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Study of Dielectric constant, Density and Refractive index in binary mixtures of n-butanol with formamide

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Abstract – In this study, the binary mixtures n-butanol with formamide were investigated, focusing on their dielectric constant, density and refractive index. The dielectric constants were measured to assess the electrostatic interactions within the mixtures, density values provided insights into the overall composition and packing of molecules. Additionally refractive index data offered information on the optical properties of the mixtures, through systematic analysis. we observed variations in these properties in n-butanol with formamide binary mixtures. These findings contribute to a deeper understanding of the physicochemical behaviour of these mixtures. From the experimental dielectric data, excess dielectric constant, Kirkwood correlation factor, Bruggeman factor are estimated and reported in the study. The results show that the dielectric constants, densities and refractive index of the binary mixtures, decreases with increasing percentage of volume of n-butanol and the study shows the presence of molecular interactions and hydrogen bonding in the binary mixtures.

***Keywords*- Binary liquid mixtures, Dielectric constant, Kirkwood correlation factor, Hydrogen bonding, Density and refractive index, Formamide–n-butanol system, Bruggeman factor**

INTRODUCTION

I. **B**inary mixtures refer to a system composed of two different substances, or components that are physically combined. These mixtures can be classified as homogeneous or heterogeneous, in a homogeneous binary mixture, the components are uniformly distributed, creating a single phase, like a solution. In contrast, heterogeneous binary mixture consists of distinct phases, a heterogeneous binary mixture consists of distinct phases, such as oil and water. At molecular level, binary mixtures involve interaction between the molecules of two distinct substances.[3,4]

II. The nature and strength of intermolecular forces between the components influence the mixture's behaviour, for example, Hydrogen bonding in water –alcohol mixtures lead to specific properties like azeotropes. Polar molecules exhibit these interactions, impacting properties such as boiling point and solubility in binary mixtures. Binary mixtures influence osmotic pressure, particularly in solution where a solvent interacts with a solute. The solubility of one component in another varies based on factors like temperature and pressure. [6,7]

Binary mixtures are integral in chemical reactions and processes. Solvent and solute combinations play a crucial role in extraction, distillation and reaction mechanism. Drug formulations often involve binary mixtures to enhance solubility control release rates, and for improving bioavailability.[3,4]

In this comprehensive experimental exploration. We meticulously investigated the binary mixture of n-butanol and formamide, probing into their dielectric constant, density and refractive index at controlled temperature 293.15K.

The subsequent calculation of key parameters, including experimental dielectric data, excess dielectric constant, Kirkwood correction factor, and Bruggeman factor, allowed for a nuanced understanding of the mixture's behavior. A significant and intriguing observation emerged from the results. A systematic decline in the dielectric constant, densities and refractive indices as the volumes decreased. This finding prompts a more profound inquiry into the molecular dynamics and intermolecular forces governing this phenomenon. The observed variations could potentially be attributed to alterations in the molecular arrangement, hydrogen bonding patterns, or other intricate interactions between n-butanol and formamide molecules. Further investigation and in-depth analyses are warranted to unravel the underlying mechanisms driving these observed changes, contributing to a deeper comprehension of the complex behavior exhibited by this binary mixture.

I. Experimental Material

The chemicals used in the present investigation are of spectroscopic grade with 99.9% purity, and were used without further purification. The solutions were prepared by mixing n-butanol with formamide at eleven different volume percentages of n-butanol with Formamide as a 100% in steps of 10%.

- **Methodology**

- **Measurement of dielectric constant**

- The dielectric constant of the binary mixture was measured using a wet sensor make by Delta-T Devices Ltd. Uk, which is based on the principle of frequency domain reflectometry (FDR) technique. When power is applied to the sensor, it creates a 100 MHz frequency Signal, this Signal is then applied to pair of stainless-steel rods, which transmit an electromagnetic field in to mixture. The field passes easily through the mixture resulting in stable voltage output that acts as a simple sensitive measure of the dielectric constant. The measurements were recorded with a calibrated meter which is connected to the wet Sensor through a cable. When probes of the sensor inserted into the mixture, pressing the read button on meter, the dielectric constant reading will appear on it. This measurement was repeated five times and the average value of reading was taken as a dielectric constant of mixture. The accuracy of measurement of the dielectric constant was ±3%.[1,2]

- **Measurement of refractive index**

- The refractive index is a useful optical property exhibiting ionic or molecular behavior of a mixture and determine basically the molecular structure, wavelength and temperature. The refractive index can offer valuable information concerning the molecular rearrangement and mixing also a few useful properties like electronic polarizability. The refractive indices values of binary mixture of n-Butanol with Formamide were measured using a digital pocket refractometer PAL-RI make by Pitago Japan. The apparatus measures the refractive index of liquids in the range of 1:3306 to 1.5284 The uncertainty in the measurement of refractive indices was ±0.0003.[1]

Measurement of density

Density of binary mixtures were measured using An Anton paar oscillation U-tube densitometer (Model DMARK Austria), calibrated with double distilled water and air. The densities of pure liquids and their mixtures were carried at single temperature, as there is no facility for temperature variation for this model.

The density values have a standard uncertainty of ± 10 cm^3.[1]

Methodology

Molar refraction, Polarizability, Solvated Radii, Molecular Polarization, and Excess Molar Volume

From experimental densities (d) and refractive indices (n) of pure substances and mixtures, we have calculated the molar refraction (R) from the equation.[1]

$$R=\left(\frac{n^2-1}{n^2+2}\right)V_m=P_A+P_E=P_T=P_D, \quad 1)$$

Where, n is the refractive index of the liquid and V_m = M/d is molecular volume, in this M and d is the molecular weight and the density of the pure liquids respectively. The right-hand side of Eq. (1) is equal to the summation of both atomic polarization (P_A) and electronic polarization (P_E) and that is equal to the distortion polarization (P_D).

Atomic (Ionic) Polarization (P_A)

Atomic or ionic polarization occurs due to the relative displacement of positively and negatively charged ions in a molecule under the influence of an external electric field. This type of polarization is significant in ionic substances and depends on the mass and charge of the ions.[1,2]

Electronic Polarization (P_E)

Electronic polarization arises due to the displacement of the electron cloud relative to the nucleus when an external electric field is applied. This displacement induces a dipole moment in atoms or molecules. It is present in all types of substance and occurs almost instantaneously due to the small mass of electrons.

Distortion Polarization (P_D)

Distortion polarization is the combined effect of electronic and atomic polarization resulting from the deformation of the charge distribution within a molecule. It represents the total polarization arising due to displacement of both electrons and ions.

The atomic polarization (P_A) was calculated from the refractive indices (n) of pure substances and mixtures by the equation:

$$P_A = 1.05\, n^2 \quad 2)$$

The permittivity at higher frequency ε_∞ is the square of the refractive index and it was calculated by the equation:

$$\varepsilon_\infty\,(Permittivityathigher\ frequency) \quad 3)$$

Equation (3) expresses the **permittivity at higher frequency (ε_∞)** in terms of the **refractive index (n)** of the liquid mixture. This relation is based on the principle that, at very high frequencies (such as optical frequencies), only **electronic polarization** contributes to the dielectric behaviour, while dipole and atomic polarizations do not respond due to their slower nature.

Since the refractive index is a measure of how light propagates through a medium, it is directly related to the electronic polarization of the substance. Therefore, the square of the refractive index gives the dielectric permittivity at high frequency.

This equation is particularly useful for separating the contribution of **electronic polarization** from the total dielectric constant, thereby helping in the analysis of intermolecular interactions in the binary mixture.[1,2]

Dipole (Orientation) Polarization

Dipole polarization arises in polar molecules possessing permanent dipole moments. In the absence of an external field, these dipoles are randomly oriented, but under an applied electric field, they tend to align along the field direction, resulting in net polarization. This type of polarization is temperature dependent.[1]

where n is the refractive index of the binary mixture. The molecular dipole polarizability (α) was calculated from the experimental densities and refractive indices of pure substances and mixtures using Lorentz formula:

$$\alpha = \left(\frac{n^2-1}{n^2+2}\right)\frac{3V_m}{4\pi N}, \quad 4)$$

where n is the refractive index of the binary mixture, and V_m = M/d is molecular volume of the mixture.

Considering spherical form of the solvated molecules, the solvated radii of the pure solvents and binary mixtures were calculated using the equation:[1]

$$V_m = \left(\frac{4}{3}\right)\pi r^3 \quad 5)$$

Molecular Polarization (P_m)

Molecular polarization is the total polarization of a molecule and is the sum of electronic, atomic, and dipole polarization contributions. It provides a measure of the overall response of a substance to an applied electric field.

From experimental dielectric constants and densities of pure substances and mixtures the molecular polarization (P_m) was estimated using the equation:[1]

$$P_m = V_m \left(\frac{\varepsilon-1}{\varepsilon+2}\right) \quad 6)$$

where ε and V_m is the static dielectric constant and molecular volume of the binary mixtures [8, 9].

Excess Parameters (Excess Density (d^E), Excess Refractive Index (n^E), Excess Molar Polarization (P_m)E, and Excess Molar Volume $(V)_m$

Excess density (d^E). The excess density was measured from the density data (d), and it was calculated using the equation:[1]

$$d^E = d_{mix} - x_1 d_1 - x_2 d_2 \quad 7)$$

where d_{mix} is the value of density of mixture, and d1, d2 are the mole fractions and densities of the first and second solvents, respectively.

Excess refractive index (n^E). From the experimental refractive index (n), the excess refractive index was calculated using the equation [8]:[1]

$$n^E = n_{mix} - (x_1 n_1 - x_2 x_2) \quad 8)$$

where is the value of refractive index of the mixture and are the volume fractions and refractive indices of the first and second solvents, respectively. [1]

Table 1 presents the measured density of the mixture at different volume fractions of n-butanol.

Volume fraction of n-butanol in formamide	Dielectric constant	Density	Refractive index
00	110.09	1.12512	1.43986
10	100.44	1.10414	1.43972
20	91.56	1.07898	1.43584
30	82.38	1.0431	1.43156
40	73.20	1.01144	1.42704
50	64.02	0.9801	1.42298
60	54.84	0.9485	1.4179
70	45.67	0.9126	1.41328
80	36.48	0.88038	1.4083
90	27.30	0.84302	1.40252
100	18.13	0.81296	1.39814

The data shows a gradual decrease in density with increasing concentration, indicating proper mixing and the influence of molecular interactions on packing of molecules.

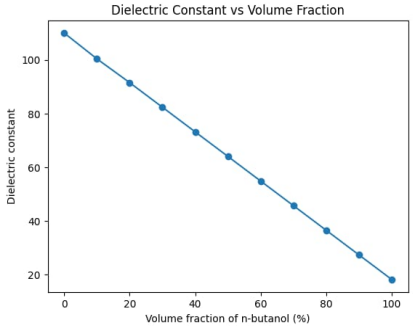

Fig a

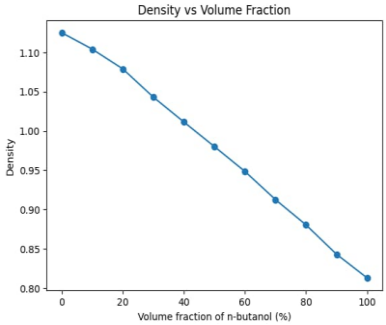

Fig b

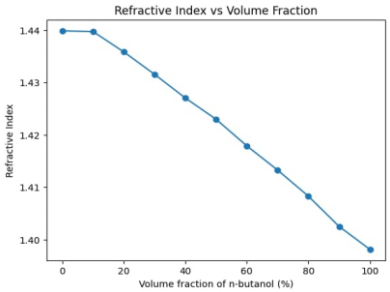

Fig c

Fig. the dielectric constant decreases with an increase in n-butanol concentration. This is because formamide is highly polar, whereas n-butanol has lower polarity. The decrease indicates a reduction in dipole–dipole interactions and changes in hydrogen bonding within the mixture. **Fig. b** the refractive index shows a gradual decrease with increasing n-butanol content. This behaviour reflects changes in molecular polarizability and density of the medium. The variation suggests modification in intermolecular interactions between the components. **Fig. c** the density of the mixture decreases with increasing volume fraction of n-butanol. This is due to the lower density of n-butanol compared to formamide. The smooth variation indicates good miscibility and suggests the presence of intermolecular interactions affecting molecular packing.

Volume fraction of n-butanol in formamide	Excess dielectric constant (ε^E)	Effective Kirkwood Correlation Factor (g^{eff})	Bruggeman factor (f_B)
00	00	1.05	1
10	-0.45	1.16	0.9
20	-0.13	1.28	0.84
30	-0.12	1.43	0.75
40	-0.10	1.62	0.68
50	-0.09	1.87	0.59
60	-0.07	2.21	0.49
70	-0.04	2.70	0.39
80	-0.042	3.48	0.27
90	-0.02	4.89	0.15
100	00	8.28	00

Table 2: Excess dielectric constant (ε^E), Kirkwood factor (g^{eff}) & Bruggeman factor (f^B)

- The **excess dielectric constant (ε^E)** is negative for most compositions.
  ➤ This indicates **weak intermolecular interactions** and possible **structure breaking** between formamide and n-butanol molecules.
- The **effective Kirkwood correlation factor (g^{eff})** increases with increasing n-butanol concentration.
- This suggests **enhanced dipole–dipole alignment** and increased molecular correlation.
- The **Bruggeman factor (f^B)** decreases continuously.
- This shows **deviation from ideal mixing behaviour**, confirming **non-ideal interactions** in the system.

Estimated values of molar volume (V_m), molar refraction (R_m), of formamide and n-butanol mixture at 298.15k temperature

Volume fraction of n-butanol in formamide	Molar volume	Molar refraction
00	0	**10.59**
10	-1.919	**11.43**
20	-3.338	**12.32**
30	-4.057	**13.35**
40	-4.696	**14.38**
50	-5.075	**15.47**
60	-5.104	**16.60**
70	-4.463	**17.87**
80	-3.662	**18.61**
90	-2.751	**20.31**
100	0	**21.96**

Table 3: Molar volume (V_m) & molar refraction (R_m)

The molar volume shows negative deviation. Indicates volume contraction due to strong molecular packing or interaction.

The molar refraction increases steadily with n-butanol concentration This suggests increase in polarizability of the mixture. The **molar polarization (P_m)** initially shows negative values and then increases. Indicates **rearrangement of molecular structure** and change in dipolar interactions. The **atomic polarization (P_a)** decreases slightly.

Estimate excess density $(d)^E$, excess refractive index $(n)^E$ excess molar polarization (pm)E, excess molar volume $(v)^E$ and deviation in molar refractive (ΔR) of formamide and n-butanol.

Volume fraction of n-butanol in formamide	Excess density	Excess refractive index	Excess molar polarization
00	0	0	0
10	0.17	0.28	-1.91
20	0.34	0.56	-3.33
30	0.49	0.84	-4.05

40	0.66	1.12	-4.69
50	0.82	1.40	-5.07
60	0.98	1.68	-5.10
70	1.14	1.96	-4.46
80	1.30	2.23	-3.66
90	1.46	2.51	-2.75
100	0	0	0

Table 5 The excess density (d^E) is positive. Indicates closer packing of molecules and strong intermolecular attraction. The excess refractive index (n^E) is also positive. Suggests increased interaction and polarizability. The excess molar polarization (P_m^E) is negative. Indicates destructive interaction between dipoles.

Table 6 excess molar volume $(v)^E$ and deviation in permittivity at higher frequency (ε_∞) of formamide and n-butanol

Volume fraction of n-butanol in formamide	**Excess molar volume $(v)^E$**	**Permittivity at higher frequency**
00	0	2.073
10	-1.9	2.072
20	-3.3	2.061
30	-4.0	2.049
40	-4.6	2.036
50	-5.0	2.024
60	-5.1	2.010
70	-4.4	1.997
80	-3.6	1.983
90	-2.7	1.967
100	-2.751	1.954

The excess molar volume $(V)^E$ is negative throughout. Confirms strong interaction and volume contraction in the mixture. The permittivity at higher frequency ($\varepsilon\infty$) decreases with increasing n-butanol. Indicates reduction in dielectric response at high frequency**.**

Results and Discussion

The dielectric constant, density, and refractive index of the mixture decrease with increasing concentration of *n-butanol*. This behaviour can be attributed to the fact that formamide is more polar and denser than n-butanol. As the proportion of n-butanol increases, the overall polarity and density of the system decrease.

The excess dielectric constant values are found to be mostly negative, indicating weak intermolecular interactions between the components. However, the increase in the Kirkwood factor suggests improved dipole alignment within the mixture, while the decrease in the Bruggeman factor confirms the non-ideal behaviour of the system.

The negative excess molar volume indicates volume contraction upon mixing, which occurs due to closer molecular packing and stronger intermolecular attractions. At the same time, the increase in molar refraction reflects enhanced polarizability of the mixture.

Molar polarization varies with composition due to molecular rearrangement, whereas atomic polarization shows a slight decrease, indicating minor structural changes at the molecular level.

The positive excess density and refractive index values suggest the presence of strong intermolecular interactions between the molecules. In contrast, the negative excess molar polarization indicates dipole opposition or reduced effectiveness of dipole alignment.

The negative excess molar volume further confirms strong interactions and compact molecular arrangement in the system. Additionally, the observed decrease in permittivity at higher frequencies is due to the reduced ability of dipoles to orient themselves under rapidly changing electric fields.

Overall, the results indicate that the binary mixture of formamide and n-butanol exhibits non-ideal behaviour. This is mainly due to intermolecular interactions such as hydrogen bonding and dipole–dipole interactions, which lead to structural rearrangement, volume contraction, and variations in dielectric and optical properties of the mixture.

Applications

The observed non-ideal behaviour of the formamide–n-butanol system. Non-ideal behaviour means strong interactions (like hydrogen bonding). This helps in choosing specific solvent mixtures for reactions where controlled interaction is needed. provides valuable insights into intermolecular interactions such as hydrogen bonding and dipole–dipole interactions. These interactions play a significant role in determining the physicochemical properties of liquid mixtures.

Such studies are useful in the selection and design of solvent systems for chemical and industrial processes, where specific solute–solvent interactions are required. The variation in dielectric properties and polarity makes this system suitable for applications in electrochemical devices, including batteries, capacitors, and sensors, where dielectric constant and permittivity are crucial parameters.

Furthermore, the non-ideal nature of the mixture can be effectively utilized in pharmaceutical formulations to enhance drug solubility, stability, and controlled release behaviour. The knowledge of excess thermodynamic properties is also important in optimizing separation techniques such as distillation and extraction, thereby improving process efficiency.

In addition, the variation in refractive index and polarizability indicates potential applications in optical materials and devices. Overall, the study of such non-ideal systems contributes significantly to the understanding and development of advanced materials, industrial processes, and molecular-level interactions in complex liquid mixtures.

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