

Intensity Modulated Fiber Optic Chemical Sensor – Molar Volumes, Refractive Indices, Electronic Polarization, Molar Refractions of Binary Liquids

V Sreehari babu¹, A. Jayanth kumar², S. Chandralingam³

Asst. Professor, Department of Physics, Guru Nanak Institutions Technical Campus, Hyderabad, India¹

Professor, Department of Physics, Institute of Aeronautical Engineering, Hyderabad, India²

Professor, Department of Physics, JNTU-Hyderabad, Hyderabad, India³

ABSTRACT: Refractive indices and densities of binary mixtures like ethanol with benzene and methanol with benzene have been measured at room temperature (303K). From the values of the measured Refractive indices and densities, molar refractions (R), molar volumes (V), and electronic polarization (ϵ) of the mixed solvents were calculated. Intensity modulated fibre optic chemical sensor probes are designed and used to sense the binary mixtures at different concentrations or mole fractions.

KEYWORDS: Fibre optic chemical sensor, refractive index, molar refraction, electronic polarization

I. INTRODUCTION

Prediction of refractive indices of binary liquid mixtures is essential for the determination of composition of binary liquid mixtures. Refractive index measurements in combination with density, boiling point, melting point and other analytical data are very useful industrially also for common substances which include oils, waxes, sugar syrups etc.[1]. Organic liquids are very important in various fields such as biomedical science, pharmaceuticals, solvent system for the refraction medium, chromatographic techniques and solvents system in spectroscopy. Physical properties of a substance depend on the internal structure or the constitution of the molecule. Thus, the determination of properties such as refractive index, molar refraction, molar polarization, electronic polarization, etc. can provide valuable informations about the structure of molecules, binary, ternary mixture of liquids[2-5]. Fiber optic sensors (FOS) have received considerable attention in the recent years because of their inherent immunity to electromagnetic interference, safety in hazardous and explosive environment, high sensitivity and long distance remote measurements. The miniature size, low cost, intrinsic safety and ease of installation of FOS makes this system ideal for applications in various engineering areas including numerous in line chemical, food, beverages or medical analysis and monitoring system. L. M. Bali et al had developed an optical sensor for determining the proportional composition of two liquids in a mixture [6]. Some others developed fiber optical chemical sensors for refractive index, PH measurements, and organic pollutants in water[7-11] with various sensing mechanisms and different sensor designs. In the present work, an intensity modulated fiber optic chemical sensor for refractive indices, molar refractions and polarizations of binary liquids (Benzene with ethanol and benzene with methanol) was developed.

II. MATERIALS & METHODS

All the chemicals used (Benzene, ethanol and methane) were of A. R. grade with purity >99%. The purity of liquids was checked by comparing experimental values of densities and refractive index of these liquids. The optical fiber used in the experiment was a standard commercial step index polymer optical fiber (POF) with a

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Polymethylmetacrilate (PMMA) core of diameter 0.980mm surrounded by a thin cladding layer of fluorinated polymer. The core refractive index (n_{core}) was 1.49 and the numerical aperture was 0.5. The refractive index of clad made of fluorinated polymer is 1.4036. Acetone is applied to the POF using a cotton bud and neutralized with the de-ionized Water. Acetone reacted with the surface of the polymer to form milky white foam on the outer cladding which was then removed by the sand paper. The MFOE 71, 9508, Mexico, LED was used which provides the radiation at the wavelength of 630 nm. The length of the optical fibre used was 30 cm with a core diameter of 1mm, from which cladding of 6 cm was removed from the central region. The photo detector used was MFOD71, 9432, Mexico which converts the light intensity into the proportionate current.

III. EXPERIMENT

Binary mixtures were prepared by mixing a known mass of each liquid in an airtight, stopper glass bottle. Refractive indices of pure liquids and binary mixtures were measured using thermostatically controlled Abbe's refractometer with accuracy 0.001 units. Calibration was performed by measuring the refractive indices of doubly distilled water. The masses were recorded on digital balance Aux 220 series to an accuracy of $\pm 1 \times 10^{-4}$ g. Care was taken to avoid contamination during mixing.

25ml specific gravity bottle was used for density measurements. It was calibrated with freshly prepared triply distilled water. The density measurements for each experimental liquid were repeated three to four times so as to get low uncertainties of $\pm 5 \times 10^{-4}$ gm/ml in density measurements.

From the measured values of densities and refractive indices, the values of molar volume (V), electronic polarization (ϵ), molar refraction were computed using the formulae:

The molar refraction R_m of pure liquid is given by

$$R_m = \left[\frac{n^2 - 1}{n^2 + 2} \right] \frac{M}{\rho} \quad \rightarrow (1)$$

Where, n- Refractive index; M- Molar mass; ρ - density

For binary mixture, Molar volume

$$V_{ms} = \frac{M_1 X_1 + M_2 X_2}{\rho_{ms}} \quad \rightarrow (2)$$

And Molar refraction,

$$R_{ms} = \left[\frac{n^2 - 1}{n^2 + 2} \right] \left[\frac{M_1 X_1 + M_2 X_2}{\rho_{ms}} \right] \quad \rightarrow (3)$$

Where, R_{ms} is molar refraction of solution; n is Refractive index of solution; M_1 and X_1 are Molar mass and mole fraction respectively of first compound; M_2 and X_2 are Molar mass and mole fraction respectively of second compound and ρ_{ms} is the density of binary mixture.

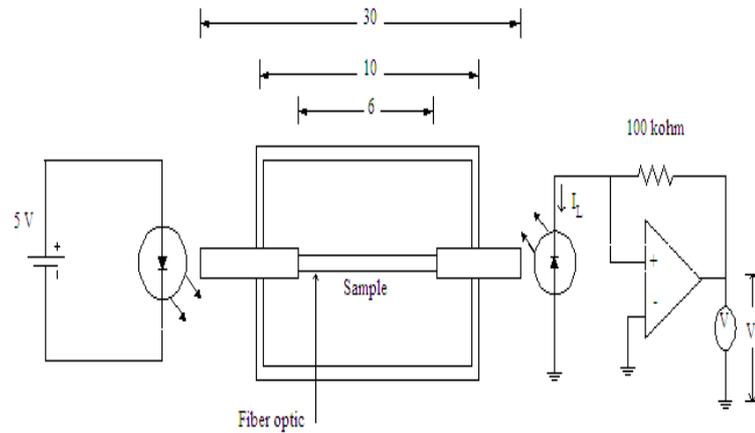


Figure 1. Experimental setup

Fig 1: Fiber optic chemical sensor design with simple electronic circuit

The experimental set-up of the proposed electronic technique to determine the molar refractions of binary mixtures of different concentrations is shown in Fig. 1. It consists of 5V constant dc supply connected to the LED. The light emitted by an LED is proportional to the forward current. Light emitting diodes are designed to produce coherent light at 630 nm wavelength with a very narrow bandwidth.

Silicon photodiode is being used as the photo detector in the circuit. The current of the photo detector is proportional to the intensity of the incident light falling on it. The photo detector is in the photovoltaic mode, which offers lower noise and therefore, is better suited for measurement and instrumentation applications. The Op-Amp's input impedance being very high, the photo diode current flows through the feedback resistor. This current is converted into a proportional voltage given by

$$V_o = I_L \times R \quad \rightarrow (4)$$

IV. RESULTS

The values of densities, refractive indices, molar volumes, electronic polarization and molar refractions for pure liquids were obtained and recorded in table 1

Table 1: Refractive index, density and molar refractions of pure liquids at 303K

Compound	Molar mass M	Refractive index n	Density ρ (g/ml)	Molar volume $V = \frac{M}{\rho}$	Molar refraction R_m
Benzene	78.112	1.501	0.8680	89.99	26.512
Methanol	32.04	1.3276	0.7860	40.763	11.2516
Ethanol	46.07	1.3582	0.7862	58.598	12.87

The values of densities, refractive indices, molar volumes, electronic polarization and molar refractions for binary mixture of ethanol and benzene at various mole fractions were obtained and recorded in table 2

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Table2: Properties of Binary mixtures of Ethanol-Benzene

Compound		Refractive index n	Electronic polarization $\epsilon = n^2$	Density ρ_{ms} gm/ml	Molar volume V_{ms}	Molar refraction R_{ms}
Mole fraction of Benzene X_1	Mole fraction of Ethanol X_2					
0.0674	0.8542	1.3829	1.9124	0.8002	63.4	14.7853
0.2769	0.7231	1.4020	1.9656	0.8113	67.721	16.3652
0.3983	0.6017	1.4183	2.012	0.8212	71.64	18.0707
0.5063	0.4937	1.4339	2.0561	0.8292	75.12	19.5592
0.5063	0.4937	1.4339	2.0561	0.8292	75.12	19.5592
0.6058	0.3942	1.4469	2.0935	0.8370	78.23	20.89
0.6974	0.3026	1.4608	2.1340	0.8439	81.071	22.2386
0.7819	0.2181	1.4727	2.1688	0.85084	83.59	23.4359
0.8216	0.1784	1.4769	2.1812	0.8538	84.79	23.9534
0.9326	0.1458	1.4924	2.2273	0.8628	89.111	25.871
0.8611	0.1389	1.4826	2.1981	0.85712	85.94	24.52
0.8971	0.1029	1.4872	2.2117	0.8599	87.004	25.03

The variation in molar refraction with various molar quantities of benzene in the binary mixture of benzene and ethanol was plotted [Fig 2]. It was observed that, as the quantity of benzene in the mixture of benzene – ethanol increases, then the molar volume, refractive index and hence molar refraction also increase showing linear trend.

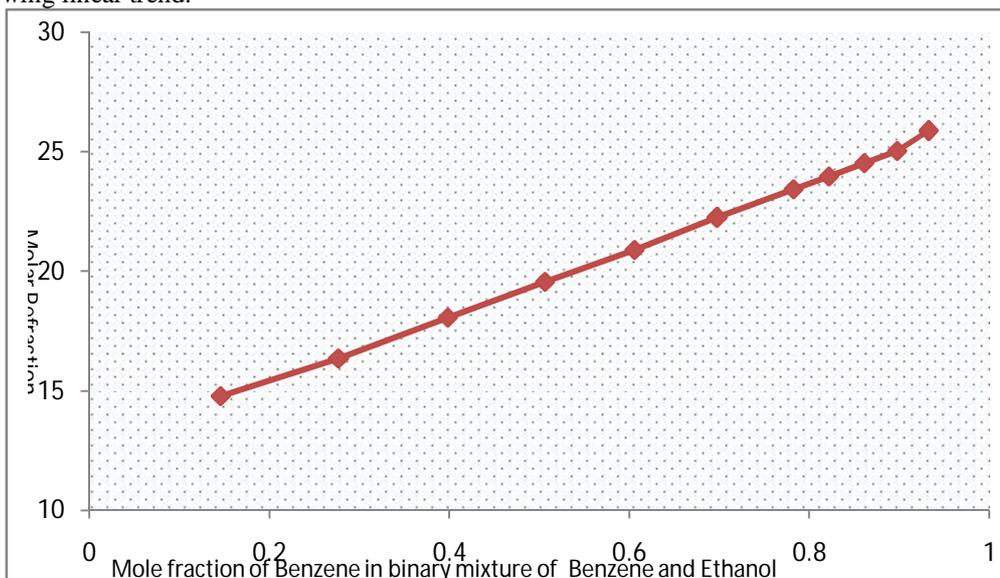


Fig 2: Variation of molar refraction with mole fraction of Benzene in Binary mixture of Benzene-Ethanol

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The values of densities, refractive indices, molar volumes, electronic polarization and molar refractions for binary mixture of methanol and benzene at various mole fractions were obtained and recorded in table 3.

Table 3: Properties Binary mixtures of Benzene-Methanol

Compound		Refractive index n	Electronic polarization n $\epsilon = n^2$	Density ρ_{ms} gm/ml	Molar volume V_{ms}	Molar refraction R_{ms}
Mole fraction of Benzene X_1	Mole fraction of Methanol X_2					
0.1976	0.8024	1.3629	1.8574	0.8071	50.98	12.8816
0.3579	0.6421	1.3918	1.9371	0.8192	59.24	14.0999
0.4878	0.5122	1.4148	2.0016	0.8297	65.70	16.4455
0.5975	0.4025	1.4327	2.0526	0.8374	71.14	18.4767
0.689	0.3110	1.4498	2.1019	0.8444	75.53	20.2911
0.7691	0.2309	1.4629	2.1401	0.8504	79.34	21.8487
0.8384	0.1616	1.4739	2.1723	0.8557	82.58	23.2026
0.8695	0.1305	1.4791	2.1877	0.8587	83.96	23.8132
0.8984	0.1016	1.4843	2.203	0.8604	85.34	24.4290
0.92652	0.07348	1.4887	2.2162	0.8624	86.65	24.9954
0.95547	0.04753	1.4936	2.2308	0.8643	88.11	25.6336

The variation in molar refraction with various molar quantities of benzene in the binary mixture of benzene and ethanol was plotted [Fig 3]. It was observed that as the quantity of benzene in the mixture of benzene –methanol increases, then the molar volume, refractive index and hence molar refraction also increase showing linear trend.

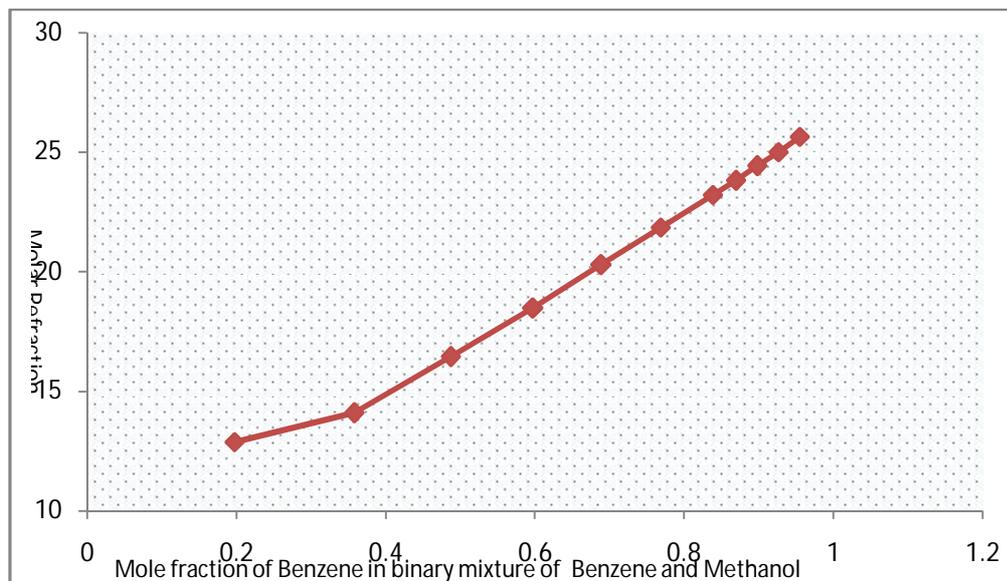


Fig-3: Variation of molar refraction with mole fraction of Solvent (Benzene) in binary mixture of benzene and ethanol

The variation in the output voltage for each value of the concentration of benzene in ethanol was measured with the proposed electronic technique and was represented in Fig.4. The output voltage decreases almost linearly with increase in the percentage of benzene in ethanol-benzene binary mixture. As the volume of ethanol in the binary

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mixture approaches zero, the refractive index of the mixture approaches the core refractive index of the fiber and hence the output voltage drops to minimum value.

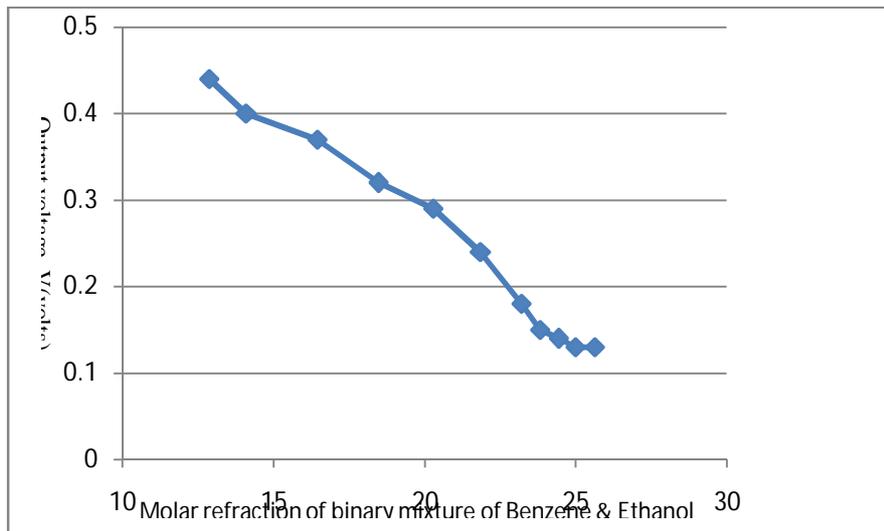


Fig-4: Output voltage vs. Molar refraction of Benzene-Ethanol binary mixture

The variation in the output voltage for each value of the concentration of benzene in methanol was measured with the proposed electronic technique and was represented in Fig.5. The output voltage decreases almost linearly with increase in the percentage of benzene in ethanol+benzene binary mixture. As the volume of methanol in the binary mixture approaches zero, the refractive index of the mixture approaches a little higher value than the core refractive index of the fiber and hence the output voltage drops to much lower values than those compared to benzene-ethanol mixture.

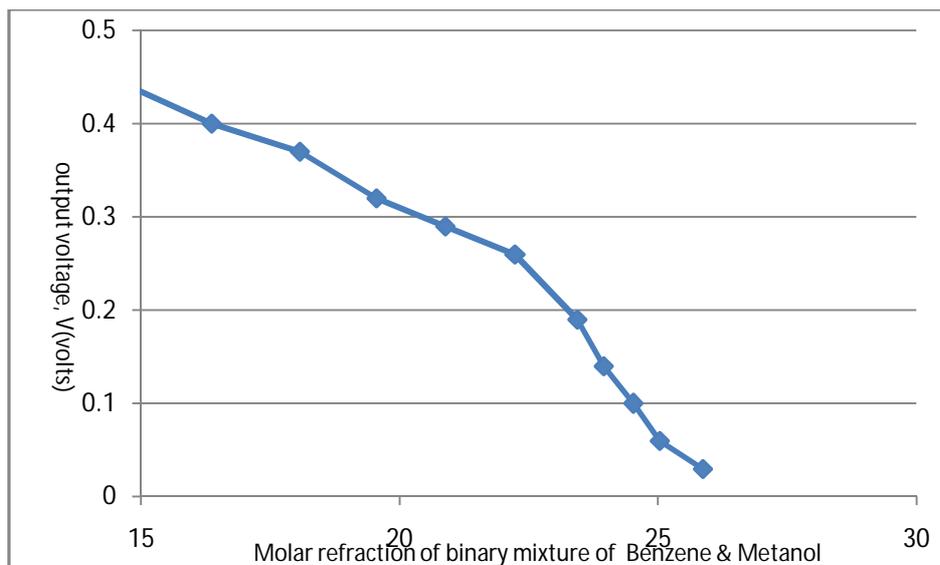


Fig-5: Output voltage vs. Molar refraction of Benzene-Methanol binary mixture

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VI. CONCLUSIONS

Refractive indices, densities of binary mixtures were determined at various concentrations. From these measured values, molar volumes, electronic polarization and molar refractions at various concentrations of binary mixtures were computed. A plastic fibre optic sensor probe was designed to measure the variations in molar refractions of binary mixtures of benzene-ethanol and benzene-methane and was calibrated. It was observed that, the refractive index value and molar refraction increase with increase in Mole fraction of benzene. Also, the molar refraction value was observed to increase with rise of refractive index of the mixture. The output voltage decreases with increase of Molar refraction (or Benzene's mole fraction) as is observed from the graphs in fig 4 and fig 5.

It could be seen that from table-2&3, the values of refractive index decreases with decrease in concentration of solution. As the concentration of solute decreases, distance between the molecules of solute increases. Hence refractive index, molar refraction and polarizability constant of ligand decreases. The substituent which has less effect of polarization has greater value of molar refraction and polarizability constant than others substituent. *This data have been used to determine solute-solute, solute-solvent and solvent-solvent interaction in the system.*

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