

Ultrasonic studies of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in Propan-2-ol + Water solvent At 303.15 K.

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Abstract

Various acoustic parameters such as isentropic compressibility (β_s) intermolecular free length (L_f) apparent molar volume (ϕ), apparent molar compressibility y (ϕ_k) molar compressibility (w), molar sound velocity (R), acoustic impedance (z) of $\text{Cu}(\text{NO}_3)_2$ in 10%, 20% and 30% Propan-2-ol + water at 303.15K have been determined from ultrasonic velocity (V), density (ρ) and relative viscosity (η_r) of the solution. These parameters are related with the molar concentration of the solution and reflects the distortion of the structure of the solvent. (*i.e.*, Propan-2-ol + water) when the solute is added to it.

Introduction

Studies on the solution of the structure of aqueous electrolytes are numerous. Viscometry^{1,2} is an important tool in order to elucidate the solute-solvent interaction and the nature of a solute as a structure maker or a structure breaker. Viscosity and density data provide an insight into the state of association of the solute and the extent of its interaction with solvent. Moreover, ultrasonic studies^{3,4} leading to several acoustic parameters provide necessary information regarding structural effects of the solute and solvent in solution. Nomoto *et al.*⁵, made successful attempts to

evaluate sound velocity in binary liquid mixtures. The nature and degree of molecular interactions in different solutions depend upon several factors, *i.e.* the nature of the solvent, the structure of the solute and also the extent of solvation taking place in the solution. Some earlier works^{6,7} dealt with the study of solute-solvent interaction from viscosity and ultrasonic measurements in both aqueous and non-aqueous media. The present work reflects the molecular interaction studies of $\text{Cu}(\text{NO}_3)_2$ in Propan-2-ol + Water solvent at 303.15K. An Attempt has also been made to evaluate the ultrasonic velocities and other acoustic parameters in $\text{Cu}(\text{NO}_3)_2$ and Propan-2-ol+Water mixture using Nomoto and

ideal mixing relations.

Experimental

The solvents used were purified by appropriate method. PROPAN-2-OL (ANALAR) and WATER was triple distilled. Purity was about 99.9%, which was in good agreement with the standard values¹³ of density, viscosity etc. the solvents of different PROPAN-2-OL contents were prepared by taking required volume of PROPAN-2-OL in distilled water. The ultrasonic velocity was measured (with an accuracy 0.5 ms⁻¹) by single crystal variable path ultrasonic interferometer (Mittal Enterprise, Model F-81) operating at a frequency of 5 MHz. Water from a thermo statically regulated bath (Toshniwal, India) equipped with Jumo D.B.P. temperature sensor was circulated with a sample holder (with double wall) to maintain the temperature of the liquid constant at 303.15 K with a precision of 0.01 K. the viscosity of the solutions was measured by a calibrated Ostwald's Viscometer. The viscometer was immersed in a Cathetometer. Ten observations were taken for each such measurement.

Results and Discussion

Table 1 shows that the relative viscosity (η_r) increases with the increasing % volume of Propan-2-ol. It may be due to increasing degree of H-bonding between (CH₃)₂ CHOH and H₂O the relative viscosity increases with increasing concentration of solute. This fact follows the work of Widemann⁸ *et al.*

The apparent molar volume (ϕ) was determined from the following :

$$\phi = \frac{M}{\rho_0} - \frac{(\rho - \rho_0)}{\rho_0} \frac{1000}{c}$$

and the results are noted in Table 1.

where M = molecular mass of the solute,

ρ_0 = density of the solvent,

ρ = density of the solution and

c = molar concentration of the solution.

The data follow Masson's equation⁹ (plot of ϕ vs. $c^{1/2}$ is linear $\phi = \phi_0 + s_v c^{1/2}$)

The values of the limiting apparent molar volume (ϕ_0) and slope (s_v) calculated from the plots are recorded in Table 2. The positive value of s_v indicates the ion-ion interaction. The increase of ϕ_0 with increasing concentration of (CH₃)₂ CHOH may be attributed to low surface charge density.

As a result the electrostatic attraction is more in a medium of low dielectric constant. The plot of $(\eta_r - 1) c^{1/2}$ is linear, which is in good agreement with the Jones-Dole equation¹⁰.

$$\eta_r = 1 + A\sqrt{C} + BC$$

$$\frac{\eta_r - 1}{\sqrt{C}} = A + B\sqrt{C}$$

The values of A and B obtained from the plot are recorded in Table 2.

Table 1. Physical properties of $\text{Cu}(\text{NO}_3)_2$ in Propan-2-ol + Water at 303.15K

Concentration	η_r	$\rho \text{ gm ml}^{-1}$	$\phi \text{ cm}^3 \text{ mol}^{-1}$
(i) 10% Propan-2-ol + water			
0.1000	1.06904	0.992542	104.4196
0.0750	1.05290	0.989083	104.0552
0.0500	1.03652	0.985610	103.6230
0.0250	1.01967	0.982119	103.0598
0.0100	1.00899	0.980012	102.5600
0.0075	1.00710	0.979660	102.4448
0.0050	1.00513	0.979307	102.3081
0.0025	1.00301	0.978954	102.1300
0.0010	1.00156	0.978742	101.9720
(ii) 20% Propan-2-ol + water			
0.1000	1.07833	0.992242	107.4828
0.0750	1.05989	0.988859	107.1100
0.0500	1.04120	0.985461	106.6677
0.0250	1.02204	0.982044	106.0914
0.0100	1.00996	0.979983	105.5800
0.0075	1.00783	0.979638	105.4621
0.0050	1.00562	0.979293	105.3223
0.0025	1.00327	0.978947	105.1400
0.0010	1.00167	0.978739	104.978
(iii) 30% Propan-2-ol + water			
0.1000	1.08525	0.991933	110.6358
0.0750	1.06512	0.988630	110.2291
0.0500	1.04473	0.985310	109.7466
0.0250	1.02385	0.981970	109.1179
0.0100	1.01072	0.979954	108.5600
0.0075	1.00841	0.979616	108.4314
0.0050	1.00602	0.979238	108.2788
0.0025	1.00348	0.978940	108.0800
0.0010	1.00177	0.978736	107.9036

Table 2. Limiting apparent molar volume (ϕ), Limiting slope (S_v), A & B of $\text{Cu}(\text{NO}_3)_2$ in Propan-2-ol + Water at 303.15 K

Parameter	10%	20%	30%
ϕ_0 ($\text{cm}^3 \text{mol}^{-1}$)	101.7	104.7	107.6
S_v ($\text{cm}^{9/2} \text{mol}^{-3/2}$)	8.6	8.8	9.6
$A \times 10^2$ ($\text{mol}^{-1/2} \text{L}^{1/2}$)	3.05	3.11	3.21
B (mol^{-1}L)	5.94	6.85	7.51

The increasing value of A with $(\text{CH}_3)_2 \text{CHOH}$ contents supports the increase in electrostatic attraction as well as in ion-solvent interactions while the increase in S_v value attribute to large size of solvent molecules and strong association between water and organic solvent through H-bonding.

Table 3. Variation of acoustic parameters of $\text{Cu}(\text{NO}_3)_2$ in Propan-2-ol + Water at 303.15 K

Conc. Mole dm^{-3}	U m/sec	$\beta_s \times 10^{-11}$ cm^2 dyne^{-1}	W	R	$Z \times 10^{-5}$ cm^2 dyne^{-1}	$L_f \times 10^{-11}$	$\phi_k \times 10^{-8}$
(i) 10% Propan-2-ol + water							
0.10000	1582	4.0257	30.2329	128.3611	15.7020	8.0369	-1383.69
0.0750	1580	4.6500	30.1565	128.6471	15.6275	8.0854	-1668.77
0.0500	1578	4.0746	30.0802	128.9370	15.5529	8.1345	-2232.30
0.0250	1575	4.1046	29.9660	129.1493	15.4684	8.1945	-3699.98
0.0100	1572	4.1292	29.8519	129.1804	15.4058	8.2435	-7448.85
0.0075	1571	4.1359	29.8139	129.1446	15.2905	8.2570	-9176.82
0.0050	1569	4.1480	29.7381	129.0266	15.3653	8.2810	-11572.51
0.0025	1566	4.1654	29.6245	128.8264	15.3304	8.3158	-16612.12
0.0010	1562	4.1876	29.4733	128.5252	15.2879	8.3602	-19906.46
0.0000	1559	4.2043	29.3602	128.2957	15.2565	8.3935	-

Table 3. Contd.

(ii) 20% Propan-2-ol + water

0.10000	1609	3.8929	31.2737	130.5912	15.9652	7.7717	-2698.77
0.0750	1607	3.9159	31.1960	130.8751	15.8910	7.8177	-3442.39
0.0500	1605	3.9392	31.1184	131.1630	15.8166	7.8643	-4926.28
0.0250	1602	3.9677	31.0022	131.3732	15.7324	7.9212	-9162.94
0.0100	1598	3.9960	30.8475	131.3209	15.6601	7.9777	-20751.40
0.0075	1596	4.0075	30.7704	131.2027	15.6350	8.0005	-26292.93
0.0050	1593	4.0240	30.6548	131.0023	15.6001	8.0335	-36356.55
0.0025	1590	4.0406	30.5394	130.8017	15.5633	8.0667	-66506.55
0.0010	1588	4.0517	30.4627	130.6650	15.5424	8.0887	-155885.96
0.0000	1585	4.0675	30.3477	130.4353	15.5110	8.1204	————

(iii) 30% Propan-2-ol + water

0.10000	1637	3.7620	32.3716	132.9051	16.2379	7.5105	-3994.1228
0.0750	1635	3.7838	32.2926	132.1863	16.1641	7.5540	-5191.5845
0.0500	1633	3.8059	32.2136	132.4716	16.0901	7.5981	-7580.2574
0.0250	1630	3.8329	32.0954	133.6795	16.0061	7.6520	-14544.425
0.0100	1626	3.8597	31.9380	133.6259	15.9340	7.7055	-34371.323
0.0075	1624	3.8705	31.8595	133.5075	15.9090	7.7272	-44535.192
0.0050	1621	3.8862	31.7419	133.3068	15.8741	7.7585	-63895.461
0.0025	1618	3.9020	31.6245	133.1062	15.8392	7.7899	-121937.87
0.0010	1616	3.9125	31.5464	132.9693	15.8164	7.8109	-295049.62
0.0000	1613	3.9275	31.4294	132.7395	15.7850	7.8450	-

The ultrasonic^{11,12} velocity (U), isentropic compressibility (β_s)¹³, Molar compressibility (W), Molar sound velocity (R), Acoustic impedance (Z)⁴, intermolecular free length (L_f) and apparent molar compressibility (ϕ_k) of $\text{Cu}(\text{NO}_3)_2$ in 10%, 20% and 30% $(\text{CH}_3)_2\text{CHOH-H}_2\text{O}$ at 303.15 K are recorded in the Table 3.

U, W, R, (L_f) increases while Z, L_f decreases with increasing contents of $(\text{CH}_3)_2\text{CHOH}$ in the solvent, suggest the powerful interaction between PROPAN-2-OL and WATER¹⁴⁻¹⁵.

The increase in U, Z while decrease in W, R, L_f with increasing concentration of the

solute represents the decrease in cohesive force. The decrease in cohesive force is responsible for the structure breaking nature of the solute. The H-bond existing between PROPAN-2-OL and WATER is disrupted by the solute molecule and thereby formation of new bonding between solute and solvent molecules has occurred.

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