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Ultrasonic Study of Molecular Interaction of *cis*-Potassium Trioxalato Aluminate (III) Trihydrate Complex with Propenol-Water Mixture at Different Temperature

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ABSTRACT

The measurement of density and ultrasonic velocity of cis-potassium trioxalato aluminate (III) trihydrate complex with propanol-water mixturehave be measured in aqueous solution at different concentration and different temperature.

The simple physical properties like density and ultrasonic velocity and viscosity are used to explain the molecular interaction in aqueous solution of propanol. The apparent molar volume, adiabatic compressibility, apparent molar compressibility, acoustical impedance, intermolecular free length, wada's constant and viscosity relaxation time have been calculated . The result are discussed in the light of solute-solvent interaction and structural effects on the solvent in solution.

Keywords: Ultrasonic velocity, density, viscosity, adiabatic compressibility, wada'sconstant ,viscosity relaxation time

I. INTRODUCTION

1.1. General Introduction:

Ultrasonic method finds extensive application for characterizing aspects of physiochemical behavior such as the nature of molecular interaction in pure liquids as well as liquid mixture [1-5]. The study of the solution properties of liquid mixture consisting of polar as well as nonpolar components finds application in industrial and technological process. Most of the work on binary mixture is channelized towards the estimation of thermodynamic parameters like adiabatic compressibility, free length etc, and their excess value so as to relate them towards explaining the molecular interaction taking place between the components of the binary mixture. Further, such studies as a function of concentration are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes [5-10]. Ultrasonic velocity measurement have been successfully employed to detect and assess weak and strong molecular interaction present in binary liquid mixture. We have measured (ρ), ultrasonic velocity (u), viscosity (η), with different mole fraction at different temperature. From this data, acoustical parameter like adiabatic compressibility (β), inter molecular free length (Lf), free volume (Vf), and their excess values are computed. Result are used to explain the nature of molecular interaction between mixing compound. Further, the experimentally measured ultrasonic velocities

at various molar concentration have been compared with theoretically estimated velocities based on empirical, semi-empirical & statistical models for the binary system.

Further, such a study of molecular interaction between solute molecule and solvent media has got great important in many fields of science including medicinal chemistry, industrial processes, biochemistry etc. The solute-solvent and solvent-solvent interaction can be studied by the measurement of relative viscosity and ultrasonic velocity of an electrolyte in solution. This type of study helps us to understand the structure making and breaking properties of solute. Ultrasonic waves in recent year, have acquired the status of an important probe for the study of structure and properties of matter in basic science ultrasonic parameter are being extensively used to study molecular interaction in pure liquid [3-5], liquid mixture [6-8] and electrolytic solution [9].

II. MATERIAL AND METHOD

2.1 Prepration of potassiumtrioxalato aluminate (III) trihydrate complex.

For preparation of complex we use the reference procedure from vogel's inorganic practical book. From this, 0.5 g of aluminium foil will taken in 250 ml beaker , 50 ml 30% KOH solution is added with content stirring in a small portion filter and remove residue. Beaker is heated up to boiling to dissolve aluminium foil completely . To this solution about 4.5g of oxalic acid is added in small in stamen and heated it in water bath Then the solution was filtered un reacted residue was clear filter was allow to settle down and then precipitation was filter . After filtration dry the ppt and weight. Take 25 ml of complex solution in a conical flask and added 6.5ml of butter solution (pH=10) and 3-4 drops of ereochrome black -T . Weight accurately 0.05 g of complex . Dissolved in water and dilute up 50 ml volumetric flask then in a conical flask 10 ml dil . H2So4 and 10 ml of complex solution is added . Then the solution of conical flask was heated upto 60 C° to and then titrate against standard KMnO4 solution. Yield of the complex is 5g m and colourof the complex is white crystals.

2.2 PHYSICAL MEASUREMENT:

Solutions of varying concentration were prepared on molarity basis from 0.04 stock solution of each complex sample with double distilled water. All the measurements were carried out at 303.15K, 308.15K, 313.15K, and . Density measurements were carried out for different solutions at 303.15K, 308.15K, 313.15K, and using a open capillary density bottle. The ultrasonic velocity in the solutions was measured using an ultrasonic interferometer at a frequency of 2 MHz with an accuracy of ±0.05 %. The relative viscosity was measured using a pre-calibrated Ostwald viscometer.

2.2.1 Methods of calculation:

THEORY AND CALCULATIONS:

The data of density (ρ), ultrasonic velocity (u) and viscosity (η) has been used to evaluate many acoustical parameters by using the following standard expressions for understanding solute-solvent, solvent-solvent interaction and structural changes.

(i) **Adiabatic compressibility:-** $\beta_s = \frac{1}{\rho_s u_s^2} \text{-------(1)}$

Where $\rho_s =$ density of solution, $u_s =$ sound velocity.

(ii) **Intermolecular free length** (L_f) **:-** $L_f = K\sqrt{\beta_s}$ ------(2)

Where 'K' is a temperature dependent constant known as Jacobson constant [m].

(iii) **Specific acoustic impedance (Z):-** $Z = u_s \rho_s$ --------(3)

(iv) **Wada's constant** (W) **:-** $W = \left(\frac{M}{\rho_s}\right) \cdot \beta_s^{\frac{1}{7}}$ ------(4)

Where 'M' molar mass of the solution.

(v) **Molar sound velocity or Rao's constant** (R) **:-** $R = \left(\frac{M}{\rho_s}\right) \cdot u_s \, 1/3$ -------(5)

(vi) **Relative association** (R_A) **:-** $R_A = \left(\frac{d_s}{d_o}\right)\left(\frac{u_o}{u_s}\right)^{1/3}$ ------(6)

Where ρ_o= density of solvent, u_o = velocity of solvent

(vii) **Apparent molar compressibility** (Φ_β): $\Phi_\beta = \left(\frac{1000}{m\rho\rho_o}\right) - (\rho_o\beta - \rho\beta_0) + \left(\frac{\beta_0 M}{\rho_0}\right)$ --(7)

(viii) **Apparent molar volume** (Φ_V):- $\Phi_V = \left(\frac{1000}{m\rho\rho_o}\right)(\rho_o - \rho) + \left(\frac{M}{\rho_0}\right)$ ----(8)

(ix) **Relative viscosity(η)**:- $\eta_r = \left[\frac{d_s . t_s}{d_w t_w}\right]\eta_w$ ----------(9)

(x) **Viscosity relaxation time :-** $\Gamma = \frac{4\eta}{3\rho . u^2}$ ----------(10)

(xi) **Absorption coefficient:** $Abs_{coeff}(a/f2) = \frac{8\pi^2\eta}{3\rho \times u^2}$ ------(11)

(xii) **Internal pressure (**π_i**)** :- $\pi_i = bRT\left(\frac{K.\eta}{u}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right)$ --(12)

(xiii) **Free volume** (V_f):- $V_f = \left(\frac{M_{eff} u}{K.\eta}\right)^{3/2}$ -------(13)

'k' is temperature independent constant equal to 4.28×10^9 for all liquids.

(xiv) **Gibb's free energy (**ΔG**)** was calculated from the relation; $\Delta G = KT \log\left(\frac{K.T.\Gamma}{\square}\right)$ ----(14)

'K' Boltzmann constant, 'ħ' is Planck constant and Γ relaxation time.

❖ **The units of** -Density(ρ):**kg cm^{-3}** ,Viscosity(η): **cp ,** Ultrasonic velocity (U) : **ms^{-1}**

Adiabatic compressibility (β_s): **cm^{2}dyne^{-1}**, Apparent molar volume (Qv): **cm^{-3} mol $^{-1}$**,Apparent molar compressibility (Qk): **cm^{-3} mol $^{-1}$bar^{-1}**, Acoustical Impedance (Z): **kg. m^{-2}s^{-1}** Intermolecular free length (L_f): **m**, Wada's constant (W**): m^3 Pas$^{-8/7}$ mol^{-1}**, Viscosity relaxation time (τ): s

III. RESULT & DISCUSSION

AL IN PROPANOL

Table 1: Density (ρ), ultrasonic velocity (u), adiabatic compressibility (β_s), intermolecular free length (L_f), acoustical Impedance (Z), Wada's constant (W), Rao's constant (R), relative association (R_A), apparent molar compressibility (ϕ_β), apparent molar volume (ϕ_V) for AL IN propanol at different temperatures.

Conc	ρ kg.m^{-3}	u m s^{-1}	β_s 10^{-11} m^{2}N^{-1}	L_f 10^{-11} m	Z x10^6 kg. m^{-2}s^{-1}	W m^3 Pas$^{-8/7}$ mol^{-1}	R	R_A	$\phi_\beta \times 10^{-1}$ m^{2}n^{-1}	ϕ_V m^3 mol^{-1}
T=303.15K										
0.000	1716.4	4364	3.0592	1.1477	7.4904	8.6695	1190.76	0.9919	_	_
0.001	1701.6	4356.8	3.0960	1.1546	7.4135	8.7300	1199.14	0.9919	5.8429	-1.3943
0.002	1697.6	4331.6	3.1396	1.1627	7.3533	8.7331	1195.01	0.9915	2.9258	-3.4296
0.003	1695.6	4322.8	3.1561	1.1657	7.3297	8.7369	1193.99	0.9910	1.9534	-2.0332
T=308.15K										
0.000	1719.3	4291.2	3.15857	1.1769	7.3779	8.6155	1168.92	0.9842	_	_
0.001	1717.2	4484.4	2.89581	1.1268	7.7006	8.7337	1223.05	0.9842	5.7800	-1.2496
0.002	1703.6	4462.4	2.94778	1.1369	7.6021	8.7811	1226.76	0.9780	2.9106	-1.5137
0.003	1699.6	4450.4	2.97068	1.1413	7.5639	8.7920	1226.34	0.9766	1.9455	-1.9233
T=313.15K										
0.000	1722	4366	3.0465	1.1646	7.5183	8.6465	1187.44	0.9849	_	_
0.001	1709.2	4468.8	2.9297	1.1421	7.6381	8.7600	1224.50	0.9849	5.7950	-1.1949
0.002	1708.8	4465.6	2.9346	1.1430	7.6308	8.7600	1223.91	0.9849	2.8982	-1.2638
0.003	1700.4	4427.2	3.0005	1.1558	7.5280	8.7754	1219.38	0.9829	1.9417	-2.1134

Table 2: Viscosity (η), viscosity relaxation time (τ), Abs coefficient, internal pressure (π_i), free volume (V_f) and Gibbs free energy (ΔG) of AL IN propanol at different temperatures.

Conc.	η x 10^{-3} Nsm^{-2}	τ x 10^{-14} s	$\alpha/f^2 \times 10^{-14}$	π_i x10^5 Pa	V_f x10^{-3} m^{3}mol^{-1}	ΔG x10^{-21}
T=303.15K						
0.000	1.20	4.8948	4.8946	2.5868	8.5558	-2.1337
0.001	1.12	4.6234	4.6233	2.4868	9.4652	-2.2374
0.002	1.17	4.8977	4.8976	2.5451	8.7882	-2.1326
0.003	1.21	5.0918	5.0917	2.5888	8.3306	-2.0620
T=308.15K						
0.000	1.19	5.0116	5.0115	2.6007	8.4480	-2.0951
0.001	1.25	4.8264	4.8262	2.6053	8.3829	-2.1647
0.002	1.30	5.1095	5.1094	2.6494	7.8459	-2.0593

0.003	1.32	5.2284	5.2283	2.6691	7.6373	-2.0168
T=313.15K						
0.000	1.14	4.6307	4.6305	2.5262	9.2464	-2.24731
0.001	1.22	4.7657	4.7655	2.5703	8.6487	-2.19335
0.002	1.27	4.9693	4.9691	2.6230	8.1343	-2.11479
0.003	1.30	5.2008	5.2007	2.6565	7.7532	-2.02927

All discussion are disscuss as shown in Table 1 and Table 2.

Density decrease and ultrasonic velocity and viscosity are increase with increase in concentration of solute. The linear behavior with increase in velocity with concentration indicates the interaction between unlike molecule, which suggests weak solute-solvent (dipole-dipole) interaction between the component molecules. As density decreases the number of solute particles in the given region decreases [17]. It shows reverse trends in ultrasonic velocity and density with increase in temperature show molecular forces are weak at high temperature. The increase in ultrasonic velocity is structure making type.

Increase in concentration of cis- potassium trioxalato aluminate (III) trihydrate complex results the linearly increases in adiabatic compressibility and free length. This trend supports weak solute-solvent interaction and suggests aggregation of solvent molecules around solute molecules [18,19]. The magnitude of adiabatic compressibility and free length decreases with increase in temperature, it clearly reveal that interaction become stronger at higher temperature [20]. The specific acoustic impedanceis the parameter related to the elastic properties of the medium. The specificacoustic impedance is the impedance offered to the sound wave by the components of the mixture. In present investigation, specific acoustic impedance decrease with increase in concentration. This trend further supports that there was no possibility of molecular interaction due to H-bonding between solute-solvents and solvent-solvent molecules which restrict the free flow of sound waves [21]. The specific acoustic impedance is directly proportional to density, ultrasonic velocity and inversely proportional adiabatic compressibility [22].

The molar compressibility (Wada's constant)and Molar sound velocity (Rao's constant) non linearly increase with increase in concentration which indicates that the magnitude of molecular interaction is enhanced in the system, which indicate interaction between solute-solvent molecule decrease. This leads to tight packing of the medium by decrease the molecular interactions [23].

Relative associationis the measure of extent of association of components in the medium. The relative association is depends on either breaking up of the solvent molecules on addition of solute to it or the solvation of present ions. The relative association non-linearly decreases with increase in concentration.

The apparent molar compressibility and apparent molar volume decreases with increase in concentration which indicates interaction between solute-solvent molecules enhanced. Some values are positive due to the compressibility of solvent due to the weak electrostatic force in the vicinity of ions. This trendssupports that the availability of more number of components in a given regions of space. This leads to tight packing of the medium and there by increases the interactions [24].

The viscosity relaxation time is the time required for the excitation energy to appear as translational energy. In present work viscosity relaxation time non-linearly decreases with increase in molar concentration and decreases with increases in temperature. Where, with increase in temperature, it shows the instantaneous conversion of excitation energy to translational energy. This indicates strong molecular interaction between the solute and solvent molecules, where it show the instantaneous conversion of excitation energy to

translational energy [25]. Absorption coefficientdecreases with increase in concentration and this trend suggest that the extent of complexity decreases with increase in concentration [26].

The internal pressure is a measure of cohesive forces between the constituent's molecules in liquids. The internal pressure is an inverse function of free volume. The internal pressure for a given system decreases with increase in concentration of solute, which indicate decrease in London force (cohesive forces) which leading to breaking the structure of solute. This suggests there is a weak interaction between the solute and solvent molecules. (or there is an decrease in the extent of complexation with increase in concentration [27].

The free volume increases with increase in concentration of solute and temperature. This increasing trend is due to stronger intramolecular interaction than intermolecular interaction which attribute to lose packing of molecules inside the shield, this suggest weak molecular interaction in components of mixtures [28]. The Gibb's free energy decreases with increase in molar concentrations of and non-linearly increases with increase in temperature the cis- potassium trioxalato aluminate (III) trihydrate complex. The increase in Gibbs free energy (ΔG) with temperature suggests longer time for rearrangement of molecules in the mixture [29]. The decreasing positive values of Gibbs free energy (ΔG) suggest the molecular dissociations [30].

IV. CONCLUSIONS

From the present investigation experimental values of density, ultrasonic velocity, viscosity and related acoustic parameter values indicate that thermodynamic parameters are sensitive to molecular interactions for ternary liquid mixtures at different concentrations and at varying temperatures. Thus it is conclude that in mixture of studied compound, both solute-solute and solute-solvent interaction is existed. Some parameters specially, free length and adiabatic compressibility indicate strong interaction between solute-solvent molecules in the studied system.

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