% ethanol content, respectively.

Finally, this sensing principle can be used for all fluids that have different refractive indices for different concentrations with an increasing sensitivity the larger the mixture refractive index as it was observed for single U-bends [14].

IV. Conclusion

In this article we have shown that using a simple low cost measurement setup it is possible to simultaneous measure and resolve methanol and ethanol concentrations in water using optical sensing techniques, in particular the evanescent-wave absorption phenomenon. The small size of the sensing element makes it suitable for in-situ measurements in pipes or similar fluid flow lines. Since this sensing method is based on the acquisition of refractive index changes it can be applied to other fluids as well that display the same phenomena, e.g. other alcohols (acetone, 1-propanol, 2-propanol) and oils. The two kinds of propanol are of particular interest since there DLFCs with those alcohols as fuels, the direct 1-propanol fuel (D1PFC) and the direct 2-propanol fuel cell (D2PFC).

### REFERENCES


