Partial Molar Volume, Partial Molar Adiabatic Compressibility and Viscosity Coefficient of Acidic Solution of Cis- Potassium Dioxalatodiaquochromate(III) Dihydrate Complex

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ABSTRACT

The ultrasonic study of oxalic acid and its complex with chromate(III) have been measured in acidic pH solution at different temperature and concentration. The apparent molar volume, adiabatic compressibility, apparent molar compressibility, partial molar volume and partial molar compressibility have been calculated and analyzed using the Jones-Dole equation. The interesting results were outcome; in solute-solvent interaction due to acidic pH solution gives more effect on bond making and breaking process.

Keywords: Ultrasonic velocity, Adiabatic compressibility, Jones-Dole equation

INTRODUCTION

The ultrasonic velocities explain the solute-solvent, solvent-solvent and solute-solute interactions in solution [1,2]. The studies of complex compounds favor the effect of size and charge of the ions on ion-solvent interactions [3,4]. The liquid mixtures containing polar and non-polar components have applications in industrial and technological process [5]. The ultrasonic parameters are used to study the molecular interactions in pure liquids. The mixing of different components gives rise to solutions that generally do not behave ideally [6,7]. Further these properties have been widely used to study the molecular interaction between the various species in the mixture [8,9].

This investigation presents the interaction between cis- potassium dioxalatodiaquochromate(III) dihydrate complex and oxalic acid in acidic pH medium.

MATERIALS AND METHODS

Preparation of cis- potassium dioxalatodiaquochromate(III) dihydrate complex

The mixture of oxalic acid (3 g) and potassium dichromate (1 g) was taken in dry mortar pastel and grind it. After that, transfer the powder into china dish with water. Heat the reaction mixture for 3 min at low flame. After heating cool the reaction mixture and pour 10 ml ethanol in it. The product thus separated was filtered, washed with ethanol.

Physical measurements

The solutions of varying concentration were prepared on molarity basis from 0.04 stock solution of each complex sample with double distilled water. The densities were measured with the help of specific gravity bottle. The ultrasonic velocity was measured by using multi-frequency interferometer (Model: F-81S, Mittal Enterprises, New Delhi,) at a frequency of 3 MHz with an accuracy of ± 0.05%. The temperature was maintained constant by using a thermostatic bath. The relative viscosity was obtained by using an Ostwald viscometer.

Methods of calculation:

1. The adiabatic compressibility was calculated from the Eq. 1:

$$\beta s = 1/U^2 \rho \tag{1}$$

where, U is the ultrasonic velocity and ρ is the density.

2. The apparent molar volume was calculated from Eq. 2 given below:

$$\phi_v = 1000(\rho_s - \rho_o)/m\rho_s - \rho_o + M/\rho_o \tag{2}$$

where ρ_s and ρ_o are the densities of the solution and water respectively, m was the molarity and M is the molecular weight of solute.

3. The apparent molar volume has been calculated at different concentration, according to Masson's equation [10]:

$$\phi_v = _{vo} + S_k \sqrt{c} \tag{3}$$

where, ϕ_{vo} is the partial molar volume at infinite dilution and is a measured of solute-solvent interaction. It is obtained from the linear plot of ϕ_v versus $\sqrt{c}$ extrapolating to infinite dilution using a least-square method. S_k is the experimental slop and measure of ion solvent interaction.

4. The apparent molar compressibility was computed from the relation:

$$\phi_k = 1000(\beta_s - \beta_o)/m\rho_0 + \beta_{sv} \tag{4}$$

where β_o and β_s are the compressibility of the solvent and solution respectively. The partial molar compressibility ϕ_{ko}, a measure of the solute-solvent interaction has been deduced from the linear plot of ϕ_k versus $\sqrt{c}$.

5. Viscosity data were analyzed using Jones-Dole equation [11]:

$$\eta/\eta_o = 1 + A\sqrt{c} + Bc \tag{5}$$

where η and η_o are the viscosities of solution and solvent respectively. A and B are the Falkenhagen and the Jones-Dole coefficient respectively. The constant A is associated with the contribution of inter -ionic electrostatic forces [12] and B is measure of order or disorder introduced by the ions into the solvent structure and was specific and an approximately additive property of ions of the electrolyte at a given temperature. On plotting η/η_o versus $\sqrt{c}$ the coefficient A and B can be obtained [13].

RESULTS AND DISCUSSION

The density (ρ), viscosity (η), and ultrasonic velocity (U) of the oxalic acid and cis-potassium dioxalatodiaquochromate(III) dihydrate complex was determined experimentally in **Table 1** and adiabatic compressibility (β_s), apparent molar volume (ϕ_v) and apparent molar compressibility (ϕ_k) values shown in **Table 2** along the concentration range 0.04 mol dm^{-3} to 0.005 mol dm^{-3} at different temperature.

Table 1: Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of oxalic acid and cis- potassium dioxalatodiaquochromate(III) dihydrate complex in acidic pH solution at different temperature.

Conc. (mol dm^{-3})	ρ (g cm^{-3})				η (cp)				U (ms^{-1})		
	298.1 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K
Oxalic acid											
0.04	1.0071	1.0059	1.0042	0.9954	0.7617	0.8328	0.6934	0.6756	1501.2	1473.6	1519.2
0.02	0.9954	0.9923	0.9975	0.9979	0.8346	0.7829	0.6888	0.5583	1517.3	1514.2	1517.5
0.01	0.9942	0.9936	0.9962	0.9854	0.7792	0.784	0.7067	0.6507	1502.2	1517.5	1512.0
0.005	0.9973	0.9960	0.9952	0.9911	0.8271	0.8052	0.6934	0.6272	1503.6	1514.6	1519.2
Cis-K[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$].2H$_2$O											
0.04	1.0002	0.9964	1.0025	1.0103	0.7566	0.7473	0.7492	0.6580	1506.0	1512.1	1578.2
0.02	0.9977	0.9893	0.9911	1.9892	0.7820	0.8384	0.7126	1.3503	1510.6	1516.2	1518.1
0.01	0.9938	0.9934	1.0059	1.9739	0.8423	0.8902	0.7232	1.7020	1515.3	1521.7	1494.0
0.005	0.9927	0.9892	0.9927	1.0013	0.9001	0.8961	0.7419	0.6613	1522.7	1525.9	1512.3

Ultrasonic velocity and density

The Values of ultrasonic velocity for cis- potassium dioxalatodiaquochromate(III) dihydrate complex were higher than oxalic acid only at lower temperature. At higher temperature of 313.15 K, the opposite trend was observed. Meanwhile, the values of density for cis- potassium dioxalatodiaquochromate(III) dihydrate complex were higher than oxalic acid only at higher temperature of 313.15 K due to formation of incompressible salt (KCl) from acidic

medium in complex solution and salt increase the mass without changing the volume very much. This shows about the impact of ligands, metal ions and acidic pH medium on the solute-solvent interaction.

Table 2: Values of adiabatic compressibility (β_s), apparent molar volume (ϕ_v) and apparent molar compressibility (ϕ_k) of oxalic acid and cis-potassium dioxalatodiaquochromate(III) dihydrate complex in acidic pH solution at different temperature.

Conc. (mol dm⁻³)	β_s (cm²dyne⁻¹)				ϕ_v (cm³mol⁻¹)				ϕ_k (cm³mol⁻¹bar⁻¹)			
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Oxalic acid												
0.04	4.41 × 10⁻⁹	4.58 × 10⁻⁹	4.31 × 10⁻⁹	4.28 × 10⁻⁹	551.51	544.35	570.65	37.40	-8.88 × 10⁻⁶	1.17 × 10⁻⁴	1.17 × 10⁻⁴	1.06 × 10⁻⁴
0.02	4.36 × 10⁻¹¹	4.40 × 10⁻¹¹	4.35 × 10⁻¹¹	4.28 × 10⁻¹¹	397.18	280.83	677.08	73.63	-2.43 × 10⁻⁴	-5.05 × 10⁻⁹	-1.74 × 10⁻⁸	-8.74 × 10⁻⁸
0.01	4.46 × 10⁻¹¹	4.37 × 10⁻⁷	4.39 × 10⁻⁷	4.36 × 10⁻¹¹	544.18	570.54	1095.55	-1255.4	-4.86 × 10⁻⁴	-3.55 × 10⁻⁸	0.0449	-1.55 × 10⁻⁷
0.005	4.43 × 10⁻⁹	4.38 × 10⁻¹¹	4.35 × 10⁻¹¹	4.33 × 10⁻¹¹	1585.47	1487.34	1877.74	-1474.55	-7.77 × 10⁻⁵	-4.30 × 10⁻⁸	-1.17 × 10⁻⁷	-3.20 × 10⁻⁷
Cis-K[Cr(C₂O₄)₂(H₂O)₂].2H₂O												
0.04	4.41 × 10⁻⁷	4.39 × 10⁻⁷	4.01 × 10⁻⁷	4.23 × 10⁻⁷	559.81	485.09	708.81	583.87	0.0112	0.0113	0.0104	0.0108
0.02	4.42 × 10⁻⁷	4.42 × 10⁻⁷	4.38 × 10⁻⁷	2.22 × 10⁻⁷	688.39	305.21	536.52	25219.44	0.0223	0.0224	0.0224	0.0166
0.01	4.44 × 10⁻⁷	4.40 × 10⁻⁷	4.45 × 10⁻⁷	2.23 × 10⁻⁷	673.24	722.40	2248.63	49744.64	0.0446	0.0448	0.0461	0.0334
0.005	4.45 × 10⁻⁷	4.42 × 10⁻⁷	4.41 × 10⁻⁷	4.30 × 10⁻⁷	1823.81	274.55	1546.29	759.36	0.0898	0.0895	0.0899	0.0864

Table 3: Partial molar volume (ϕ_{vo}), partial molar compressibility (ϕ_{ko}) at infinite dilution and experimental slope of oxalic acid and cis- potassium dioxalatodiaquochromate(III) dihydrate complex in acidic pH solution at different temperature.

Set I	Temp	ϕ_{vo}	Sv	ϕ_{ko}	B
Oxalic acid	298.15 K	1603	-6497	-0.000396	-0.5295
	303.15 K	1516	-6205	-0.000084	3.664
	308.15 K	2256	-9364	-0.02838	1.413
	313.15 K	-2336	13110	-0.000077	8.85
Set II	**Temp**	ϕ_{vo}	**Sv**	ϕ_{ko}	**B**
cis- potassium dioxalitodiaquochromate(III) dihydrate complex	298.15 K	1942	-7841	0.1140	-9.972
	303.15 K	407.4	-9947	0.1138	-12.82
	308.15 K	2535	307.6	0.1157	1.964
	313.15 K	3338	-1115	0.1034	-28.55

Table 4: Value of Jones-Dole equation of oxalic acid and cis- potassium dioxalatodiaquochromate(III) dihydrate complex in acidic pH solution at different temperature.

Conc. (mol. dm⁻³)	(η/η_o-1)/√c Jones-Dole Equation				(η/η_o-1)/√c Jones-Dole Equation			
	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
	Oxalic acid				**Cis- K[Cr(C₂O₄)₂(H₂O)₂].2H₂O**			
0.04	-0.5097	0.0248	-0.4137	-0.2732	-0.5403	-0.4914	-0.0449	-0.3971
0.02	-0.1133	-0.3908	-0.6285	-1.5469	-0.5525	0.0820	-0.4063	6.2872
0.01	-0.8131	-0.5399	-0.6515	-0.8949	-0.0703	0.7419	-0.4341	13.8123
0.005	-0.3518	-0.4009	-0.5813	-1.7310	0.8650	1.1449	-0.2644	-1.0581

The increases in ultrasonic velocity also indicate association among the molecules and greater solute-solvent interaction. Ultrasonic velocity increases with increase in concentration of the metal complexes may be due to: (i) a decrease in compressibility caused by the introduction of incompressible ions of acidic pH solution; and (ii) a change of acidic pH solvent structures around the ion. From above the contribution of (i) was generally larger and depends more on concentration than on the kind of ions [14].

Adiabatic compressibility

The adiabatic compressibility shows the ion-solvent molecular attraction and gives the resultant compactness. The adiabatic compressibility values decrease with increasing the concentration of the solute might be due to aggregation of acidic pH solvent molecules around the solute molecules [15]. There was possibility of H-bond formation between acidic pH solvent and metal complex. So, the H-bond strengthens the intermolecular force resulting in decrease in compressibility and increase in ultrasonic velocity.

Apparent molar volume and apparent molar compressibility

The values of apparent molar volume and apparent molar compressibility were lower in the case of oxalic acid in a comparison to those of metal complex shows the greater solute-solvent interactions [16]. The variation in apparent molar volume due to the geometrical arrangements of the metal complex in acidic pH solution phase.

Partial molar volume, partial molar compressibility and experimental slope

The values of partial molar volume (ϕ_{vo}), partial molar compressibility (ϕ_{ko}) at infinite dilution and experimental slope of oxalic acid and cis- potassium dioxalatodiaquochromate(III) dihydrate complex in acidic pH solution at different temperature shown in **Table 3**.

Partial molar compressibility was a measure of interaction between these solutes and water molecules i.e. hydrophobic interactions and therefore more of a structure making property. The negative value of ϕ_{ko} for oxalic acid was shows the loss of structural compressibility of oxalic acid molecules due to the increased electrostrictive forces of acidic pH solution but in metal complex the ϕ_{ko} value was positive shows the structural compressibility though there was presence of acidic pH medium. At 308.15 K, the structural compressibility was more than other temperature [17,18].

The values of partial molar volume (ϕ_{vo}) was increased with increasing temperature but the Sv (slope) value shows positive higher value at 308.15 K temperature gives in **Table 3**, it means the metal complex was highly stable at 308.15 K temperature.

The Jones-Dole coefficient (B) show the positive value at 308.15 K (**Table 4**) obtained from Jones-Dole equation indicates a strong attraction of solvent molecules with ions, which gives the complex forming behavior of acidic pH solution.

CONCLUSION

The density, viscosity and ultrasonic properties helps to understand the solute-solvent interaction in acidic pH solution of oxalic acid and its chromate(III) complex at different temperature and concentration and the further calculated properties such as apparent molar volume, adiabatic compressibility, apparent molar compressibility, partial molar volume and partial molar compressibility were shows the compactness, stability, hydrophobic and hydrophilic nature of cis- potassium dioxalatodiaquochromate(III) dihydrate complex. Due to acidic pH solution, the large effect shows on compressibility, stability and ion -solvent interaction of cis- potassium dioxalatodiaquochromate(III) dihydrate complex.

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