Section A-Research

Hydrogen bonding and molecular interaction between 2-amino-5-bromobenzoic acid with n-alkanols

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Abstract:

The ultrasonic velocity (U), viscosity (η) and density (ρ) have been measured for binary liquid mixture containing 2-amino-5-bromobenzoic acid + ethanol, 2-amino-5-bromobenzoic acid + propanol and 2-amino-5-bromobenzoic acid + butanol at 299 K and 2 MHz frequency for different molar concentration. The adiabatic compressibility (β_{ad}), acoustic impedance (Z) intermolecular free length (L_f) and intermolecular free volume (V_f) are calculated from the experimental data. The molecular interaction present in the solvent mixture and hydrogen bonding is analyzed on the basis of this parameter. Furthermore, FTIR spectra confirmed the rupture or reduction of hydrogen bond.

Section A-Research

1. Introduction

The investigation of intermolecular interactions is crucial to the advancement of molecular sciences. Numerous studies have been conducted using a variety of physical techniques, including infrared [1, 2], the Raman effect [3-7], nuclear magnetic resonance, the dielectric constant [8], ultra-violet [9] and the ultrasonic approach [10, 11]. Recent years have seen a significant increase in the use of ultrasound for probing binary liquid mixtures' physico-chemical properties, that helps in comprehend the liquid state [12-14]. In industrial and technical operations, the study of the solution characteristics of liquid mixtures including both non-polar and polar components is useful. The majority of research on binary mixes is focused on estimating thermodynamic characteristics, such as L_f and β_{ad}, and their excess values in order to connect them to the binary mixtures constituent molecules' molecular interactions. Such concentration-dependent studies are also helpful for understanding the structure and complex molecular bonding and other molecular process [15-18]. Alcohols are organic liquids that can be associated with any group and are self-associated. They have a three-dimensional hydrogen band network [19, 20], therefore, it is intriguing to investigate the molecular interactions in binary mixes that contain alcohol as one of the components. Studies of liquid mixes that create hydrogen bonds in the system as a result of solute-solvent interactions and are becoming more and more popular. Alcohol solutions were subjected to ultrasonic measurements, which have proven to be very helpful in studying the structure of molecular interaction. Numerous uses for

determining ultrasonic velocity, density, viscosity, and their excess characteristics include evaluating behaviour and qualitatively estimating molecular interactions in the solutions.

In the present work, investigated acoustic Parameters, namely the Adiabatic Compressibility (β), Free Length (L_f), Free volume (V_f), and Acoustic Impedance (Z) for the binary mixtures containing 2-amino-5-bromobenzoic acid + ethanol, 2-amino-5-bromobenzoic acid + propanol and 2-amino-5-bromobenzoic acid + butanol at 299 K are made. In addition to the thermo physical and acoustic parameters, FTIR studies were also conducted for the hydrogen bonding of binary mixtures like 2-amino-5-bromobenzoic acid with ethanol, propanol and butanol, to determine how two miscible organic liquids interact with one another intermolecularly.

2.Experimental Techniques

The study of hydrogen bonding and molecules interaction of binary liquid mixtures has been carried out by using aromatic alcohols such as ethanol, propanol and butanol, supplied from Merck Co. which was 99.9% pure. These aromatic alcohols were used without any purification and mixed with 2-amino-5-bromobenzoic acid. Utilizing a multi-frequency 2 MHz) Ultrasonic Interferometer (Model: M-82S) obtained from M/S Mittal Enterprises, New Delhi, the ultrasonic velocity in the liquids and their mixtures was determined. Density measurements were made using an electronic balance machine and a 50 ml specific gravity bottle with an accuracy of 0.001 Nsm^{-2} and the sample's viscosity was measured using an Ostwald viscometer.

Sample preparation: Sample solutions are prepared at different volume percentages in 1- alcohols in step of 50% volume within a 0.01% error limit. The liquid systems of different desired concentration for the study have been prepared by weight fraction at laboratory temperature.

Suitable concentration in step of 0.02moleL^{-1} is used for all the systems. The complex in dilute solution also has been prepared by weight fraction to set same concentration. The fresh composition of liquid mixture has been performed and the mixtures were prepared freshly and stored in air tight bottles.

2.1Density Measurement

An apparatus called specific gravity bottle of capacity 50 ml is used to measure the density of pure liquids and mixes. The density of the experimental sample with different primary alcohols are calculated using the equation

$$\rho_s = \frac{m_s}{m_w}\,\rho_w$$

where ρ_s, ρ_w and m_s, m_w are the densities and masses of sample liquids and water respectively.

2.2 Viscosity measurement

The viscosity was determined using an Ostwald's viscometer kept in a constant temperature water-bath at 299K with accuracy ±0.001 Ns m^{-2}, using the value of viscosity of water at 299K from literature. The equation used for the computation of viscosity is,

$$\eta_s = \left(\frac{\rho_s t_s}{\rho_w t_w}\right)\eta_w$$

Where, ρ_s and ρ_w are the densities of the solution and water, t_w, t_s are the corresponding flow times of water and sample solution. η_s, η_w are the viscosities of water and sample respectively at temperature 299K.

2.3 Ultrasonic velocity measurement

The ultrasonic velocity measured by Ultrasonic interferometer with a tolerance of 0.005% from Mittal Enterprises in New Delhi, which operates at 2 MHz of fixed frequency. A quartz crystal fastened to the bottom of the measurement cell is excited at its resonant frequency by the high frequency generator. The measuring cell has a 12cc capacity. The reflector plate in the liquid can be raised or lowered by a fine micrometre screw with a minimum count of 0.01 mm at the top of the cell. A shielded cable is used to link the measuring cell to the high frequency generator's output terminals. Normal or quartz crystal ultrasonic waves are reflected from the reflector plate. In the space between the quartz crystal and the reflector plate, stationary waves are created. The micrometer is steadily moved until a predetermined number of maximum anode current readings (n) are crossed. The micrometer's overall movement is measured and noted (d).

The liquid's ultrasonic waves have a wavelength of $\lambda = 2d/n$. $U = \lambda f$ is the liquid's ultrasonic wave velocity.

2.4 Determination of thermo-acoustic parameters

The following standard formulas are used to derive the various thermo-acoustic parameters: Adiabatic compressibility (β)

The adiabatic compressibility (β) has been calculated from Laplace's equation

$$\beta = \frac{1}{\rho U^2}$$

Intermolecular free path length (L_f)

The intermolecular free length, which is separation between the surfaces of adjacent molecules, is calculated using the equation

$$L_f = \sqrt{\beta} K_T$$

Intermolecular Free Volume (V_f)

Intermolecular free volume (V_f) the important properties for studies the physio-chemical variability of the liquid mixtures and pure liquid. The free space and its associated qualities are closely related to molecular structure and can reveal intriguing details regarding interactions that could take place when two or more liquids are combined. The structural configurations, coupled with the shape and size of the molecules, have an impact on the molecular interactions between like and dissimilar molecules. A liquid can be thought of as being made up of individual molecules that are all moving in their own volumes V_f at average potentials caused by their nearby neighbors. In other words, a liquid's molecules are not completely close together, and there are few open spaces between them for movement and its volume V_f is called the free volume. Eyring and Kincaid [21] explained the free volume that enables a specific liquid molecule to travel and adhere to ideal gas laws. Free volume is evaluated by using the equation

$$V_f = \left[\frac{MU}{K\eta}\right]^{\frac{3}{2}}$$

Acoustic Impedance (Z)

Acoustic impedance Z is evaluated by using the equation, $Z = U\rho$

where ρ, η and M are the density, viscosity and molecular weight of the mixtures. K_T is the temperature dependent constant called as Jacobson's constant with value $K_T = 206$ and $K = 4.28 \times 10^9$ is the independent constant respectively

2.5 Fourier-transform infrared (FTIR)

The spectrometric instrument were used for measuring the infrared spectra of the binary mixtures at room temperature using JASCO FTIR 4100 type spectrometer at 299 K for absorption spectra [22-24]. The infrared (IR) spectra is significantly altered by hydrogen-bonding interactions, including frequency shifts of the order of hundreds of cm^{-1} and increases in IR bands intensity for associated to the functional groups which is directly involvement in the hydrogen-bonded bridges through their vibrational modes.

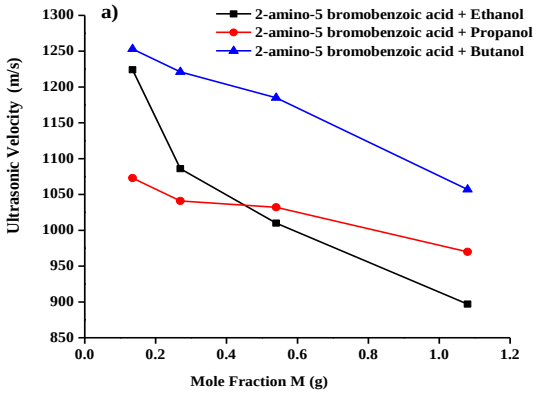
3. Result and Discussion

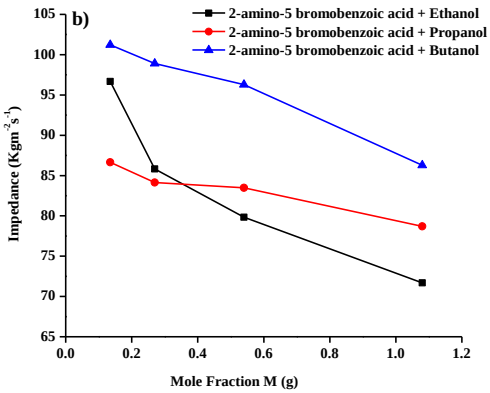
Table1. Lists the experimental ultrasonic velocity like ultrasonic, adiabatic compressibility, free volume, free length and acoustic impedance values for the three binary mixtures of 2-amino-5-bromopyridine with ethanol, 2-amino-5-bromopyridine with propanol, and 2-amino-5-bromopyridine with butanol at 299K.

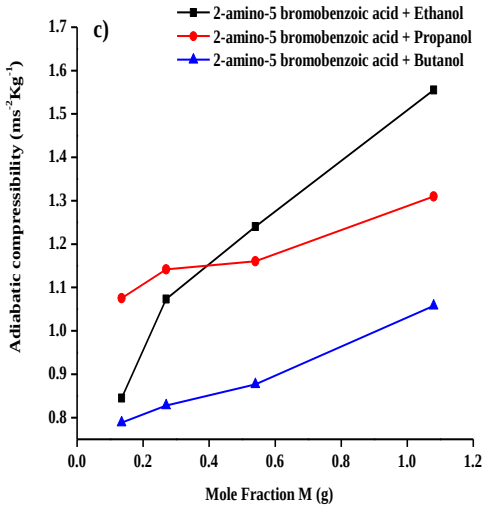
Name of Sample	Mole fraction (g)	Ultrasonic Velocity (m/s)	Impedance z × 10^{-4} ($Kgm^{-2}s^{-1}$)	Adiabatic compressibility β× 10^{-9} ($ms^{-2}Kg^{-1}$)	Intermolecular free length L_f × 10^{-7}(m)	Intermolecular free volume V_f × 10^{-10} (m^3mol^{-1})
2-amino-5 bromobenzoic acid + Ethanol	0.135	1224	96.6715	0.8451	1.8937	0.33177
	0.270	1086	85.8146	1.0730	2.1338	0.77514
	0.540	1010	79.8283	1.2402	2.2941	1.92114
	1.08	897	71.6873	1.5551	2.5688	4.32813
2-amino-5 bromobenzoic acid + Propanol	0.135	1073	86.659	1.0754	2.1362	0.08050
	0.270	1041	84.135	1.1417	2.2011	0.17997
	0.540	1032	83.486	1.1606	2.2192	0.46125
	1.08	970	78.694	1.3100	2.3577	1.12551
2-amino-5 bromobenzoic acid + Butanol	0.135	1253	101.211	0.7885	1.8292	0.083675
	0.270	1221	98.907	0.8280	1.8744	0.223639
	0.540	1185	96.284	0.8764	1.9284	0.596631
	1.08	1057	86.268	1.0577	2.1185	1.210786

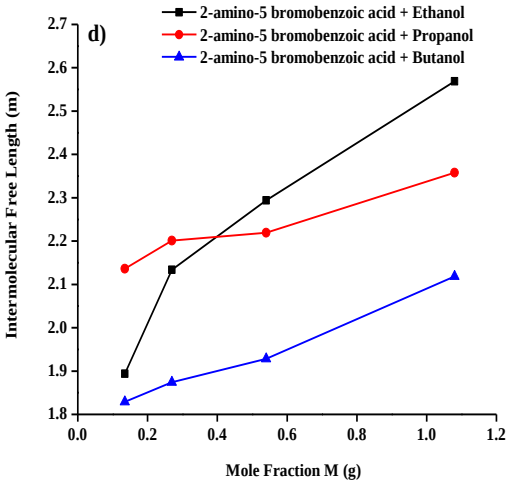
Name of Sample	Trial No.	Mole fraction (g)	Density of Sample **ρ** (Kg/m^3)	Viscosity of sample **η** (mP)
2-amino-5 bromobenzoic acid + Ethanol	1	0.135	789.80	8.059
	2	0.270	790.19	8.122
	3	0.540	790.38	8.249
	4	1.08	799.19	8.526
2-amino-5 bromobenzoic acid+ Propanol	1	0.135	807.64	18.160
	2	0.270	808.22	20.609
	3	0.540	808.98	21.816
	4	1.08	811.28	22.630
2-amino-5 bromobenzoic acid+ Butanol	1	0.135	807.75	20.667
	2	0.270	810.05	20.914
	3	0.540	812.53	21.104
	4	1.08	816.16	23.488

Table2. Values of Density, Viscosity of the samples of 2-amino-5- romobenzoic acid + ethanol, 2-amino-5-bromobenzoic acid + propanol and 2-amino 5- bromobenzoic acid + butanol at 299 K.


a)
2-amino-5 bromobenzoic acid + Ethanol
2-amino-5 bromobenzoic acid + Propanol
2-amino-5 bromobenzoic acid + Butanol
Ultrasonic Velocity (m/s)
Mole Fraction M (g)


b)
2-amino-5 bromobenzoic acid + Ethanol
2-amino-5 bromobenzoic acid + Propanol
2-amino-5 bromobenzoic acid + Butanol
Impedance (Kgm^{-2}s^{-1})
Mole Fraction M (g)


c)
2-amino-5 bromobenzoic acid + Ethanol
2-amino-5 bromobenzoic acid + Propanol
2-amino-5 bromobenzoic acid + Butanol
Adiabatic compressibility (ms^{-2}Kg^{-1})
Mole Fraction M (g)


d)
2-amino-5 bromobenzoic acid + Ethanol
2-amino-5 bromobenzoic acid + Propanol
2-amino-5 bromobenzoic acid + Butanol
Intermolecular Free Length (m)
Mole Fraction M (g)

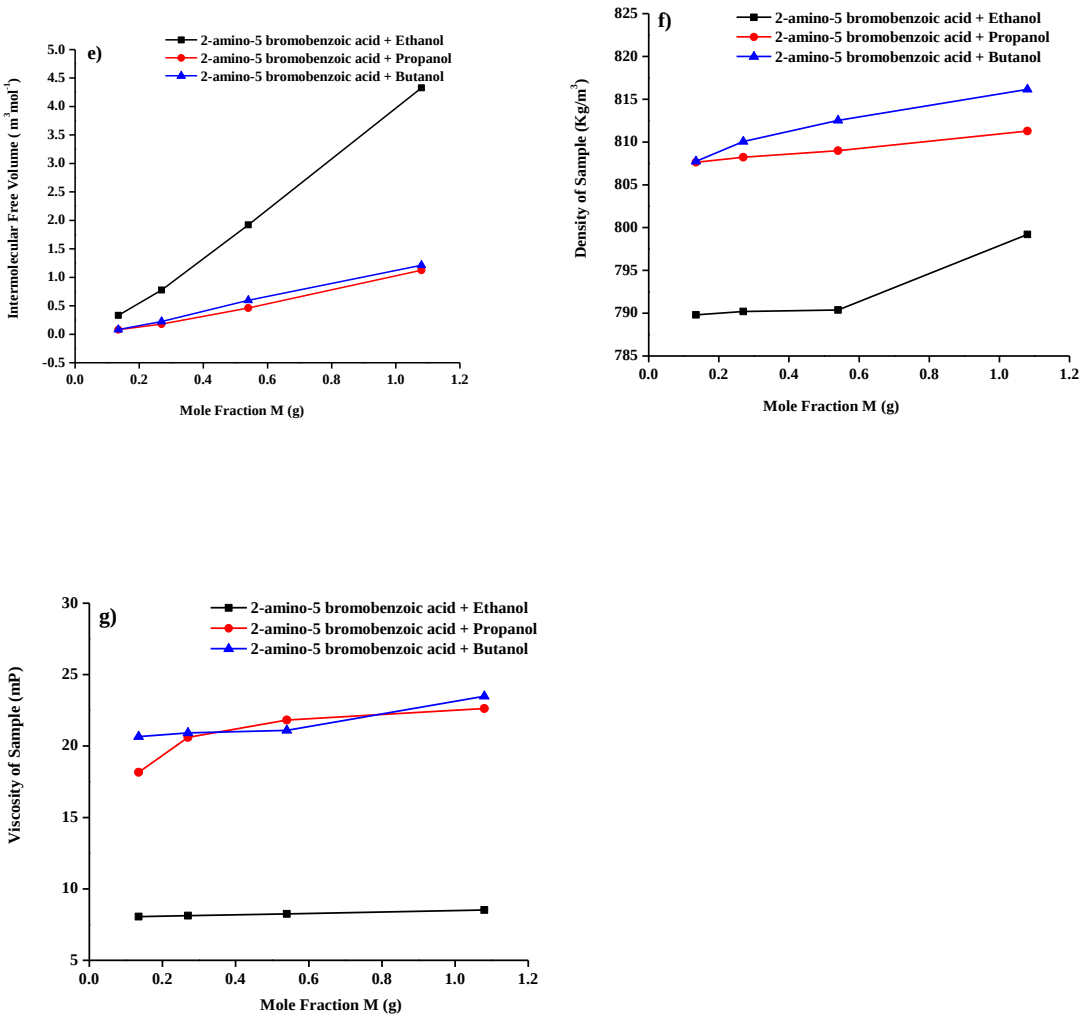


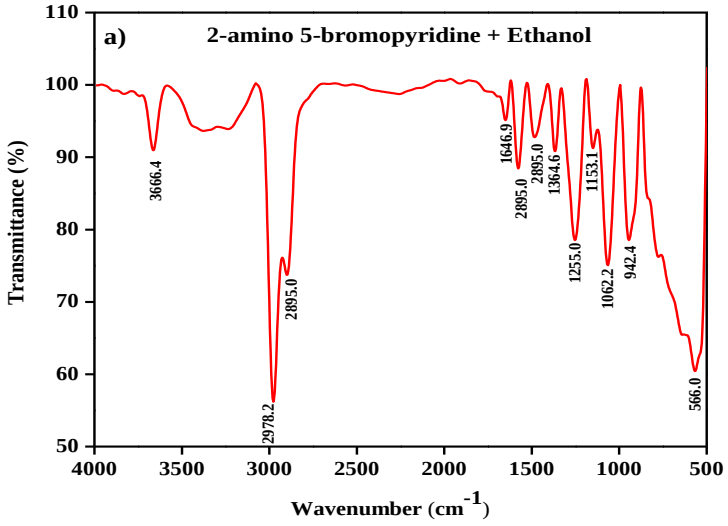
Figure 1. Mole fraction with respect to a) Ultrasonic velocity, b) Impedance, c) Adiabatic compressibility, d) Intermolecular free length, e) Intermolecular free volume, f) Density of Sample and g) Viscosity of samples.

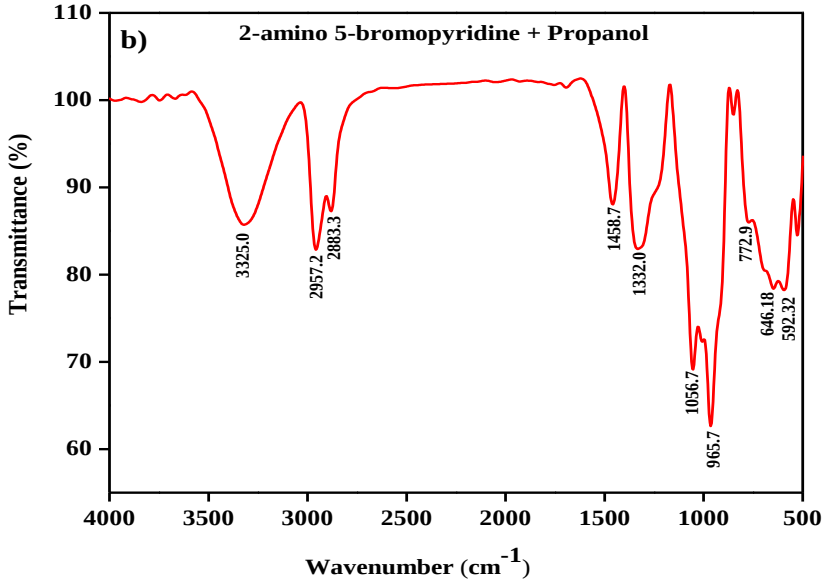
From the Table 1 and figure 1(a and b) show that, ultrasonic velocity, impedance decreases with increase in the mole fraction in the case of 2-amino-5-bromobenzoic acid + ethanol, 2-amino-5-bromobenzoic acid + propanol and 2-amino-5-bromobenzoic acid + butanol. This is brought on

by the formation of intermediary compounds between binary liquids. In Table 1 and fig1 (c, d and e) the Adiabatic compressibility, Intermolecular free length, Intermolecular free volume increases with increase in mole fraction. From the Table 2 and fig 1 (f and g) show that, density and viscosity of the samples increases with respect to the increase in the mole fraction in all types of 2-amino 5-bromopyridine + ethanol, 2-amino 5-bromopyridine + propanol and 2-amino 5-bromopyridine + butanol. Due to the liquid mixes' increased free length and adiabatic compressibility, the ultrasonic velocity has decreased. It has been found that the sound velocity increases as the number of CH groups or chain length increases at a certain concentration. In all systems, the adiabatic compressibility and free length rise as the mole fraction rises. This could result in a particular molecular interaction occurring between the molecules of liquid mixture. The ultrasonic velocity in liquid systems is determined by the adiabatic compressibility and free length. With rising mole fraction, internal pressure decreases and free volume rises. The nature and strength of the forces that exist between the molecules may be revealed by the internal pressure. The reduction in free volume demonstrates how the strength of contact steadily declines as solute concentration rises. It indicates a minimal contact between the molecules of the solute and solvent [25]. Acoustic impedance increase in 2-amino 5-bromopyridine + ethanol, whereas decreases in the case of 2-amino 5-bromopyridine + propanol and 2-amino 5-bromopyridine + butanol. It has been noted that generally speaking, a reduction in free energy favours the creation of reaction products. This finding supports the hypothesis that hydrogen bonds originate in binary mixes.

Hydrogen Bond by FTIR spectrum

A hydroxyl group's hydrogen-oxygen bond produces a distinctive infrared absorption band, but as we might expect, hydrogen bonding has a significant impact on this absorption.





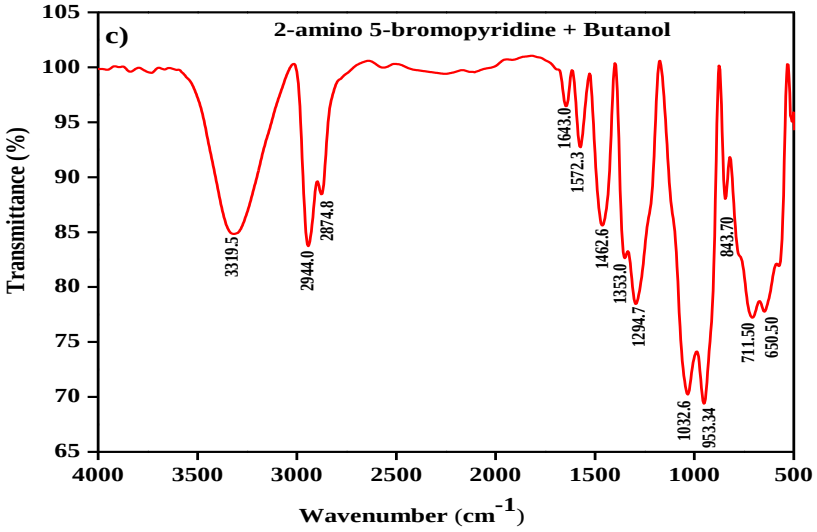


Figure 2. FTIR spectrum of a) 2-amino 5-bromopyridine + ethanol, b) 2-amino 5-bromopyridine + propanol and c) 2-amino 5-bromopyridine + butanol.

Ethanol in the 2-amino-5-bromobenzoic acid binary mixture liquid is showing the absorption fairly sharp absorption band at spectra band at 3666.4 cm^{-1} owing to a free or unassociated hydroxyl group as shown in figure 2(a). However, there is a reasonably wide band near 350 cm^{-1}, which is typical of hydroxyl groups with hydrogen bonds. Since hydrogen bonding weakens the link, the absorption frequency will be reduced, causing a change in frequency of around 300cm^{-1}. Because the hydroxyl groups are linked to aggregates of different sizes and shapes, the association band is wide. This results in a spectrum of closely spaced absorption frequencies and various different types of hydrogen bonding. Figures 2(b) and 2(c) of the FTIR analysis demonstrate the broad absorption spectra band, which is centred at 3325.0 cm^{-1} and 3319.5 cm^{-1}, respectively, which is stretching frequency of the O-H bond in propanol and butanol. The band at

2957.20 cm^{-1}, which applied to the sample of propanol and 2929.84 cm^{-1}, applied to the stretching frequency of the C-H bond (CH_2 asymmetric [26])

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Author Contributions

The manuscript was written through contributions of all authors. All authors read and approved the final version of the manuscript. Authors [a] and [b] contributed equally.

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Abbreviations

FTIR – Fourier Transform Infra-Red Radiation.

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