American Journal of Engineering Research (AJER)
e-ISSN : 2320-0847 p-ISSN : 2320-0936
Volume-02, Issue-10, pp-338-343
www.ajer.org

Research Paper Open Access

Entropy and Enthalpy variations with Acoustic parameters of Cholesteryl oleyl carbonate

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Abstract: - The ultrasonic velocity (U), density (ρ), viscosity (η) have been measured for Cholesteryl oleyl carbonate at different temperatures. From the experimental data, , Free Volume (VF)), Internal Pressure (πi), Relaxation time (τ), Gibbs Free Energy (ΔG), Absorption Coefficient (α) and Enthalpy (H), Entropy(S) have been calculated.Entropy is a thermodynamic state property, its value depends only on the state of a system, not on the history of the system. Therefore, to determine the change in entropy of a system from one state to another, it is sufficient to evaluate the change for a reversible process between those two states; the change in entropy for any other process connecting the same two states will be the same as the change for the reversible process The properties have been used to discuss the presence of significant interactions between the component molecules.

Keywords: - *Cholesteryl oleyl carbonate, Ultrasonic Velocity, Enthalpy(H), Entropy(S),Gibbs Free Energy (ΔG), Absorption Coefficient (α)*

I. INTRODUCTION

The study of intermolecular interaction plays an important role in the development of molecular sciences. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like Infrared [1,2], Raman effect [3,4], Nuclear Magnetic resonance, Dielectric constant[5], ultra violet[6] and ultrasonic method [7,8]. Cholesterol (**$C_{46}H_{80}O_3$, MOL WT-681.14**) is a steroid alcohol that is essentially insoluble in aqueous solutions. Cholesterol can be esterified with a fatty acid to form cholesteryl esters. The latter form discrete lipid droplets in cells, especially in cells of steroidogenic tissues, and in the lipid core of low-density lipoproteins in the blood. Cholesterol is a fatty lipid sparingly insoluble in water but soluble in a number of organic solvents. Cholesteric materials are temperature sensitive and have color changing ability upon temperature.Not only emulsifying and humectant properties but also liquid crystal properties of cholesterol and its derivatives (salts and esters) make them useful in the commercial applications of cosmetics and pharmaceuticals. Measurement of Ultrasonic Velocity is generally made either by continuous wave method or by pulse methods. In the present study, the ultrasonic velocity was measured using a multi ultrasonic Interferometer (Mittal Enterprises Make) for the observation of ultrasonic velocity (C) and knowing the frequency we can find out various parameters such as adiabatic compressibility, acoustic impedance and temperature variation using temperature bath. The density at room temperature was measured using specific gravity bottle and single pan microbalance. Acoustical parameters were calculated using the measure values of velocity, density. The values of ultrasonic velocity, Free Volume (VF)), Internal Pressure (πi), Relaxation time (τ), Gibbs Free Energy (G), Absorption Coefficient (α),Enthalpy(H), Entropy(S),of cholesteryl oleyl carbonate at different temperatures (303K to 323K) are given in Table 1. When a liquid freezes the mobile molecules of the liquid phase are forced to assume fixed positions in the solid phase This will normally reduce the molecular disorder of the system, so there will usually be an entropy decrease that accompanies freezing. Since entropy is a thermodynamic state property, its value depends only on the state of a system, not on the history of the system. Therefore, to determine the change in entropy of a system from one state to another, it is sufficient to evaluate the change for a reversible process between those two states; the change in entropy for any other process connecting the same two states will be the same as the change for the reversible process. At the transition temperature, any transfer of heat between the system and its surroundings is reversible, because the two phases in the system are in equilibrium.

II. SOME FORMULAE OF THE PARAMETERS TO BE CALCULATED

Gibbs free energy is calculated from acoustic relaxation time (τ) following Eyring rate process theory [19]:

$$\Delta G = RT \ln(KT\tau / h)$$

Where K = 1.23×10^{-23} J/K, T is the temperature, τ is the relaxation time, h = 6.626×10^{-34} Js (Planck's Constant) **.** Acoustic relaxation time (τ) is calculated using the following relation:

$$\tau = 4\eta / 3\rho C^2$$

Acoustical relaxation time indicates the the presence of interactions. The internal pressure is calculated from the free volume concept on the basis of statistical thermodynamics as,

$$\pi i = bRT [K \eta / C]^{1/2} [\rho^{2/3} / M^{7/6}]$$

Absorption coefficient (α) is calculated from the following equation $\alpha = \omega^2 \tau / 2C$ [19] where $\omega = 2\pi f$, C is the ultrasonic velocity, η is viscosity, ρ is the density and M is the molecular weight of the cholesteryl oleyl carbonate taken .The enthalpy (H) is calculated from the relation

$H = \pi i$ **(Vf)**

Entopy(S) is calculated from the relation G =H –T S

Fig 1:

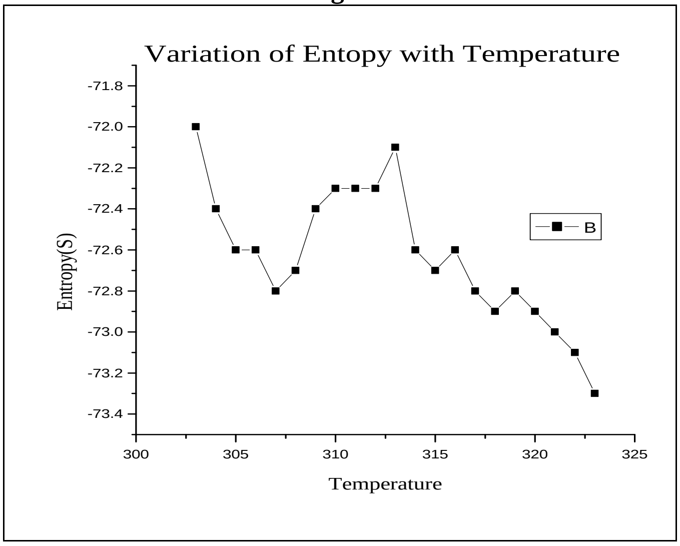

Fig 2:

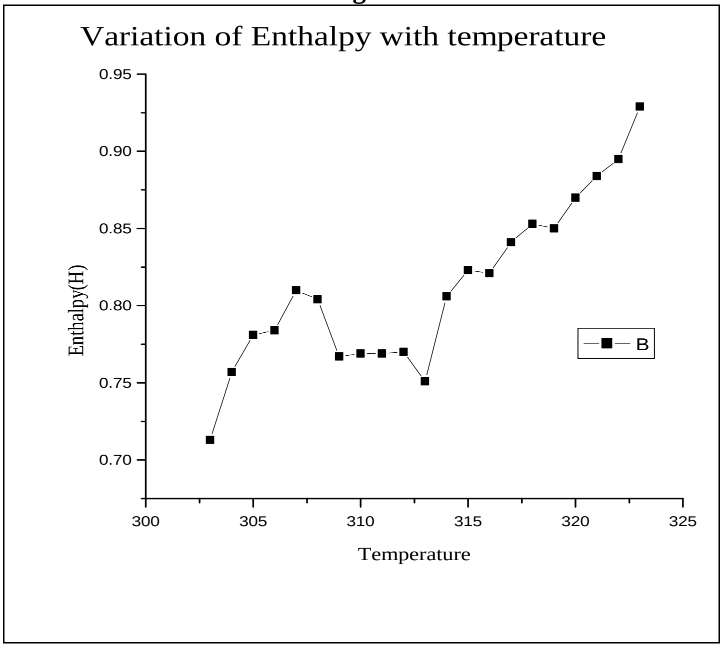

Fig 3:

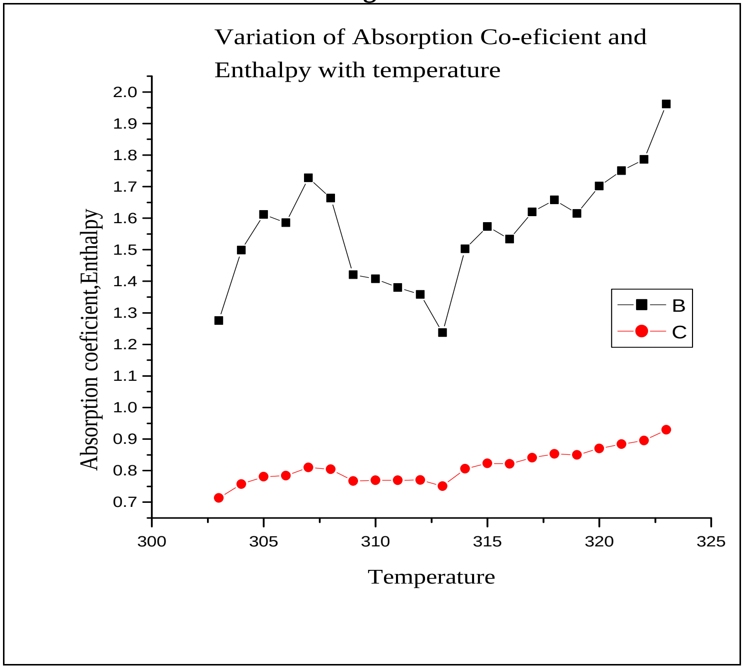

Table 1:

Abs. Temp	C m/s	τ (relaxation time)	ΔG	πi	α	Vf
303	1748	1.11E-09	2.20E+04	6.11E+05	1.275022155	1.17E-06
304	1568	1.17E-09	2.22E+04	5.95E+05	1.498288025	1.27E-06
305	1492	1.20E-09	2.24E+04	5.87E+05	1.611565767	1.33E-06
306	1504	1.19E-09	2.24E+04	5.88E+05	1.585643054	1.33E-06
307	1420	1.23E-09	2.26E+04	5.80E+05	1.727882688	1.40E-06
308	1456	1.21E-09	2.27E+04	5.84E+05	1.663199766	1.38E-06
309	1616	1.15E-09	2.26E+04	5.99E+05	1.420397546	1.28E-06
310	1624	1.14E-09	2.27E+04	6.00E+05	1.407639041	1.28E-06
311	1644	1.13E-09	2.27E+04	6.01E+05	1.379806776	1.28E-06
312	1660	1.13E-09	2.28E+04	6.03E+05	1.357724825	1.28E-06
313	1764	1.09E-09	2.28E+04	6.12E+05	1.237459938	1.23E-06
314	1548	1.16E-09	2.30E+04	5.92E+05	1.502899463	1.36E-06
315	1500	1.18E-09	2.32E+04	5.88E+05	1.573109748	1.40E-06
316	1524	1.17E-09	2.32E+04	5.90E+05	1.533663903	1.39E-06
317	1468	1.19E-09	2.33E+04	5.84E+05	1.619692135	1.44E-06
318	1444	1.20E-09	2.34E+04	5.82E+05	1.657627099	1.47E-06
319	1468	1.19E-09	2.35E+04	5.84E+05	1.614606747	1.46E-06
320	1416	1.20E-09	2.36E+04	5.79E+05	1.701693416	1.50E-06
321	1388	1.21E-09	2.37E+04	5.76E+05	1.750711048	1.53E-06
322	1368	1.22E-09	2.38E+04	5.74E+05	1.786463329	1.56E-06
323	1284	1.26E-09	2.40E+04	5.65E+05	1.961563587	1.65E-06

Fig 4:

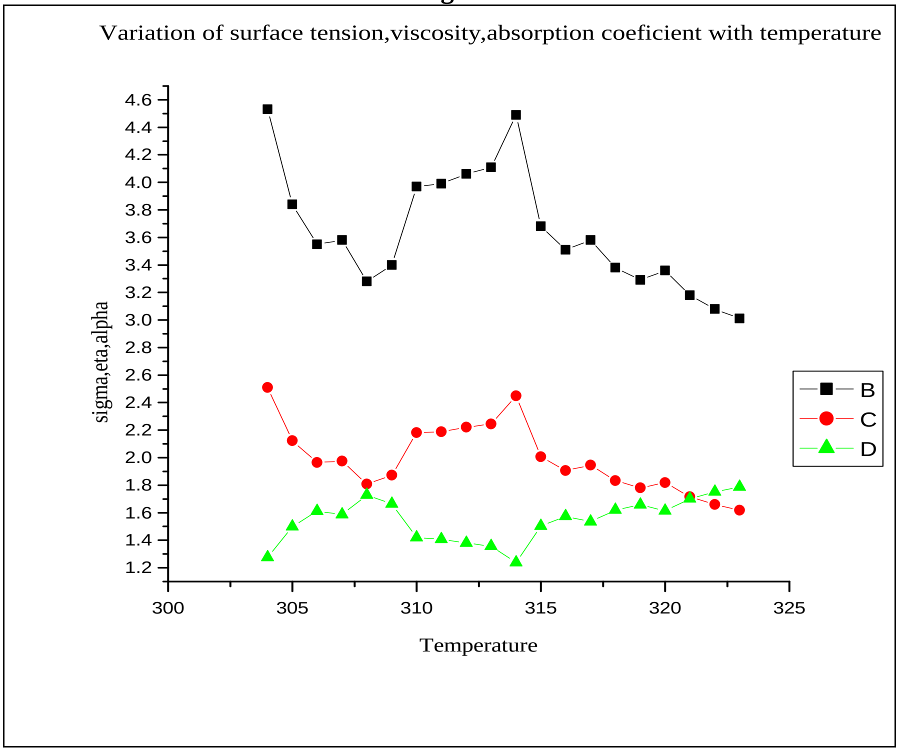

Table2:

Absolute Temp(T)	**C(m/s)**	**Sigmax10^{-4}(σ)**	**Eta(η)**	**ρ □□k g/m3)**	**□ □ □ □ □ H □**	**S**
303	1748	4.53	2.510051	982.9000	7.13E-01	-7.20E+01
304	1568	3.84	2.124227	980.7000	7.57E-01	-7.24E+01
305	1492	3.55	1.964224	978.6000	7.81E-01	-7.26E+01
306	1504	3.58	1.975388	976.5000	7.84E-01	-7.26E+01
307	1420	3.28	1.807604	974.3000	8.10E-01	-7.28E+01
308	1456	3.40	1.87161	972.2000	8.04E-01	-7.27E+01
309	1616	3.97	2.180629	970.1000	7.67E-01	-7.24E+01
310	1624	3.99	2.188548	968.0000	7.69E-01	-7.23E+01
311	1644	4.06	2.220686	965.9000	7.69E-01	-7.23E+01
312	1660	4.11	2.244912	963.9000	7.70E-01	-7.23E+01
313	1764	4.49	2.449869	961.8000	7.51E-01	-7.21E+01
314	1548	3.68	2.006363	959.7000	8.06E-01	-7.26E+01
315	1500	3.51	1.906749	957.7000	8.23E-01	-7.27E+01
316	1524	3.58	1.94553	955.7000	8.21E-01	-7.26E+01
317	1468	3.38	1.832349	953.6000	8.41E-01	-7.28E+01
318	1444	3.29	1.781042	951.6000	8.53E-01	-7.29E+01
319	1468	3.36	1.818934	949.6000	8.50E-01	-7.28E+01
320	1416	3.18	1.71683	947.6000	8.70E-01	-7.29E+01
321	1388	3.08	1.660052	945.6000	8.84E-01	-7.30E+01
322	1368	3.01	1.618347	943.6000	8.95E-01	-7.31E+01
323	1284	2.73	1.466207	941.6000	9.29E-01	-7.33E+01

An increase of entropy can cause numerous side-effects: Changes of volume, form, phase,magnetism,etc. Entropy decreses with temperature upto 307 K but there is maximum entropy at 313 K, which may point to BP II and BP I [3] phase transitions.

III. RESULTS AND DISCUSSION

Table 1 represents the experimentally measured values of ultrasonic velocity(U) , Gibbs free energy(ΔG), Classical Absorption Coefficient, Free Volume (VF) ,), Internal Pressure(πi), Relaxation time(τ), at different temperatures. Table 2 represents the variation of Enthalpy(H), Entropy(S),surface tension,viscosity,density. The excess values of relaxation time, internal pressure, and Gibbs free energy indicate that the interaction between the molecules does not seem to vary very much in strength with changing frequency. Hence, intermolecular interaction in the case of cholesteryl oleyl carbonate is large. However, with rise in temperature increase in free volume and decrease in internal pressure are noticed.From the table (1) Gibbs Free Energy, Classical Absorption Coefficient increases with the increase in temperature.Increase in Gibbs' free energy suggests shorter time for rearrangement of molecules. Relaxation time is the time taken for the excitation energy to appear as translational energy. The above fact confirms the minimum interaction between the molecules in cholesteryl oleyl carbonate . Viscous relaxation time and the Gibbs' free energy both decreases as temperature increases. As temperature increases, excitation energy increases and hence relaxation time decreases. Further, since the kinetic energy of the molecule increases, longer time is taken for rearrangement of molecules and this suggest a decrease in Gibbs' free energy. Free volume is the average volume in which the centre of a molecule can move due to the repulsion of the surrounding molecules. . This suggests that there is a closed packing of molecules inside the shield. Such an increase in internal pressure generally indicates association through hydrogen bonding and hence supports the present investigation. Figure 1 shows variation of entropy with temperature. From the graph it is observed that the entropy decreases with the increasing value of temperature, but a clearly visible change of the temperature evolution occurs at 307 and 313 , which may point to BP II and BP I [3] phase transitions. Recently the stabilization of blue phases over a temperature range of more than 60 K including room temperature (260–326 K) has been demonstrated [17,18] . Highly chiral liquid crystals, on the other hand, may exhibit one or more blue phases (BP) as they are heated from the helical phase to the isotropic phase. In addition, the blue phases possess a much higher viscosity than either the helical or isotropic phase. In both cases, it is likely that the crystalline ordering of the blue phases is responsible for giving these liquids properties which one usually associates with solids. The phase of a thermotropic liquid crystal is temperature dependent. As temperature is varied, the conditions on the translational and orientational order of the constituent molecules which produce the most energetically favorable system may also change.

IV. CONCLUSION

The results obtained for the present study indicate that the thermodynamic parameters are sensitive to the molecular interaction present in cholesteryl oleyl carbonate . From Ultrasonic velocity and related acoustical parameters for cholesteryl oleyl carbonate at varying temperature, it is concluded that there exists a strong molecular interaction due to hydrogen bonding.

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