Chapter II

Fiber optic sensor for determining the quality of alcohol-water mixtures

2.1 Introduction

Water is an almost universal solvent and aqueous solutions of alcohols have found widespread use in several sectors such as beverage industries, personal care products, pharmaceutical and chemical industry, chromatography solvents to food additives, supercritical water technology etc [1]. They have also found use in bio science as solvents assisting protein denaturation due to the promotion of the R-helix structure of peptides and proteins [1]. Hence in-situ detection and quantification of alcohol with high sensitivity and selectivity is a critical factor in many industrial as well as biotechnical applications. Moreover accurate measurement of ethanol is unavoidable in clinical and forensic analysis in order to analyze human body fluids like blood, serum, urine and breath. In order to manage fermentation process and thus to control the quality of products, detection of ethanol is important in food [2,3] and beverage industries [4,5].

This wide application range is due to the fact that a lot of physical and chemical properties of alcohol-water mixtures exhibit nonlinear dependence on solvent composition and shows peaks at certain critical concentrations depending on the nature of alcohol [6-9]. With increasing chain length, the solubility of alcohols in water decreases and among monohydroxyl alcohols that are miscible with water in any proportion, tert-butyl alcohol (TBA) possesses the biggest alkyl group. The TBA-water mixture is characterized by anomalies like a sharp minimum of the Excess molal volume and a maximum of the molal heat capacity at TBA molar fraction 0.04 [10]. Sato et al. have shown in a series of publications that the thermodynamics of mixing of short alcohols such as ethanol [11], methanol [12], 1-propanol [13] and 2-propanol [14] with water are complex functions of the liquid composition.

While much is known about the macroscopic chemical behavior of these solutions, the solvation structure is poorly understood for many
aqueous alcohols. Since alcohol molecules possess alkyl and hydroxyl groups, the way of dissolution in water is highly complicated due to the hydrophilic and hydrophobic interactions of alcohol and water molecules in solution, which in turn cause the anomalies [15]. Binary mixtures of alcohol and water were studied extensively using various techniques like X-ray absorption and X-ray emission (XA and XE) [16], ultrafast spectroscopy [17], Infrared (IR) absorption spectroscopy [18], neutron diffraction [19,20,21], Small-angle X-ray Scattering (SAXS) [22,23], light scattering [24-26], microwave analysis [27], time resolved spectroscopy [28], computer simulations [29-34] etc., in the light of hydrogen-bond network, aggregation, hydrophobic interaction, ‘clathrate’ formation, and ‘hydrophobic hydration’ for several years to correlate solution structure with the observed anomalies. Even after being investigated for decades, the structure and topology of the hydrogen-bonded network in aqueous solutions of alcohols is an area where open questions still remain and the conclusions drawn from experimental studies are conflicting [16,19]. The observed anomalies with alcohol-water mixtures were first attributed to the ice-like or clathrate-like structures created in surrounding water due to the hydrophobic head groups present in alcohol [21,25,26,35-38]. The results shown by neutron diffraction experiments [19] and x-ray emission spectroscopy [16] clearly challenge the “iceberg” model and suggest that rather than being enhanced or depleted, the structure of water in the mixture is close to that of the pure liquid. However, there are obvious inconsistencies between these experimental studies. The small fraction (~0.13) of water molecules predicted by Dixit et al. [19] to exist singly with no hydrogen-bonds to other water molecules is suggested to be incompatible with the simulated XE spectra of Guo et al.[16]. According to theoretical studies based on the RISM (Reference Interaction Site Model) approach, alcohol molecule resides in the cavity of the H-bonding network created by the surrounding water molecules which, in turn, lowers the compressibility of the medium [34]. However, with further addition of alcohol, the tetrahedral network structure gradually converts to the zigzag chain structure of alcohol increasing the compressibility of the water–alcohol mixtures [34]. Recently Naiping et.al. have reported the influence of structure formation with ethanol and water on the taste or brand preference of the otherwise colorless and tasteless water-ethanol solution called vodka [39].
Thus understanding the structure of molecules in alcohol-water solutions and the evaluation of alcohol concentration in alcohol-water mixture is currently a considerable challenge. During the last decades many analytical methods have been developed for the measurement of ethanol and other alcohols \[40,41\] and can be classified into three major categories namely chromatographic\[42-44\], resistive\[45-60\], capacitive \[61\] and optical\[62,63\]. Among these techniques, the chromatographic method is the most accurate and sensitive with a lower limit of ethanol detection on the order of 0.005% v/v reported by Zimbo et.al. \[44\]. Drawbacks of this method include high cost, as well as the necessity for sample pretreatment and long operation times. Somewhat less precise but more rapid measurements are achieved by the use of resistive methods where enzymes \[46- 49\], metal oxides \[50-53\] nanoparticles \[54-59\] and polymers \[60\] are used as sensing materials. Enzyme based ethanol concentration detection is based on either of two enzymes, alcohol oxidase or alcohol dehydrogenase, by monitoring \(O_2\) consumption or \(H_2O_2\) formation \[46-48\]. The specificity of the enzyme binding sites provides highly selective and accurate sensors. The disadvantage of the sensors lies in their instability due to protein denaturing when exposed to high temperature, pressure, or pH extremes. Regarding nanoparticle based detection, Hsueh et.al. reported a highly sensitive ethanol vapor sensor based on ZnO nanowire \[54\]. A zinc oxide based ceramic semiconductor ethanol gas sensor was reported by Bhooloka Rao \[55\] while Tan et.al. \[56,58,59\] presented different sensors based on nano-sized \(\alpha-Fe_2O_3\) with \(SnO_2\), \(ZrO_2\), \(TiO_2\) solid solutions. A polymer based sensor was designed by Lee et.al \[60\] while Dubas et.al \[64\] developed an absorbance based ethanol sensor using dye–Chitosan polyelectrolyte multilayers.

Among various sensing techniques, the simplest approach in the determination of alcohols is an optical sensor based method. Optical sensors generally have the advantages of low-cost manufacturability, safety, and miniaturization and are intended for use in real-time, in situ monitoring. Several authors have reported optical ethanol sensors based on fluorescence \[65-72\], Raman spectroscopy \[73\], Fabry Perot cavity \[74\] and optical fibers \[75-80\].

Due to their inherent advantages, fiber optic sensors are an ideal choice and have been implemented for the detection of ethanol \[81-83\]. Passive
nonselective fiber-optic sensors based on determination of refractive index changes as a function of the alcohol content using surface plasmon resonance [84] have been reported by Matsubara et. al. Recently fiber optic sensors incorporating an active sensitive terminal have been developed for monitoring lower alcohols in gas or liquid mixtures. An optical fiber long-period grating with solgel derived SnO$_2$ coating was successfully implemented by Gu et.al. [85,86] while Penza et.al. [87,88] have reported the sensitivity of Langmuir–Blodgett (LB) films with single-walled carbon nanotubes (SWCNTs) for ethanol vapour detection.

This chapter describes the fabrication of an extrinsic fiber optic sensor probe by using etched plastic clad silica (PCS) fiber. Also we discuss the theory and principle of operation of the designed fiber optic probe and the successful utilization of the probe for quantifying alcohol concentration in their binary mixtures with water. The designed sensor works on the principle of hydrophilic adhesion of molecules on to the silica fiber and can be effectively utilized for determining the concentration of ethanol, methanol and 2-propanol in their binary mixtures with water.

### 2.2 Fabrication of fiber probe

The designed sensor probe consists of two fibers, one of which transmits light into the medium to be investigated and the second fiber directs the modulated light back into the photo detector. We have used plastic clad, step index silica fiber with a core diameter of 400 µm (Newport F-MBC, 0.37 NA) having a length of 50 cm for the probe preparation. After removing the sheath from the tip of both the fibers (around 1mm), the tip is dipped in acetone for removing the cladding. The prepared tip of each of the fiber is then dipped in hydro fluoric acid (48%) for about 30 minutes for etching. Etching produces a tapered region with a core of reduced diameter and both the fibers are then aligned parallel and glued together at one end as shown in figure 2.1 to form the sensor probe.
2.3 Theory

The principle underlying the working of the sensor probe is explained by Kumar et.al [89]. Consider the fiber structure shown in figure 2.2. Light from a multimode fiber of core diameter \( d \), is coupled into the decladded fiber region of smaller diameter \( d_e \) through an intermediate taper which is also decladded. The core refractive indices of all these three regions are same \( (n_i) \)
When light propagates from a fiber of diameter \( d \) to a region of diameter \( d_e \) through a tapered region, the fraction of optical power coupled is given by Kumar et al. [89] as

\[
P = P_0 \left[ \frac{n_i^2 - n_c^2}{R^2 (n_i^2 - n_{cl}^2)} \right]
\]

(2.1)

where \( P_0 \) is the input power, \( n_i \) is the core refractive index, \( n_{cl} \) the cladding refractive index and \( n_l \) the refractive index of the medium surrounding the taper and \( R = d/d_e \). From (1) it is clear that the coupled power \( P \) decreases with the increase in \( n_l^2 \). Thus power lost to the surrounding medium through the tapered region \( P_0 - P \) is proportional to the refractive index of the surrounding medium, \( n_l \).

2.4 Simulation studies

In order to study the working of the sensor probe a planar structure with parameters similar to that of the fiber is simulated using BeamPROP software package of RSoft.
A structure as shown in figure 2.3 is simulated where there is a core at the center having a width of 400 μm and refractive index 1.45. Laterally, the core extends to cladding of thickness 10 μm on either side with a refractive index of 1.4. Then on either side there is a layer analogous to sheath with a thickness of 105 μm making the total lateral width 630 μm. Axially, the core extends to a tapered region without the cladding and sheath layer. Then there is a layer corresponding to etched layer having width less than 400 μm. Two such structures are aligned exactly parallel like the fiber probe. Light of wavelength 532nm is coupled to one of the fibers and light propagation was simulated using the software. The field patterns thus
obtained for structures with different parameters are shown in figure 2.4a, 2.4b, 2.4c, 2.4d, 2.4e, 2.4f, 2.4g, 2.4h, 2.4i and 2.4j. The simulation result of an un-etched fiber probe is presented in figure 2.4a, where there is neither tapered region nor diameter reduction. In this case the unaltered fiber core of the two fibers extends out without cladding. From the simulation result it is obvious that the coupled light pass through the fiber and field coupling between the two fibers does not exist. Figure 2.4b shows the results where the fibers are reduced to a diameter of 200 µm but without a tapered region. In this case also there is no evidence for field coupling.
Fiber optic sensor for determining the quality of alcohol-water mixtures

Figure 2.4 Fibers etched to 200μm dia with c) 60 μm taper
d) 100 μm taper

e) 160 μm taper
f) 200 μm taper
Fiber optic sensor for determining the quality of alcohol-water mixtures

Figure 2.4 Fibers etched to 200 μm dia with g) 260 μm taper  
h) 300 μm taper

Figure 2.4 i) Fiber etched to 100 μm dia with 200 μm taper  
j) Fiber etched to 300 μm dia with 300 μm taper
Figures 2.4c, 2.4d, 2.4e, 2.4f, 2.4g and 2.4h shows the results for probes with tapered regions of different lengths and a narrowed core of width 200 μm. The height of the tapered region is 60 μm in the case of figure 2.4c while it is 100 μm, 160 μm, 200 μm, 260 μm and 300 μm respectively for figures 2.4d, 2.4e, 2.4f, 2.4g and 2.4h. Figure 2.4i shows the result for the probe where the tapered region has a height of 200 μm and the etched core has a width of 100 μm. From the graphs it is evident that there exists field coupling from the input fiber to the other and its strength varies with the dimension of the tapered region.

2.5 Experimental

The experimental setup used for the study is presented in figure 2.5. The emission from a 20mW diode pumped solid state laser source (λ=532 nm) is launched into one of the fiber arms of the sensor. The modulated optical signal is collected by the second arm, which is coupled to the detector head (Newport 818-SL) of a power meter (Newport 1815-C). To move the fiber probe in and out of liquid, the liquid carrying beaker is kept on a translation stage which can be moved with a resolution of 10μm.
2.6 Results and Discussions

We used pure water as the test medium to investigate the response of the fiber probe to liquid medium. Water was taken in the beaker and the probe was immersed in and then pulled out from water using the translation stage. The output power is plotted as a function of the liquid level displacement from the tip of the fiber probe and is shown in figure 2.7. The curve ABCD is the response obtained while moving the probe into water from air and DEFG represents the response obtained for the probe displacement in the opposite direction. The point ‘A’ represents the output power when the probe was in air while ‘B’ indicates the point where the tip touched water surface. The point ‘C’ represents the intersection point of water surface and the tapered region. When the fiber probe is in air, a part of light intensity leaks through the etched region of the input fiber and gets coupled into the output fiber as shown in the simulation results. The coupled light then reflects back from the tip of the second fiber and is collected back.
Fiber optic sensor for determining the quality of alcohol-water mixtures

at the receiver. This power remains constant, and can be termed as the reference value. The detector output reduces from the reference value when the probe is immersed in water. A sharp increase in output is obtained when the probe tip is pulled out of water surface as shown by the curve FG in figure 2.7. The marking ‘F’ corresponds to the point where the probe tip is just out of water surface. The marking ‘B’ corresponds to the point at which the probe tip touch water surface while moving in and ‘F’ the point at which the tip leaves the water surface while moving out. A separation of around 750μm is observed between ‘B’ and ‘F’ and this is due to the surface tension effect of water.

![Figure 2.7 Response of the probe when dipped and pulled out of water](image)

To explain this phenomenon of sharp increase in output, another experiment was conducted. Light was allowed to pass through a silica fiber which has a decladded region and the output was recorded. Then a medium of higher refractive index was added around the decladded region and the varying intensity as a function of time was recorded. The experiment was
done with liquids like ethanol (RI 1.36), 2-propanol (RI 1.375) and water (RI 1.33). Another medium with a higher refractive index was made by mixing ethyleneglycol and water having a measures refractive index 1.43. The experiment was repeated for this liquid too. The result thus obtained is shown in figure 2.8. From the basic theories of decladded optical fiber, it is clear that the output should decrease when a medium with refractive index higher than 1 is added around the decladded region. From the result it is observed that for water the output increases while for all other liquids it decreases. Silica is hydrophilic in nature and hence water molecules adsorb on to the fiber [90]. This enhances back reflection of light into the core at the core medium interface and hence causes the increase in output. Adsorption does not happen in the case of alcohols and the medium with refractive index 1.43. An entirely opposite response was obtained when the silica fiber was replaced with a polymer optical fiber and the result is shown in figure 2.9. In this case the output power reduced when water was the ambient medium while it increased when ethanol was introduced.

Figure 2.8 Response of decladded PCS fiber towards various ambient liquids
As per equation 2.1, the optical power leaking through the tapered region is proportional to the refractive index around the tapered region. From the simulation studies as well it is clear that the input light leaks through the tapered region and couples to the second fiber. A fraction of light reflects back from the tip of the second fiber and is collected back at the detector and this represents the intensity at the point ‘A’ in figure 2.7. When the tip touches water surface back reflection reduces due to absorption by water. This causes the reduction in output at the point ‘B’. As the tapered region intersects with water, though more power leaks out, the increase in absorption cause the further reduction of output power at point ‘C’. Since silica is hydrophilic water molecules adsorb on to it and once the fiber comes out of water they act as scattering centers. This increases the field coupling and causes the drastic increase in output marked by FG in the response curve.

As time progresses the output intensity drops to reference value due to evaporation of the adsorbed molecules and is shown in figure 2.10. This response of the probe can be utilized as a liquid level sensor.
To further verify these conclusions, the experiment was repeated using ethanol water mixtures. Ethanol was mixed with de ionized water at various volumetric ratios using ultrasonicator to prepare the test solutions at required concentrations. Efforts were taken to conduct experiments at constant temperature of 25\(^\circ\)C. The beaker filled with the test solution was kept on the translational stage (figure 2.5) and after immersing in it, the probe was pulled out. The initial intensity maximum and the time taken by the intensity to drop to the reference value were recorded for each ethanol concentration. The evaporation rate of ethanol is higher than that of water and it is obvious that in this mixture with water the evaporation rate increase with the increase in ethanol concentration. The time taken by the response to reach reference as a function of ethanol volumetric concentration is given in figure 2.11. From the response given in figure 2.11, it is evident that the output drops to reference value at a faster rate when the ethanol
concentration is higher. As the ethanol concentration in the solution became high (more than 80%) the sudden rise in the intensity was not observed. This proves the assumption of molecular adsorption on to the fiber. These adsorbed molecules cause the sudden increase in output and eventually on evaporation the output drops to reference value. Since ethanol does not have hydrophilic head groups adsorption does not occur.

Another interesting observation from the experiment with ethanol water solution is that the initial intensity maximum varies with ethanol concentration. The plot in figure 2.12 gives the output intensity as a function of ethanol concentration where the X axis gives the volumetric percentage of ethanol in the solution and Y axis gives the ratio of the maximum output to that of the reference value. Even though the maximum output and the ratio of maximum output to the reference value gives the same trend, the method of taking the ratio helps in reducing noise due to the ambient light. We repeated
the experiment several times by varying the input power, wavelength of the laser etc but the curve peaks around 60% V/V concentration and when converted to mole fraction of ethanol it is around 0.3.

The experiment was repeated with aqueous mixtures of methanol and 2-propanol and the results obtained are shown in figure 2.13 and figure 2.14 respectively.

From the results obtained using the probe for ethanol, methanol and 2-propanol it is obvious that the probe can be used as a sensor for determining the volumetric concentration of alcohol-water binary mixture. In the case of ethanol it is evident from figure 2.12 that the response is almost linear in the ethanol volumetric concentration range 0% to 60% and 60% to 90%. In the case of methanol the response is linear (figure 2.13) in the volumetric concentration range 50% to 100% while for 2-propanol (figure 2.14) the linear range for volumetric concentration is in between 0% to 40% and 40% to 100%.

Figure 2.12 Sensor output as a function of ethanol concentration
Fiber optic sensor for determining the quality of alcohol-water mixtures

Figure 2.13 Sensor output as a function of methanol concentration

Figure 2.14 Sensor output as a function of 2-propanol concentration
The results reveal that the phenomenon is related to molecular level and hence rather than volumetric ratio mole fraction gives a better insight. In order to compare the results the sensor parameter was normalized and plotted as a function of alcohol mole fraction. The results thus obtained for methanol, ethanol and 2-propanol are shown in figure 2.15 while that for tert-butanol is shown in figure 2.16. The plots give the variation of the sensor parameter as a function of alcohol mole fraction. The X axis gives the mole fraction of alcohol in the solution while the Y axis gives the normalized ratio of the initial maximum output (detector output just after pulling out the probe from liquid) to that of the reference value (detector output just before immersing the probe into the liquid).

Figure 2.15 Normalized sensor parameter as a function of alcohol mole fraction.
It is evident from figure 2.15 that methanol and ethanol show maximum output intensity at the alcohol mole fraction of 0.3 and 2-propanol at 0.15. Tert-butanol shows a different type of response in which the output intensity starts to decrease at the mole fraction of 0.05 and shows a dip at 0.1 (figure 2.16). These critical mole fractions obtained using the fiber probe is similar to the values available in the literature and hence the response can be explained only in terms of cluster formation in the alcohol water mixture. Butanol and higher alcohols are more hydrophobic in nature and the alcohol molecules take part directly in the micellization process and become unique components of the micelle aggregate whereas the less hydrophobic alcohols, methanol to propanol, are mainly soluble in aqueous solution [91].

In its pure form water molecules form cluster of around 30 molecules and on addition of alcohol molecules these clusters start to break due to hydrophobic interaction between water and alcohol molecules [91]. In the case of methanol, ethanol and 2-propanol, the large structure of water break down completely at the critical concentration causing a drastic reduction in the cluster size of water. This reduction in size of the water cluster eventually
Fiber optic sensor for determining the quality of alcohol-water mixtures

reduces scattering which in turn causes a decrease in light coupling. Further addition of alcohol reduces the hydrophilic head groups per unit volume and hence the output power reduces continuously.

In the case of tert-butanol, the decrease in intensity after first critical point at 0.05 can be attributed to the breakdown of water structure. Unlike in the case of other alcohols, micellization occurs in tert-butanol-water mixtures. The tert-butanol molecules encapsulate water molecules and this causes a drought in hydrophilic head groups in the solution. This can be the cause of the sharp dip at mole fraction of 0.1.

Conclusions

In this chapter we discussed the design and fabrication of an intensity modulated extrinsic optical fiber sensor probe. The probe was fabricated by chemically etching a plastic clad silica fiber using hydro fluoric acid. The theory of working was explained and the simulation results using RSoft was presented. The effective use of the probe as a water level detector was explained. The probe was used for the measurement of critical concentration of binary mixtures of alcohol and water. The critical mole fractions obtained using the robust and inexpensive probe are 0.3 for methanol and ethanol, 0.15 for 2-propanol and 0.05 and 0.1 for tert-butanol, which agrees well with the values found using methods like neutron diffraction studies and microwave analysis. The results also give an evidence for micellization in tert-butanol water mixtures. The probe can be effectively used for quality evaluation of alcohol-water mixtures which has applications in food and beverage industries.

References

Fiber optic sensor for determining the quality of alcohol-water mixtures


Fiber optic sensor for determining the quality of alcohol-water mixtures

Fiber optic sensor for determining the quality of alcohol-water mixtures


Fiber optic sensor for determining the quality of alcohol-water mixtures

Fiber optic sensor for determining the quality of alcohol-water mixtures

Fiber optic sensor for determining the quality of alcohol-water mixtures

