Original Research

Molecular interaction studies of butyl formate with n-alcohols in carbon tetrachloride at 303K

Sampandam Elangovan*, Senbeto Kena, Kebede Legesse & Misganu Chewaka

Department of Physics, College of Natural and Computational Sciences, Wollega University, Ethiopia

Abstract	Article Information
In ternary mixes of butyl formate with 1-Butanol, 1-Pentanol, and 1-Hexanol, ultrasonic velocities (U), viscosities (ρ), and carbon tetrachloride densities (ρ) have been recorded at 303K. A number of acoustic parameters, including adiabatic compressibility (β), free length (L_f), free volume (V_f), and internal pressure (π_i), have been computed using the experimental data. In addition, the molecular interactions, including hydrogen bonds, that occur in combinations of solutes and solvents were utilized to ascertain and clarify the parameter values that were found to be excessive. From what we can see, the effects of homo and hetero association on molecules in alcohols increase as the carbon atom chain lengthens.	

INTRODUCTION

In a liquid state, the molecular interactions between polar and non-polar components greatly affect the system's chemical and physical characteristics. The dye, petrochemical, and pharmaceutical industries are just a few that depend on research into molecular interactions in liquid mixtures (Khursan et al., 2022; Chandrasekar et al., 2015; Nayeem et al., 2015). Research by Sanguri et al. (2015), Nithiyanantham & Palaniappan (2011), and Naik et al. (2015) suggests that ultrasonic analysis can be a sensitive method for determining the type of interaction between molecules in liquid mixtures. The ester butyl formate is different. The chemical and pharmaceutical industries utilize it as an intermediary and solvent in the manufacturing of many commodities. The textile, leather, latex rubber, electroplating, and coagulating industries also make use of it (Elangovan and Mullainathan 2013). The polarity and robust three-dimensional hydrogen bond network of alcohols make molecular interaction investigations of alcohol-containing liquid mixes quite interesting. (Franks et al., 1966; Kumari et al., 2022; Mirzaev et al., 2005) They can also be linked to any other group that exhibits polar attraction, on varying degrees. This experiment made use of carbon tetrachloride, a solvent that is not polar. The following liquid mixing systems have not had their

molecular interactions studied at 303K, as far as we can tell from a literature review: Carbon tetrachloride linked to butyl formate and 1-butanol make up the first system. Carbon tetrachloride, 1-pentanol, and butyl formate make up System II. Carbon trichloride, 1-hexanol, and butyl formate make up System 3.

MATERIALS AND METHODS

The Indian firm S.D. Fine Chemicals supplied all of the chemicals. Used in their unrefined forms, all of the compounds were of analytical purity. With a precision of $\pm$ 0.1 ms-1, the ultrasonic velocity (U) in the liquid mixtures was measured using a 2 MHz ultrasonic interferometer (Model F-81) manufactured by Mittal Enterprises in New Delhi.A specific gravity bottle with a 10-milliliter capacity that had been adjusted with deionized, double-distilled water was used to determine the densities of all the substances. A calibrated Ostwald viscometer was used to measure the viscosities of the solutions. The density was precisely measured to within $\pm$ 0.05 kgm-3. There is a margin of error of around 0.1% in the observed viscosity.

The following acoustical parameters have been computed using the experimental data.

$$\lambda = \frac{2d}{n}$$
Ultrasonic wavelength

Where d is the distance moved by the reflector and n is the number of oscillations produced by the ultrasonic interferometer.

Ultrasonic velocity $\quad U = f\lambda$

Where f is the frequency of ultrasonic wave

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

Where U is the ultrasonic velocity and ρ is the density of the liquid mixture.

Free length $\quad L_f = K_T\sqrt{\beta}$

Where K_T is the temperature dependent constant having value of 198.53×10^{-8} in MKS system.

$$V_f = \left[\frac{M_{eff}U}{\eta K}\right]^{3/2}$$
Free Volume

It is possible to get the effective molecular weight (Meff=m1x1+m2 x2+m3x3) of a liquid by multiplying its mole fraction by its molecular weight (m). The solution's viscosity is represented by η. For all systems containing liquids, the temperature-independent constant K is 4.28×109. For this experiment, we utilized n-butyl formate with a fixed mole fraction (x1) of 0.4 to make carbon tetrachloride and 1-alcohol solutions in varying amounts.

$$\pi_i = bRT\left[\frac{K\eta}{U}\right]^{1/2}\left[\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right]$$
Internal pressure

When all liquids have a cubical packing percentage of 2, represented as b. The temperature independent constant K, the experimental temperature T, and the universal gas constant R make up the equation.

$A^E = A_{exp}-A_{id}$
Here $A_{id} = \Sigma A_i x_i$

A_i represents any acoustical parameter and x_i is the corresponding mole fraction.

RESULTS AND DISCUSSION

The following experimental parameters are presented in Table 1: density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (β), free length (Lf), free volume (Vf), and internal pressure (πi). The density of any mixture of liquids decreases as the mole percentage of 1-alcohols rises. It is possible that the components were mixed in a less strict liquid system, leading to the higher concentration of 1-alcohols (Singh et al., 2020; Elangovan & Mullainathan, 2013).

Table 1

Variation of acoustical parameters in the Butyl formate +1-Alcohols+ Carbon tetrachloride

x_2	x_3	ρ (kgm^{-3})	η $\times 10^{-3}$ (Nsm^{-2})	U (ms^{-1})	β $\times 10^{-10}$ (m^{2}N^{-1})	L_f $\times 10^{-10}$ (m)	V_f $\times 10^{-7}$ (m^{3}mol^{-1})	π $\times 10^{12}$ (Nm^{-2})
			System I: Butyl formate +1-Butanol + Carbon tetrachloride					
0.0000	0.6443	837	0.803	1181	8.5659	0.5813	0.2193	0.7261
0.1131	0.5335	835	0.921	1174	8.6891	0.5851	0.1977	0.8389
0.2247	0.4241	833	0.949	1169	8.7846	0.5881	0.1879	0.9216
0.3350	0.3161	832	0.957	1165	8.8557	0.5912	0.1803	1.0067
0.4438	0.2094	831	1.039	1161	8.9276	0.5932	0.1663	1.1469
0.5513	0.1040	828	1.068	1159	8.9908	0.5953	0.1574	1.2759
0.6575	0.0000	827	1.175	1157	9.0329	0.5973	0.1435	1.4811
			System II: Butyl formate + 1-Pentanol + Carbon tetrachloride					
0.0000	0.6442	841	0.946	1184	8.4820	0.5782	0.2022	0.7896
0.0973	0.5429	838	1.063	1176	8.6286	0.5832	0.1853	0.8896
0.1968	0.4393	836	1.089	1171	8.7232	0.5863	0.1777	0.9610
0.2986	0.3333	834	1.108	1167	8.8042	0.5893	0.1707	1.0399
0.4028	0.2248	833	1.181	1161	8.9061	0.5924	0.1596	1.1608
0.5094	0.1137	831	1.209	1160	8.9430	0.5944	0.1521	1.2755
0.6187	0.0000	829	1.316	1159	8.9800	0.5954	0.1400	1.4579
			System III: Butyl formate +1-Hexanol + Carbon tetrachloride					
0.0000	0.5435	845	1.087	1186	8.4134	0.5762	0.1888	0.8483
0.1309	0.4328	842	1.204	1177	8.5730	0.5813	0.1750	0.9388
0.2507	0.3315	840	1.231	1172	8.6669	0.5843	0.1688	1.0019
0.3608	0.2385	837	1.243	1168	8.7576	0.5884	0.1636	1.0670
0.4622	0.1528	835	1.321	1163	8.8543	0.5914	0.1540	1.1743
0.5561	0.0736	834	1.351	1161	8.8954	0.5925	0.1475	1.2767
0.6431	0.0000	831	1.457	1160	8.9431	0.5945	0.1371	1.4350

A change in the cohesive force acting on the components of the liquid mixture or an alteration in the effective molecular area could lead to a greater viscosity (η) value, which signifies an increase in the friction resistance force. Once the liquids are mixed, the change in intermolecular free length determines the variance in ultrasonic velocity. Furthermore, the solute and solvent will interact with a larger force, generating hydrogen bonds,

which will increase the free length of the mixture (Mallick et al., 2018; Elangovan & Mullainathan, 2013). Table 1 displays the statistical association between alcohol content and free length (Lf) in this investigation. In this case, for all three liquid systems, the ultrasonic velocity (U) drops as the mole proportion of alcohols increases. (Chauhan et al., 2016; Praharaj et al., 2013) The trend was caused by structural changes in the selected liquid systems that decreased the intermolecular forces. According to the data shown in Figure 1, the ultrasonic velocities changed consistently with increasing alcohol chain length.
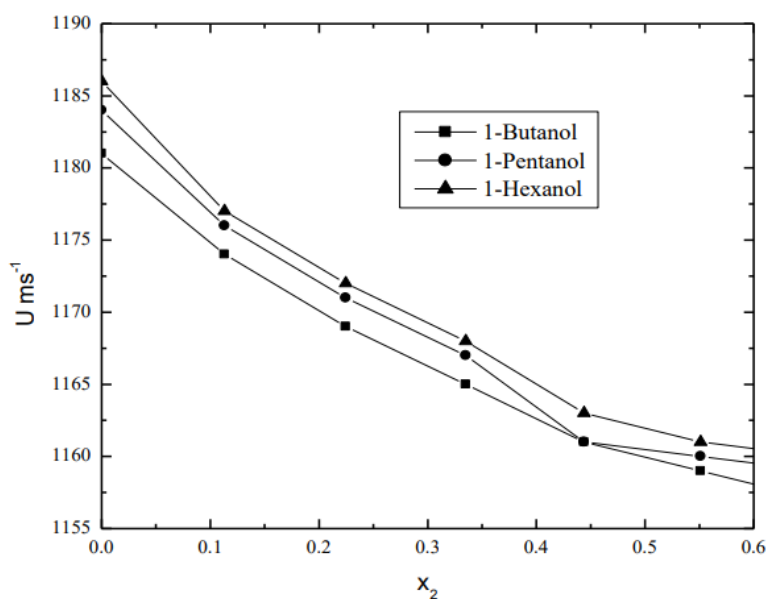

Figure. 1. *Variation of ultrasonic velocity with n-alcohol concentrations*

The adiabatic compressibility (β) is enhanced as the mole percentage of alcohols rises. As the concentration of alcohol increases, the free volume (Vf) drops. Naturally, the inverse trend is shown by the internal pressure (Φi). Figure 2 shows that the internal pressure changes as a function of the alcohol mole fraction. According to Kumar and Chauhan (2015) and Manukonda et al. (2013), a packed configuration can result from dipolar-type interaction. Perhaps this is because the carbonyl group in butyl formate forms hydrogen bonds with the hydroxyl group in alcohols, as shown by the formula C= O---HO. As the length of the alcohol chains rose, hetero- and homo-association decreased. The proton-donating ability of the higher alcohols changed, which is likely the source of this.

Table 2 presents excess values of numerous acoustic parameters, which help to better understand the type and strength of molecular interaction in liquid systems. Dispersion forces should favorably contribute to excess values, according to Elangovan and Mullainathan (2013), but unlike components should interact adversely with one other. On the flip side, interactions involving dipole-induced dipoles, charge transfer, and hydrogen bonding should have a negative impact.
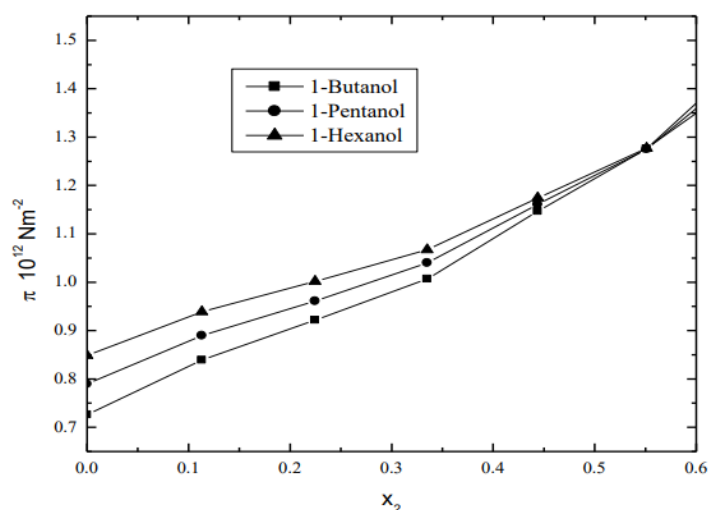
Figure 2 *Variation of internal pressure with n-alcohol concentrations*

Table 2

Variation of excess values of acoustical parameters in the Butyl formate + 1- Alcohols + Carbon tetrachloride systems at 303K

x_2	x_3	η^E $\times 10^{-3}$ (Nsm^{-2})	β^E $\times 10^{-10}$ (m^2N^{-1})	$L_f^{\ E}$ $\times 10^{-10}$ (m)	$V_f^{\ E}$ $\times 10^{-7}$ (m^3mol^{-1})	π^E $\times 10^{12}$ (Nm^{-2})
		System I: Butyl formate +1-Butanol + Carbon tetrachloride				
0.0000	0.6443	-0.0350	-0.3794	-0.0257	-0.0097	-0.0321
0.1131	0.5335	-0.0429	-0.4049	-0.0272	-0.0092	-0.0390
0.2247	0.4241	-0.0463	-0.4286	-0.0287	-0.0091	-0.0449
0.3350	0.3161	-0.0489	-0.4525	-0.0302	-0.0092	-0.0514
0.4438	0.2094	-0.0552	-0.4749	-0.0315	-0.0088	-0.0610
0.5513	0.1040	-0.0590	-0.4971	-0.0329	-0.0087	-0.0705
0.6575	0.0000	-0.0675	-0.5193	-0.0343	-0.0082	-0.0851
		System II: Butyl formate + 1-Pentanol + Carbon tetrachloride				
0.0000	0.6442	-0.0418	-0.3749	-0.0255	-0.0089	-0.0349
0.0973	0.5429	-0.0427	-0.3468	-0.0234	-0.0074	-0.0357
0.1968	0.4393	-0.0393	-0.3149	-0.0211	-0.0064	-0.0346
0.2986	0.3333	-0.0353	-0.2808	-0.0187	-0.0054	-0.0331
0.4028	0.2248	-0.0325	-0.2458	-0.0163	-0.0044	-0.0320
0.5094	0.1137	-0.0279	-0.2065	-0.0137	-0.0035	-0.0294
0.6187	0.0000	-0.0246	-0.1679	-0.0111	-0.0026	-0.0272
		System III: Butyl formate +1-Hexanol + Carbon tetrachloride				
0.0000	0.5435	0.0614	0.4753	0.0325	0.0106	0.0479
0.1309	0.4328	0.0437	0.3111	0.0211	0.0063	0.0340
0.2507	0.3315	0.0219	0.1542	0.0104	0.0030	0.0178
0.3608	0.2385	0.0008	0.0061	0.0004	0.0001	0.0007
0.4622	0.1528	-0.0198	-0.1328	-0.0088	-0.0023	-0.0176
0.5561	0.0736	-0.0401	-0.2641	-0.0175	-0.0043	-0.0379
0.6431	0.0000	-0.0627	-0.3854	-0.0256	-0.0059	-0.0618

As the carbon chain length grows, the excess parameters βE and πE become increasingly positive for 1-butanol to 1-hexanol. This is due to the fact that hydrogen bonding is becoming weaker. The loss of the packing environment and the significant disturbance of symmetry caused by the --OH group occur with higher concentrations of n-alcohols; hence, the excess negative values decrease and become positive at 1-hexanol. The most significant excess negative πE values were observed in 1-butanol, 1-pentanol, and 1-hexanol, according to the present study. The pattern in the fluctuation of the acoustic parameters indicates that the hetero association and homo association of molecules diminish as the carbon atom chain length in alcohols grows.

CONCLUSIONS

Hydrogen bonding is postulated to facilitate molecular contact in the chosen liquid systems, according to the sign of the calculated excess values and the experimentally measured acoustical properties. As the length of an alcohol chain increases, the strength of its hydrogen bonds decreases. The diminished proton-donor capacity of the stronger alcohols is one probable cause.

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DECLARATION

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

All data included in the article are available from the corresponding author upon request

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