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Acoustic and thermodynamic properties of cholesterol in ethanol and 1-propanol solution in different concentration at 303K

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Abstract

Ultrasonic velocity and density are measured in the mixture of cholesterol in ethanol and 1-propanol solution at different concentration to study the thermodynamic properties. Acoustical parameters like adiabatic compressibility, intermolecular free length, acoustic impedance and surface tension are calculated using the ultrasonic velocity and density. These data are particularly discussed with respect to the concentration of cholesterol. The variation of ultrasonic velocity shows a dip at higher concentration of cholesterol. These properties are used to illustrate the nature of interactions between component molecules.

Keywords: Cholesterol-acoustical properties-ethanol-1-propanol-molecular interactions.

Introduction

Cholesterol is a sterol. It is interacted with lipoproteins and with bile salts. Moreover, studies of cholesterol aggregation in aqueous medium are essential for an understanding of the physico-chemical properties of cholesterol. The physical state of the cholesterol/lipids in relation to the bio chemical environment can be understood on the basis of their interaction with an aqueous system. Knowledge of the physico-chemical properties of cholesterol aggregates in aqueous medium are thus essential for an understanding of structural properties. Aqueous solutions of cholesterol have been little investigated to understand the cholesterol – cholesterol and cholesterol-water interactions to form the complex systems.

Ultrasonic parameters are used extensively to study molecular interactions in liquid mixtures. In the recent years, it has been found that, the acoustical properties of solution should be an important parameter in the study of several chemical reactions and in the investigation of molecular interactions. Thermodynamic properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture from ideality. Recently, more number of researchers has studied the properties of cholesterol/lipids. Researchers had examined cholesterol aggregates in water employing a dialysis technique and studied the micelle equilibrium, critical micelle concentration and solubility of cholesterol[1-4].

The same author(s) have studied the ultrasonic study and allied properties of cholesterol in chloroform solution at 294K[5]. In this work, the thermodynamic properties of cholesterol like adiabatic compressibility, intermolecular free length, acoustic impedance and surface tension are studied in ethanol and 1-propanol solution at 303K by ultrasonic velocity measurement and the non-linear variations have been calculated by (B/A) Hartmann and baluu and Empirical relation.

Material and Methods

In the present investigation, cholesterol (Merck) of molecular weight of 386.66 gm/mol was taken. Cholesterol was added in Ethanol (AR-Grade) at different concentration. Density and ultrasonic velocity was measured in different concentrations of mixed solution at 303K. Ultrasonic interferometer (Mittel Enterprises, New Delhi) of fixed frequency (2 MHz) was used for measuring ultrasonic velocity. Density of a binary mixture was measured using gravimetric method. These values were found to be accurate up to ± 0.1 kg/m^3. The same experiment was repeated in 1-propanol solution with different concentration of cholesterol. Acoustical parameters, acoustical impedance, intermolecular free length, compressibility, internal pressure, volumetric parameters, relaxation time and classical absorption coefficient are calculated using as usual formula.

Results and Discussion

The experimental values of ultrasonic velocity, adiabatic compressibility, density, intermolecular free length for the system of cholesterol in ethanol and in 1-propanol at 303K are presented in Table 1 and Table 2. The adiabatic compressibility, βs, of donor-acceptor for solutions have been determined from the sound velocity, using an expression

Table-1
Experimental values of ultrasonic velocity, density, compressibility, acoustic impedance, intermolecular free length, surface tension and relative association of cholesterol in ethanol at different concentrations

Concentration of cholesterol (mg)	Velocity (U) (m/s)	Density (ρ) (kg/m^3)	Adiabatic compressibility (β) 10^{-10} ($kg^{-1}ms^2$)	Acoustic impedance (Z) $X10^5$ (kg/m^2s)	Free length (L_f) 10^{-10} (m)	Surface Tension (σ) (N/m)	Relative association (R_A)
0	1159.21	784	9.492	9.088	1.319	19494	0.000
20	1156.87	790	9.455	9.142	1.316	19589	1.008
30	1163.70	794	9.301	9.239	1.305	19856	1.011
40	1158.40	791	9.418	9.166	1.314	19657	1.009
50	1163.94	795	9.285	9.254	1.304	19889	1.013
60	1166.55	793	9.264	9.253	1.303	19911	1.010
70	1180.40	802	8.949	9.467	1.280	20490	1.016
80	1169.67	803	9.107	9.388	1.292	20227	1.021
90	1182.33	804	8.893	9.510	1.277	20602	1.033
100	1184.87	808	8.813	9.578	1.271	20770	1.084
125	1177.64	802	8.993	9.443	1.284	20414	1.017

Table-2
Experimental values of ultrasonic velocity, density, compressibility, acoustic impedance, intermolecular free length and surface tension of cholesterol in 1-propanol in different concentrations

Concentration of cholesterol (mg)	Velocity (U) (m/s)	Density (ρ) (kg/m^3)	Adiabatic compressibility (β) 10^{-10} ($kg^{-1}ms^2$)	Acoustic impedance (Z) $X10^5$ (kg/m^2s)	Free length (L_f) 10^{-10} (m)	Surface Tension (σ)	Relative association (R_A)
0	1206.25	803	8.555	9.691	1.252	21205	0.000
20	1203.60	771	8.952	9.281	1.281	20285	0.961
30	1196.68	801	8.717	9.587	1.264	20893	0.999
40	1194.94	805	8.705	9.613	1.263	20935	1.004
50	1206.12	805	8.535	9.714	1.250	21254	1.003
60	1206.74	808	8.502	9.747	1.248	21332	1.005
70	1208.38	808	8.478	9.761	1.246	21376	1.004
80	1208.82	809	8.460	9.778	1.245	21418	1.006
90	1206.11	808	8.507	9.747	1.248	21325	1.006
100	1209.31	809	8.450	9.786	1.244	21439	1.0064
125	1214.20	810	8.379	9.830	1.239	21577	1.005

$\beta s = 1/U^2 d$ Where, βs, U, and d refer to the adiabatic compressibility, velocity and density of the solutions respectively. Similarly, $\beta_o = 1/U_o^2$ d Where, β_o, U_o, and d refers to the adiabatic compressibility, velocity and density of the solvent respectively. The compressibility lowering is expressed as,

$$\Delta \beta = \beta s - \beta_o$$

The variation of ultrasonic velocity with concentration of cholesterol for two different systems is shown in Figure-1. It is observed that the ultrasonic velocity varies non-linearly with increasing the concentration of cholesterol. It shows some dip at a concentration of 40mg and 80mg of cholesterol with ethanol. The sources of non-linear variations are observed with 1-propanol as reported earlier with chloroform[6]. The deviation in adiabatic compressibility can be explained by taking into consideration of the following factor.

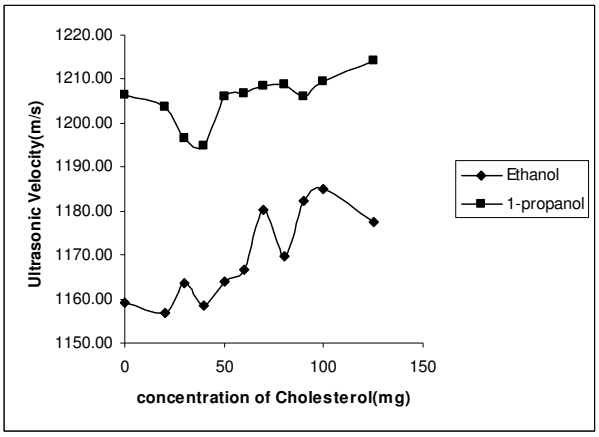

Figure-1
Variation of ultrasonic velocity of cholesterol in ethanol and 1-propanol solution

Loss of di-polar association and difference in size and shape of the component molecules
Which lead to decrease in velocity and increase in compressibility.
Dipole-dipole interaction or hydrogen bonded complex formation between unlike molecules
Which lead to increase in sound velocity and decrease of compressibility.

The actual deviation depends on the resultant effect. The observed decrease/increase in adiabatic compressibility, intermolecular free length and acoustic impedance with composition is an evidence of significant interaction between the component molecules in the binary mixtures.

The variations of adiabatic compressibility of cholesterol in ethanol and 1-propanol are shown in figure-2. Increase in the compressibility value indicates the weakening of molecular interactions[7]. The compressibility decrease with increase in the concentration of cholesterol and it increases at a concentration of 80mg. According to the Fort and Moore, compressibility studies of binary liquids mixture involve hydrogen bonding[8]. According to them, hydrogen bonding between unlike components made a negative contribution to compressibility. The increase in velocity and decrease in compressibility forms a tight bond system. Hence, it is observed that the compressibility of a binary mixture non-linearly varies with concentration of cholesterol.

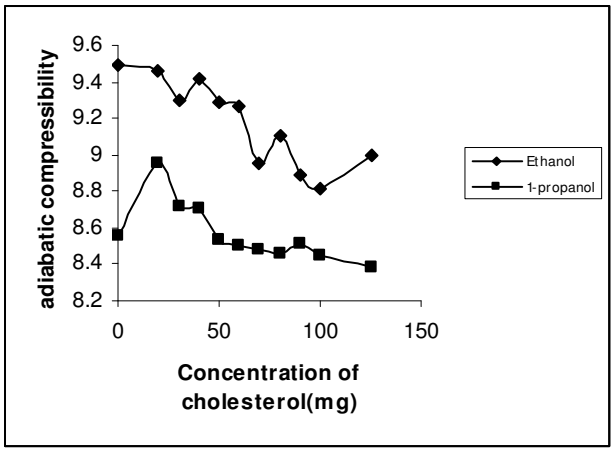

Figure-2
Variation of adiabatic compressibility of cholesterol in ethanol and 1-propanol solution

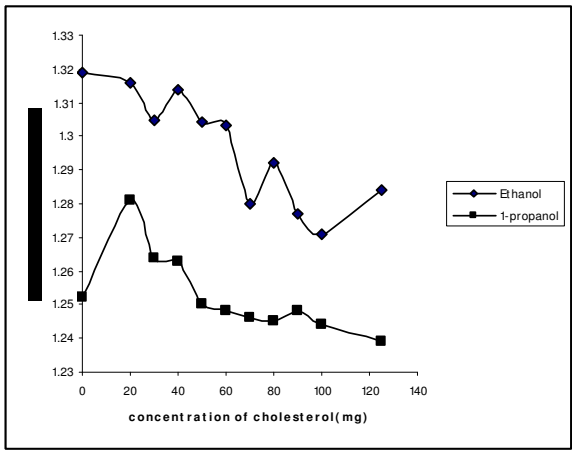

Figure-3
Variation of intermolecular free length of cholesterol in ethanol and 1-propanol solution

The variation of ultrasonic velocity in a solution depends on the intermolecular free length of mixing[9]. Ultrasonic velocity increases on decrease of free length and vice-versa. The computed values are given in table-1. The intermolecular free length decreases with concentration of cholesterol and it is shown in figure-3. This is an indication that the structural readjustment in the liquid binary mixture proceeds in the direction of less compressible phase or closer packing of molecules. A sudden increase in molecular free length shows a looser packing molecules or weak interaction[10]. Acoustic

impedance is almost reciprocal of compressibility. The increase in velocity, impedance and decrease in compressibility and free length with the addition of ethanol and 1-propanol indicates that, intermolecular forces increase with addition of solvents[11]. The calculated values of acoustic impedance are shown in table-1 and table-2. Compressibility decreases with increase in the concentration, whereas, impedance increases for a given concentration. A sudden decrease of impedance at a particular concentration may be due to the complex formation in the solution, and this may be on the basis of the interaction between solute and solvent molecules[12]. The non linear variation of surface tension also supports this interaction1[13]. Relative association was found as non linear variations with ethanol and 1-propanol and it shows the weak and strong interactions and this conclusion is fortified by the values of relative association and it is shown in Figure-4 [14]. Table-3 shows the variations of the B/A values calculated from Hartmann and Ballou relation and the variations are shown in Figure-5. The values of lowering compressibility were computed using the above formula and the variations are shown in figure 6. The lowering compressibility values are positive at lower concentration. It is almost linear decreasing in ethanol solution while it randomly varies in 1-propanol solution. It confirms the interaction between the solvent and solute molecules[15].

Nonlinearity parameter of salts-polyvinyl alcohol mixed solution calculated by Harymann and Ballou relation: In the last few years a number of theoretical methods have been proposed for estimating the nonlinearity parameter (B/A) for pure liquids and liquid mixtures[16]. This parameter has been further correlated with other thermo acoustical parameters which are used to deduce the available volume and intermolecular free length of liquid mixtures. General formulation for non-linearity in terms of acoustical parameters of liquids has been made using the experiment for sound velocity (U) and introducing the contribution due to isobaric acoustic parameters (k) and the isothermal acoustic parameter (k"). The expression for B/A is given by.

$$B/A = 2k + 2\gamma k"$$

Computations of k and k" require only the knowledge of thermal expansion co-efficient. Detailed method of calculation is given by Hartmann and Balizer obtained the following relation for B/A[17-18]

$$B/A = 2+ ((0.98 \times 10^4)/U) \quad (1)$$

Empirical relation proposed by Ballou is given by

$$B/A = -0.5 + ((1.2 \times 10^4)/U) \quad (2)$$

Where U is the velocity in m/s. Table-3 shows the variations of the B/A values calculated from Hartmann and Ballou relation and it shows decreased trend with increase in concentration. The B/A values for the liquids have been interpreted as the quantity representing the magnitude of the hardness of liquids. The B/A values are concenerned with interactions between the components of the binary systems[19]. The interaction between the components of the binary mixtures is weaker at a particular concentration of cholesterol.

From the graphs of ultrasonic velocity, density, compressibility, molecular free length, impedance and surface tension with concentration of cholesterol, it is clear that, ultrasonic velocity increases with concentration of cholesterol in binary mixture of ethanol up to 70mg. Here, ethanol promotes acyl-chain order. At a concentration of 80mg, a sudden decrease of velocity occurs due to weak interaction between solute and solvent molecules. It may be due to H---O---H bonding interactions.

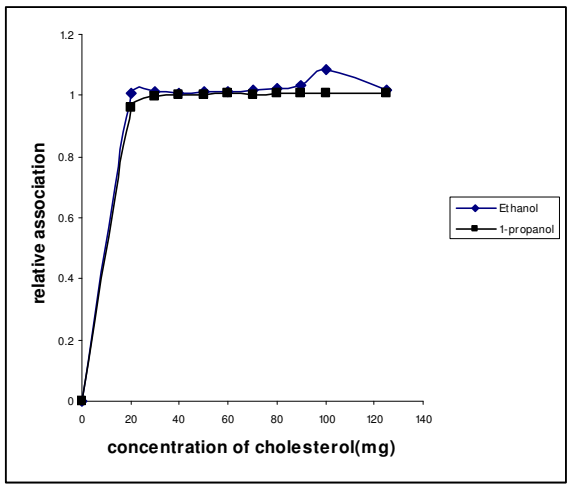

Figure-4
Variation of relative association of cholesterol in ethanol and 1-propanol

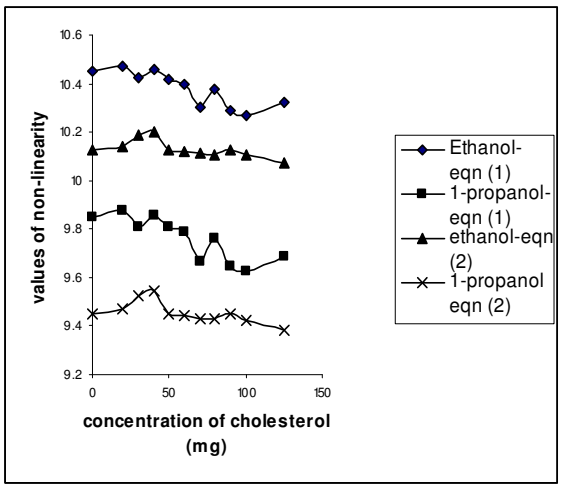

Figure-5
Variation of non-linearity (B/A) of cholesterol in ethanol and 1-propanol solution using equation (1) and equation (2) solution

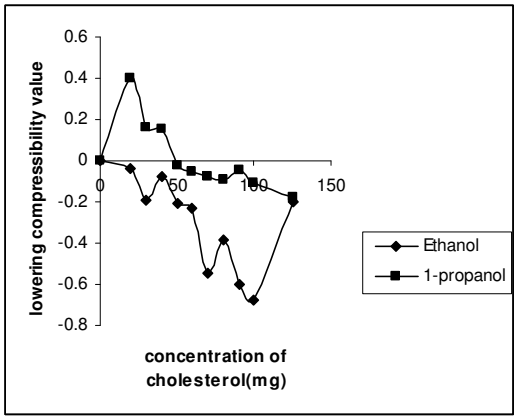

Figure-6
Variation of lowering compressibility values of cholesterol in ethanol and 1-propanol

Table-3
Non-linearity (B/A) values of a binary mixtures of cholesterol in ethanol and in 1-propanol solution at different concentrations using different equations

Concentration of cholesterol (mg)	Cholesterol in ethanol		Cholesterol in 1-propanol	
	Equation (1)	Equation (2)	Equation (1)	Equation (2)
0	10.454	9.852	10.124	9.448
20	10.471	9.873	10.142	9.470
30	10.421	9.812	10.189	9.527
40	10.460	9.859	10.201	9.542
50	10.419	9.809	10.125	9.449
60	10.400	9.787	10.121	9.444
70	10.302	9.666	10.110	9.430
80	10.378	9.759	10.107	9.427
90	10.288	9.649	10.125	9.449
100	10.271	9.627	10.104	9.423
125	10.321	9.689	10.071	9.383

Cholesterol molecules may act as a structure breaker, at higher concentration and ethanol disorders the hydrocarbon interior by tilting the cholesterol chain. An increase in ethanol concentration allows the liquid-ordered phase to exist at higher concentrations. Recall that at low concentration, ethanol disorders the hydrocarbon interior by tilting the lipid chain[20]. Similarly, ultrasonic velocity increases up to a concentration of 80mg and there is a closer interaction between cholesterol and 1-propanol mixture. While, at a concentration of 90mg, there is a weaker interaction. Further increase in the concentration, indicates the strong interaction with 1-propanol. The weak interaction might be due to the two lone pairs of electrons of cholesterol. It shows some immiscibility of solute and solvent molecules and this behavior is the result of structural changes occurring due to the formation of hydrogen bond complexes in the solution. But, in the case of cholesterol with 1-propanol solution, it shows the closer interaction between the solute and solvent molecules. The present study points out clearly that the emergence of a new complex structure is temporarily formed in this system at a particular concentration. Hence, it is concluded that, some disordered structure is formed in the solution and it may be due the formation of micelle. Further study may give more details about complex ion formation.

Conclusion

The ultrasonic velocity and other acoustical parameters of cholesterol in ethanol and in 1-propanol solution were studied. The variations in the acoustical parameters might be due to the formation of complex structures. The present study points out clearly that the emergence of a new complex structure is temporarily formed in this system at a particular

concentration. Hence it is concluded that, some disordered structure is formed in the solution and it may be due the formation of micelle. Further study may give more details about complex ion formation.

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