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MOLECULAR INTERACTIONS STUDY BETWEEN BUTYL ACETATE WITH ALKANES USING ULTRASONIC TECHNIQUES

Abstract

Ultrasonic velocities for binary mixtures of butyl acetate as a main component with alkanes like heptane, decane, dodecane and tridecane have been measured at 303.15, 308.15 and 313.15K temperatures with different compositions. The obtained experimental data have been utilized to find out excess or deviation properties such as deviations in ultrasonic velocity (Δu), and intermolecular free length (L_f). The deviation in ultrasonic velocities and excess intermolecular free length convey prevailing trends of curves that are both positive and negative which attributes the different molecular interactions for proposed binary mixtures.

Keywords: butyl acetate; Alkanes; ultrasonic velocity; intermolecular free length; molecular uinteractions

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I. INTRODUCTION

Butyl acetate is used as an ingredient in cleaners, fragrances, and as an extractant in the production of pharmaceutical preparations. It is sometimes referred to as butyl ethanoate. This organic substance is mostly utilized as a solvent in the lacquer manufacturing process. Additionally, it is utilized in a variety of food products, including baked goods, cheeses, candies, and ice cream, as a synthetic fruit flavoring. Additionally, nail polish and other nail-care products are made with butyl acetate as a solvent. It is utilized in the production of safety glass, plastics, photographic films, and synthetic leather cleansers. It works great as a solvent to prepare polymers and resins. Because butyl acetate is frequently used in paint formulations in conjunction with alcohols like n-butanol, it improves both the solvency and the resistance to blushing. Due to its high solvency and low water absorption capacity, it can also be used as an extractant in pharmaceutical preparations and as a raw material for essences and fragrances. Given that butyl acetate is a polar solvent, combining it with non-polar solvents like alkanes yields some intriguing findings about the density and viscosity of binary mixtures as well as insights into the potential effects of the molecular interaction between butyl acetate and alkanes. Understanding the thermoacoustic characteristics of mixtures with butyl acetate as a major component and the molecular interaction studies in binary liquid mixtures of butyl acetate with alkanes are of interest to us in light of the aforementioned salient features.

Few studies have been done on the physicochemical characteristics of binary mixtures of butyl acetate with alkanes like heptane, decane, dodecane, and tridecane, according to a review of the literature. Resa reported the isentropic compressibilities and ultrasonic velocities of mixtures containing butyl acetate and aromatic hydrocarbons (toluene, ethylbenzene, p-xylene, mesitylene, isopropylbenzene, butylbenzene, isobutylbenzene, or t-butylbenzene) that were measured using the Grunberg and Nissan model at various

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temperatures and atmospheric conditions [1]. Gonzalez discussed alkanes (n-hexane, n-heptane, n-octane, n-nonane) or esters (ethyl acetate, vinyl acetate, propyl acetate, isopropyl acetate, butyl acetate) + olive oil at temperatures between 288.15-298.15 K are enclosed in binary systems at ultrasonic velocity [2]. These physical characteristics were used to calculate the corresponding derived magnitudes, changes in isentropic compressibilities, and changes in refractive indices on mixing. Density, viscosity, refractive index, and speed of sound have all been reported by Aminabhavi and Banerjee for binary mixtures of acrylonitrile with methyl, ethyl, propyl, butyl, and 3-methyl butyl-2-acetate in the temperature range of 298.15 to 308.15) K [3]. The obtained experimental data is utilized in this study to identify certain properties of excess or deviation. Pycnometers were used to measure the experimental density, cannon Fenske viscometers (Rosella, NJ) were used to measure viscosity, and Mittal Single Crystal Interferometers (model M-84, New Delhi) were used to measure sound speed. It is concluded that, with the exception of the deviation in the viscosity property, the results of the studied excess or deviation properties show systematic dependence on the size of esters used. The density, viscosity, refractive index, and sound speed of binary mixtures of 2-chloroethanol with methyl, ethyl, n-propyl, and n-butyl acetate have all been studied by Aralaguppi [4]. Volume excess for (methanol + butyl acetate) and (vinyl acetate + butyl acetate) has been determined by Resa [5]. The Van Laar and Wilson equations have been used to correlate the activity coefficients. For binary mixtures of n-butylamine with butyl acetate, methyl acetate, and iso-amyl acetate, Sankara Reddy have measured excess volume, speed of sound, and viscosity at 303.15 K over the whole composition range [6]. The collision factor theory (CFT) developed by Schaaff was used to report sound speeds. The Grunberg and Nissan model was used to correlate the viscosity data. Chandrasekhar have determined excess molar volumes and speed of sound of ethyl acetate and butyl acetate with 2-alkoxyethanols at 308.15 K [7]. Jyostna have measured densities and viscosities of binary liquid mixtures of acetonitrile and N-methyl acetamide with aromatic ketones at 308.15

K [8-9]. Patwari determined densities, viscosities and speeds of sound of binary liquid mixtures of sulfolane with ethyl acetate, n-propyl acetate and n-butyl acetate at temperatures of (303.15, 308.15 and 313.15) K [10]. Lie-Chiahave measured VLE for binary mixtures of 2-butanol + butyl acetate [11]. They have used various activity coefficient models to correlate the experimental data. Sastry and Patel have reported densities, excess molar volumes, speeds of sound, excess isentropic compressibilities and relative permitivities for alkyl (methl, ethyl, butyl, and isoamyl) acetates with glycols at different temperatures [12]. Qin have determined excess volumes of binary mixtures of alkyl esters and ketones with aromatic hydrocarbons [13].

Recent study shows many technical applications of new materials that can produce strong ultrasonic vibrations observed in the field of physics, chemistry, biology, medicine, and industry which have been made possible by the quick development of ultrasonic technology and the introduction of new materials in research. These days, studying ultrasonic absorption and velocity in a variety of media like liquids, liquid-liquid mixtures, suspension, electrolyte solution, polymers, etc.is a pretty useful way to look at specific physical characteristics of the media. Extensive research has been conducted on the interferometric method which involves stimulating a liquid column to resonance.

II. MATERIALS AND METHODS

The analytical grade butyl acetate, heptane, decane, dodecane, and tridecane provided by Sigma-Aldrich have been deployed for the ultrasonic velocity's measurements. For these chemicals, the mass fraction purity was substantially greater than 0.99. To reduce the water content and stabilize these chemicals, they were placed over 0.4 nm molecular sieves and distilled right before to use. The analysis of the purity for the used chemicals using GC-8610 revealed that it was >0.995. The fluid which serves as binary Mixtures were made by combining known masses of pure liquids in airtight stoppered bottles.

Mass measurements were performed for each using a Mettler one-pan balance (AE, 240, Switzerland). The conclusive result subsequently was found that the mole fraction's uncertainty amounted less than + 0.0001. The methods for measuring sound speed can be broadly classified into two groups.

1. The Continuous Wave Method

This method includes interferometric and optical methods that are based on the study of acoustic gratings[14]. Variable path interferometers have been used extensively, and new developments allow sound speed measurements to be accurate to a few parts per million [15]. Hunter and Dardy used a double crystal detector to measure sound speed at 500 MHz [16]. Other kinds of interferometers were also used to measure sound speed and investigate the resonance of liquid filling cavities. Dobbs and Finegold used a cylinder made of barium titanate that was plated so that one half functioned as a receiver and was filled with the experimental liquid [17]. Fort and Moore used a single crystal interferometer operating at 400 KHz to measure the ultrasonic sound speeds of binary liquid mixtures [18].

2. Pulse Technique

The pulse technique allows sound speed in liquids to be measured by measuring the transit time for a given path.[19-20]. This method measures the time difference between two ultrasonic wave echoes traveling between a transducer and a reflector in order to calculate velocity. Compared to pulse techniques, the ultrasonic interferometer has some clear advantages [21-22]. One benefit of using an optical interferometer is that differential path length, as opposed to total path length, can be used to measure these parameters accurately. Furthermore, the interferometer only needs a straightforward frequency measurement, whereas the pulse technique requires a more complex time interval measurement. Therefore, it is discovered that an interferometer is a better tool for determining the

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temperature and pressure coefficients of sound speed. Del Grasso has addressed the advantages of the ultrasonic interferometer in great detail [22]. However, the narrow band of applicable frequencies (10 to 100 MHz) limits the interferometric method.

The variable path single crystal interferometer F-81 (Mittal Enterprises, New Delhi, India) operating at a frequency of 2 MHz was used in this study to measure the speed of sound in pure liquids and binary mixtures. The interferometer cell has 1.6 cm inner diameter stainless steel tube makes up the 12 cm3 interferometer cell. A quartz crystal with a gold plating is fixed to the cell's bottom. This crystal emits ultrasonic waves, which travel until the movable reflector reflects them back. The diameter of the reflecting surface is 1.4 cm. Using a Teflon coupler and a steel rod, this is connected to a micrometer screw assembly that can measure up to 0.01 centimeters. A threaded cup and teflon ring are used to secure the micrometer assembly and reflector to the liquid cell. The necessary stability for the measuring cell is provided by a heavy pedestal. To keep the experimental liquid at a consistent temperature throughout the experiment, provisions have been made for water to be circulated at any desired temperature from a thermostatically controlled bath into a jacket surrounding the measuring space. An electrically powered quartz transducer connected to a liquid column makes up the interferometer. the quartz crystal's distance down the liquid column. The column vibrates in resonance whenever the distance between the reflector and the quartz transducer is an integral multiple of half wavelength. Sharp dips in the r-f voltage across the transducer result from this increase in the transducer's motional impedance. A half wavelength ($\lambda/2$) is the distance traveled by the reflector between any two successive dips.

The experimental liquid was placed inside the interferometer cell, which was wired shielded to the high frequency generator's output terminal. A thermostat controlled to within + 0.01 K was used to circulate water, keeping the cell temperature at 303.15 K. The

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micrometer screw was gradually turned until the anode current meter displayed a maximum and the micrometer reading was recorded after the liquid reached the bath's temperature. By turning the screw downward, the quartz transducer and reflector plate were separated in length. A number "n," in this case forty, was counted after multiple maxima were passed in order to increase measurement accuracy. After adjusting the anode current to its maximum, the micrometer's reading was once more noted. The formula for the total distance traveled by the reflector was $d = \lambda/2$. With the quartz crystal's accuracy (f) known with precision (2MHz), the sound speed (u) was computed using the formula $u = \lambda/f$. The micrometer screw was turned upward to determine the value of u. The accuracy of the sound speed values was within 0.15%. In continuation with our earlier research, the present study reports ultrasonic velocities for 9 samples having different mole fraction between 0.1 to 1 at 203.15, 205.15, and 213.15K temperatures [23].

III. RESULTS AND DISCUSSIONS

The deviation properties of the binary liquid mixtures have been evaluated using the eq. (1-3)

$$\Delta y = y_{mix} - (x_1 y_1 + x_2 y_2) \quad (1)$$

where y_{mix} indicates the property of the mixture viz, speed of sound (u), and intermolecular free length (L_f), y_1 and y_2, x_1 and x_2 refer to the property and mole fraction of pure components 1 and 2 respectively and Δy indicates the deviation in observed property (Δu) The excess free length can be calculated by following equation

$$L_f = K \cdot (K_S)^{1/2} \quad (2)$$

In above Eqs. (2), K is the temperature dependent Jacobson's constant, Ks is isentropic compressibility which can be calculated by following equation

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$K_s = [1 / (u^2 \rho)]$ (3)

Graphical representation of Δ*u* as a function of mole fraction of Butyl acetate(x_1) at 303.15, 308.15 and 313.15 K is given in Figure 1. By interpreting, it can be seen that for the systems Butyl acetate + Dodecane and Butyl acetate + Tridecane, Δ*u* shows positive deviation, whereas for the system Butyl acetate + Heptane, Δ*u* values are found to be negative at all studied temperatures. When compared to other systems, the Δu values for the butyl acetate + decane system exhibit a different trend. It is observed that the Δ*u* is found to be positive at 313.15 K and negative at 303.15 and 308.15 K. When the temperature of Butyl acetate + Heptane increases, it is observed that the values of Δu become less negative and a minima is reached at mole fraction $x_1 = 0.5$. Values of Δ*u* show a systematic increase with increasing temperature in the systems Butyl acetate + Dodecane (maxima at x_1=0.6) and Butyl acetate + Tridecane (maxima at x_1=0.5). The increasing strength of interaction between component molecules of binary liquid mixtures is demonstrated by positive deviations in Δu values. The mixture is predominant, leading to an expansion faster than the speed of sound, as indicated by the negative deviation.

Intermolecular free length is a crucial physical characteristic of liquid mixtures that primarily influences sound velocity. As the sound velocity drops, the intermolecular free length also drops. The shape of the molecule and their interactions with one another both affect the structural arrangements. Figure 2 demonstrates that the curve obtained for L_f^E and the systems of butyl acetate + heptane, butyl acetate + dodecane have positive values of L_f^E; the other two systems, butyl acetate + decane exhibit both positive and negative deviations and butyl acetate + tridecane exhibit negative deviations at all temperatures. Weak molecular interactions and improper interstitial accommodation between the component molecules are indicated by positive values of L_f^E. Dipole-induced dipole, dipole-dipole, and charge transfer interactions between the components of the binary liquid mixtures are among the various forces acting between them;

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these forces contribute negatively to the excess values, while dispersion forces operate positively. In every instance of these four binary mixtures under study reveals that dispersion forces are present

IV. CONCLUSIONS

Values of Δu and L_f^E were calculated based on measurements of ultrasonic velocities for binary mixtures of butyl acetate with heptane, decane, dodecane, and tridecane at (303.15, 308.15, and 313.15) K. For mixture, Butyl acetate + Dodecane and Butyl acetate + Tridecane, Δu shows positive, Butyl acetate + Heptane negative while Butyl acetate + Decane shows positive-nigative deviations It appears that the molecules in butyl acetate and n-alkanes are interacting through weak dipole-dipole forces. Furthermore, it is noted that temperature has a considerable impact on the properties of Δu that have been studied. The intermolecular free length L_f investigated over entire composition range for binary mixtures shows weak molecular interactions and improper interstitial accommodation between the component molecules are indicated by positive values of L_f^E for partial systems. The dipole-induced dipole, dipole-dipole, and charge transfer interactions between the components of the butyl acetate binary liquid mixtures are predominant.

Figures

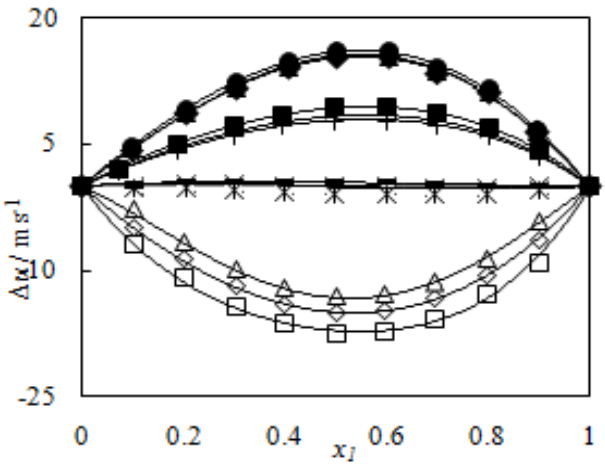

Figure 1: Curves of deviation in ultrasonic velocitty Δu Vs mole

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fraction for the binary mixture of
Butyl acetate+ Heptane at (□, 303.15; ◊, 308.15;Δ, 313.15)K,
Butyl acetate+ Decane at (×, 303.15; ж, 308.15;▬, 313.15) K,
Butyl acetate+ Dodecane at (O, 303.15; +, 308.15; ■, 313.15)K,
Butyl acetate+ Tridecane at(♦, 303.15;▲, 308.15 ; ●, 313.15) K

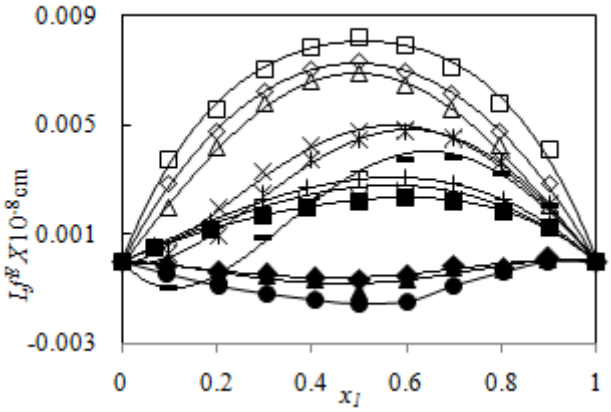

Figure 2: Curves of excess intermolecular free length L_f^E Vs mole fraction for the Binary mixtures of

Butyl acetate+ Heptane at (□, 303.15 ; ◊,308.15 ; Δ,313.15)K,
Butyl acetate+ Decane at (×, 303.15 ; ж, 308.15 ; ▬, 313.15) K,
Butyl acetate+ Dodecane at (O, 303.15 ; +,308.15 ;■, 313.15) K,
Butyl acetate+ Tridecane at (♦, 303.15; ▲, 308.15 ; ●, 313.15) K.

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