Research Article

Density, Viscosity and Ultrasonic Studies of Potassium Sulfate in Propan-2-ol +Water Mixture at 303.15K

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Abstract

The measurement of ultrasonic velocities, densities and viscosities of potassium sulfate in 10, 20 and 30% propan-2-ol+water helps to understand the intra and inter molecular interactions between the molecules of the components. The various acoustic parameters such as isentropic compressibility, intermolecular free length, apparent molar volume etc. of K_2SO_4 in 10, 20 and 30% propan-2-ol+water at 303.15K have been determined. These parameters are related with the molar concentrations of the binary solutions and reflect distortion of the structure of mixed solvents on addition of potassium sulfate. The variation of these parameters has been discussed in the light of solute-solute and solute-solvent interactions. The structure making or structure breaking capacity of potassium sulfate in propan-2-ol+water has been discussed. The results showed that the electrolyte under investigation acts as structure breaker in the mixed binary solvent.

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Introduction

Ultrasonic are the science of acoustic and the technology of sound. The frequency range of ultrasonic waves is greater than 20 kHz which is beyond the audible limit but infrasonic waves are lower than the audible limit. Human ears do not respond to either of these frequencies. Ultrasonic technique is used for the investigation of solute- solvent interactions in solutions. Various acoustic parameters such as isentropic compressibility (βs), intermolecular free length (L_f), apparent molar volume (φ_v), molar sound velocity(R), acoustic impedance (Z), apparent molar compressibility (φ_k) of K_2SO_4 in 10, 20 and 30% propan-2-ol+water at 303.15K give important information regarding the ion-solvent interaction between inorganic salt in aquo-organic solvent. Nomato et al. made successful attempts to evaluate sound velocity in binary liquid mixtures. The nature and degree of molecular interaction in different solutions depend upon several factors like the nature of the solvent, the structure of solute and also the extent of solvation. In present communication, the density, viscosity and ultrasonic velocity of K_2SO_4 solutions at 10, 20 and 30% propan-2-ol+water mixture at 303.15K have been studied and an attempt has been made to enquire about the net structure breaking or net structure making effect [1-5] in propan-2-ol+water mixtures.

Experimental
Materials

Reagent grade propan-2-ol was purchased and used without further purification. Samples of analytical reagents K_2SO_4 (E Merck) was dried at 120^oC in an oven. Solutions were then prepared from the dried sample by using doubly

distilled water. Before using the solvent, it was dried over molecular sieve and all solutions were prepared in doubly distilled water.

Mixture preparation

Binary mixtures were prepared by taking appropriate amounts of doubly distilled water and organic solvent on measuring cylinder. The binary solvent compositions are 10, 20, 30% of organic solvent in conductivity water at the experimental temperature.

Density measurement

Density of mixed binary solvents and solutions of potassium sulfate in 10, 20 and 30% propan-2-ol-water are determined by using pycnometer tube whose capacity is 50cm^3. It was thoroughly cleaned by benzene, alcohol and doubly distilled water.

Viscosity measurement

The viscosities pure the binary solvents and the solutions (0.1, 0.075, 0.050, 0.025, 0.01, 0.0075, 0.0050, 0.0025 and 0.001M) are determined by Ostwald Viscometer. From this data the relative coefficient of viscosities are determined.

Ultrasonic measurement

Ultrasonic velocities of the solutions were measured by using ultrasonic interferometer at 303.15K with the help of thermostat maintained at the required temperature accurate to ±0.05K. The estimate error of the ultrasonic velocity was in the order of ±0.5%.

Results and Discussion

Measurement of ultrasonic velocity with the help of the ultrasonic interferometer is based on finding the wavelength in the medium. Plate current is corresponding to the variations of the reflector distance (d) by integral multiple (n) of half the wavelength (λ).

$$d = n\frac{\lambda}{2} \qquad \text{or,} \quad \lambda = 2\frac{d}{n}$$

Again U= f λ, So, U= f $2\frac{d}{n}$, U is measured in ms^{-1}.

Table 1. Density, Viscosity, Ultrasonic velocity and acoustic parameters for K$_2$SO$_4$ at 303.15K in 10% Propan-2-ol

Conc. (mol dm^{-3}) 10% Propan-2-ol in water	Density (ρ) (g ml^{-1})	Viscosity (η_r x 10^3) (kg m^{-1}s^{-1})	Apparent molar volume 'φ$_v$' (ml mol^{-1})
0.1000	0.9972	1.0707	106.8610
0.0750	0.9938	1.0539	106.5581
0.0500	0.9903	1.0369	106.1988
0.0250	0.9868	1.0196	105.7305
0.0100	0.9847	1.0087	105.3150
0.0075	0.9843	1.0068	105.2192
0.0050	0.984	1.0048	105.1056
0.0025	0.9836	1.0028	104.9575
0.0010	0.9834	1.0014	104.8261
0.0000	0.9833	1.0006	104.6141

One reading was noted for ten maxima that gives the value of n. the frequency of radiations (f) was taken as 5 MHz.

$$U = 5 \times 2\frac{d}{10} = d \times 10^6 \, m$$

Table 1 shows that the relative viscosity (η_r) increases with the increase in percentage volume of propan-2-ol. It may be due to increasing degree of hydrogen bonding between propan-2-ol and water. The relative viscosity increases with the increasing concentration of the solute. This fact follows the work of Widemann et.al. the apparent molar volume(φ_v) was determined from the following equation and the results are noted in Table 1.

$$\varphi_v = \frac{M}{\rho_0} - \frac{(\rho - \rho_0)}{\rho_0} \frac{1000}{C}$$
(1)

Where M= molecular mass of the solute, ρ_0 = Density of the solvent, ρ = density of solution, C = molar concentration of the solution.

Table 2. Density, Viscosity, Ultrasonic velocity and acoustic parameters for K_2SO_4 at 303.15K in 20% Propan-2-ol

Conc. (mol dm^{-3}) 20% propanol-2 in water	Density(ρ) (g ml^{-1})	Viscosity (η_r x 10^3) (kg m^{-1}s^{-1})	Apparent molar volume 'φ_v' (ml mol^{-1})
0.1000	0.9852	1.0760	108.5191
0.0750	0.9818	1.0579	108.1950
0.0500	0.9783	1.0396	107.8106
0.0250	0.9748	1.0210	107.3096
0.0100	0.9727	1.0093	106.8650
0.0075	0.9724	1.0073	106.7625
0.0050	0.972	1.0052	106.6409
0.0025	0.9717	1.0029	106.4825
0.0010	0.9715	1.0015	106.3419
0.0000	0.9713	1.0009	106.1102

Table 3. Density, Viscosity, Ultrasonic velocity and acoustic parameters for K_2SO_4 at 303.15K in 30% Propan-2-ol

Conc. (mol dm^{-3}) 30% Propan-2-ol in water	Density(ρ) (g ml^{-1})	Viscosity (η_r x 10^3) (kg m^{-1}s^{-1})	Apparent molar volume 'φ_v' (ml mol^{-1})
0.1000	0.9711	1.0802	113.1773
0.0750	0.9677	1.0611	112.8320
0.0500	0.9643	1.0418	112.4224
0.0250	0.9609	1.0221	111.8886
0.0100	0.9588	1.0098	111.4150
0.0075	0.9585	1.0077	111.3058
0.0050	0.9582	1.0054	111.1763
0.0025	0.9578	1.0031	111.0075
0.0010	0.9576	1.0015	110.8577
0.0000	0.9575	1.0011	110.6101

Table 4. Ultrasonic velocity and acoustic parameters for K_2SO_4 at 303.15K in 10% Propan-2-ol

Conc. (mole dm^{-3})	Ultrasonic velocity 'U' (m/s)	Isentropic Compressibility β_s x 10^{-11} (cm^2 dyne^{-1})	Molar compressi-bility 'W' (cm^2 dyne$^{1/2}$)	Molar sound velocity 'R' (dm^{6}s^{-3}mol^{-1})	Acoustic impedance Z x 10^{-4}(g cm^{-2} s^{-2})	Inter molecular free length L$_f$ x10^{-6} (m)	Apparent molar compres-sibility φ_k x 10^{-14} (cm^2 dyne^{-1})
0.1000	1555	4.1472	4.0268	98.9048	15.5065	4.0656	-6.2239
0.0750	1554	4.1668	4.0379	99.2219	15.4437	4.0752	-6.5724
0.0500	1553	4.1869	4.0494	99.5512	15.3794	4.0850	-7.1149
0.0250	1551.5	4.2099	4.0605	99.8722	15.3102	4.0962	-11.9581
0.0100	1550.5	4.2243	4.0672	100.0636	15.2678	4.1032	-12.1010
0.0075	1550	4.2287	4.0683	100.0935	15.2567	4.1054	-11.5677
0.0050	1549.5	4.2327	4.0689	100.1133	15.2471	4.1073	-10.4476
0.0025	1548.5	4.2399	4.0696	100.1325	15.2310	4.1108	-11.7502
0.0010	1548	4.2435	4.0699	100.1420	15.2230	4.1126	-9.0908
0.0000	1547	4.2495	4.0696	100.1307	15.2117	4.1154	-

Table 5. Ultrasonic velocity and acoustic parameters for K_2SO_4 at 303.15K in 20% Propan-2-ol

Conc. (mol dm^{-3})	Ultrasonic velocity 'U' (m/s)	Isentropic Compressibility β_s x 10^{-11} (cm^2 dyne^{-1})	Molar compressi-bility 'W'(cm^2 dyne$^{1/2}$)	Molar sound velocity 'R'(dm^{6}s^{-3}mol^{-1})	Acoustic impedance Z x 10^{-4}(g cm^{-2} s^{-2})	Inter molecular free length L_fx10^{-6} (m)	Apparent molar compres-sibility φ_k x 10^{-14} (cm^2 dyne^{-1})
0.1000	1561.52	4.1628	4.0737	100.2492	15.3841	4.0732	-6.1994
0.0750	1560.96	4.1802	4.0854	100.5844	15.3255	4.0817	-6.5513
0.0500	1560.48	4.1977	4.0975	100.9339	15.2662	4.0903	-7.0853
0.0250	1560	4.2154	4.1098	101.2859	15.2069	4.0989	-8.5672
0.0100	1559.2	4.2288	4.1168	101.4872	15.1663	4.1054	-11.9834
0.0075	1559	4.2312	4.1177	101.5142	15.1597	4.1066	-11.4583
0.0050	1558	4.2384	4.1184	101.5342	15.1438	4.1100	-10.3554
0.0025	1557	4.2451	4.1187	101.5439	15.1294	4.1133	-11.6333
0.0010	1556	4.2515	4.1187	101.5430	15.1165	4.1164	-8.1032
0.0000	1555	4.2578	4.1187	101.5422	15.1037	4.1195	-

Table 6. Ultrasonic velocity and acoustic parameters for K_2SO_4 at 303.15K in 30% Propan-2-ol

Conc. (mol dm^{-3})	Ultrasonic velocity 'U' (m/s)	Isentropic Compressibility β_s x 10^{-11} (cm^2 dyne^{-1})	Molar compressi-bility 'W'(cm^2 dyne$^{1/2}$)	Molar sound velocity 'R'(dm^{6}s^{-3}mol^{-1})	Acoustic impedance Z x 10^{-4}(g cm^{-2} s^{-2})	Inter molecular free length L_fx10^{-6} (m)	Apparent molar compres-sibility φ_k x 10^{-14} (cm^2 dyne^{-1})
0.1000	1571.08	4.1720	4.1315	101.9120	15.2568	4.0777	-6.1334
0.0750	1570.5	4.897	4.1435	102.2574	15.1977	4.0864	-6.4785
0.0500	1569.8	4.2082	4.1555	102.6027	15.1376	4.0954	-7.0003
0.0250	1569	4.2274	4.1675	102.9483	15.0765	4.1047	-8.4471
0.0100	1568	4.2421	4.1746	103.1518	15.0340	4.1119	-11.8738
0.0075	1567.75	4.2448	4.1755	103.1786	15.0269	4.1132	-11.3261
0.0050	1567.5	4.2475	4.1764	103.2055	15.0198	4.1145	-10.3542
0.0025	1567.25	4.2506	4.1777	103.2431	15.0111	4.1160	-10.1870
0.0010	1567	4.2528	4.1783	103.2591	15.0056	4.1171	-10.7397
0.0000	1566	4.2587	4.1779	103.2480	14.9945	4.1199	-

The data follow the Masson's equation (plot of φ_v verses $C^{1/2}$ is linear).

$$\varphi_v = \varphi_v^0 + S_v\, C^{1/2} \qquad\qquad (2)$$

Most of the interactions occurring in liquid phase can be studied from various physico-chemical parameters [6-8]. Viscosity is the parameter which controls the flow of a liquid. It depends on factors like nature of the liquid and intermolecular forces. The viscosity data at different concentrations and different temperatures determine the structural aspect of the solution taking into account of the various molecular interactions. The concentration dependence of the viscosity coefficient (η) of a solution in aqueous, non-aqueous solvents has been expressed in terms of the semi empirical Jone- Dole equation. According to Jones - Dole, the molar concentration "C' and the relative viscosity of an electrolyte solution are related in the form of an equation (3).

$$\eta_r = 1 + A\, C^{1/2} + B\, C \qquad Or, \qquad (\eta_r - 1) = A\, C^{1/2} + B\, C \qquad\qquad (3)$$

The constant A and B are the inter-ionic and solute-solvent interaction coefficient, respectively. η_r is the relative viscosity = η/η_0.

The apparent molar volume (ϕ_v) of a solution is generally calculated from the density data by the standard procedure.

$$\beta_S = \rho^{-1} U^{-2} \qquad (4)$$

Where, U is the ultrasonic velocity of the solution and ρ is the density of the solution.

The apparent molar properties are found to depend on the concentration of the solution. The apparent molar compressibility (ϕ_k) is computed from the relation(5).

$$\phi_k = \frac{1000\beta_S}{C} - \frac{\beta_S^0}{\rho_0}\left(\frac{1000\rho}{C} - M\right) \qquad (5)$$

where, β_S^O is the isentropic compressibility of the solvent. $\beta_{S,}$ ρ , ρ_O, M and C have their usual meaning. The ϕ_k values vary linearly with $C^{1/2}$ and the limiting apparent molar compressibility (ϕ_k^O) is obtained for a set of solution of variable concentrations using the linear extrapolation of ϕ_k verses $C^{1/2}$ according to the equation(6),

$$\phi_k = \phi^O_k + S_k C^{1/2} \qquad (6)$$

The intermolecular free length (L_f) i.e. the distance covered by a sound wave between the surfaces of two molecules according to Jacobson is given by the equation (7).

$$L_f = K^{1/2} \beta_S \qquad (7)$$

where, K is a temperature dependent constant. The molar sound velocity (R) can be calculated by using the equation

$$R = U^{1/3} V_m = U^{1/3} M \rho^{-1} \qquad (8)$$

where, V_m is the molar volume of the solution, U is the ultrasonic velocity of the solution. M is the molecular mass of the solute and ρ is the density of the solution.

The ultrasonic velocity also affects the acoustic impedance 'Z' which is given as

$$Z = U \rho \qquad (9)$$

Molar compressibility (W) can be calculated from the equation (10).

$$W = \beta_S^{-1/2} V_m = \beta_S^{-1/2} M \rho^{-1} \qquad (10)$$

The density of the solution increases with increase in concentration of all the experimental solvents. The apparent molar volume (φ_v) increases with increase in concentration and almost linearly increases with the square root of the concentration of the solutions (**Figure 1**). From the above table it is seen that φ_v^o values are all positive indicating a strong solute solvent interaction. This interaction depends upon the nature of the solute and structure of solvent.

The viscosity [9-11] data shows that the viscosity (η_r) increases with increase in concentration of the solution. The variation of relative viscosities with $C^{1/2}$ described in the equation (3) is linear as shown in **Figure 2**. The slope of the above mentioned plot is the constant B which measures the effective solvodynamic volume of the solvated ions. When the solute dissolves in the solvent, some of the solvent molecules are attached to the ions because of the ion-solvent interactions and this causes the increase in viscosity of the solution (a positive contribution to the B coefficient). Positive values of S_v and the limiting slope also give the same suggestion.
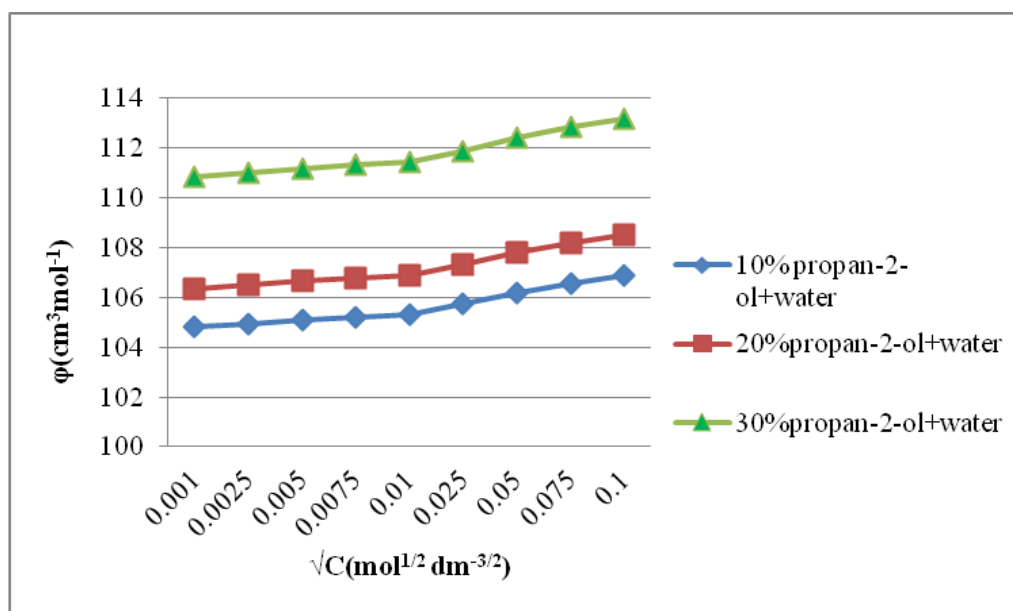
Figure 1. Plot of Apparent molar volume (φ) vs $\sqrt{C}$ of potassium sulfate at 303.15K for 10% propan-2-ol+water, 20% propan-2-ol+water and 30% propan-2-ol+water
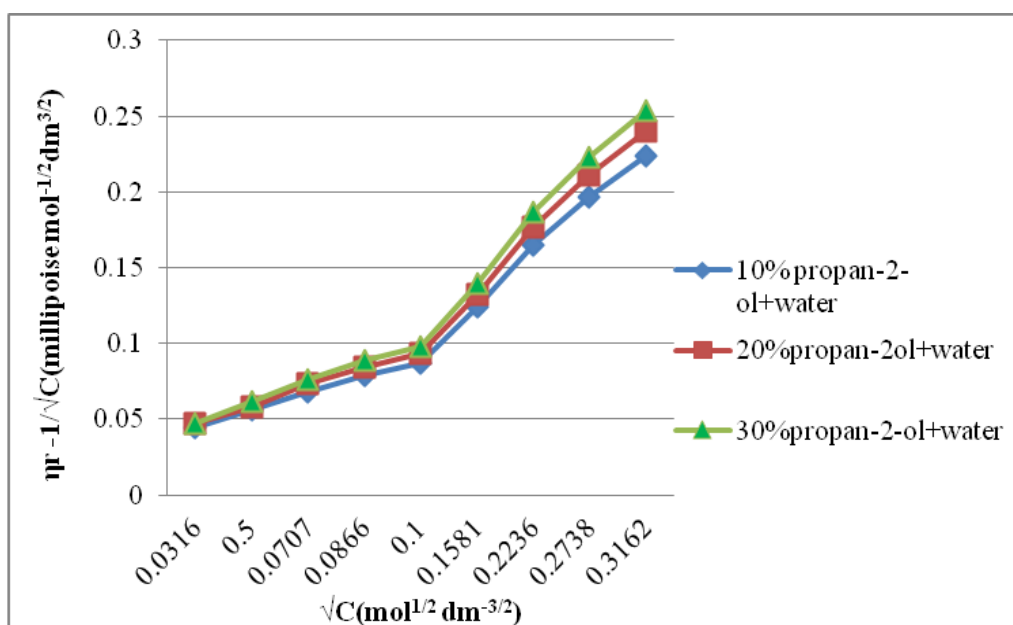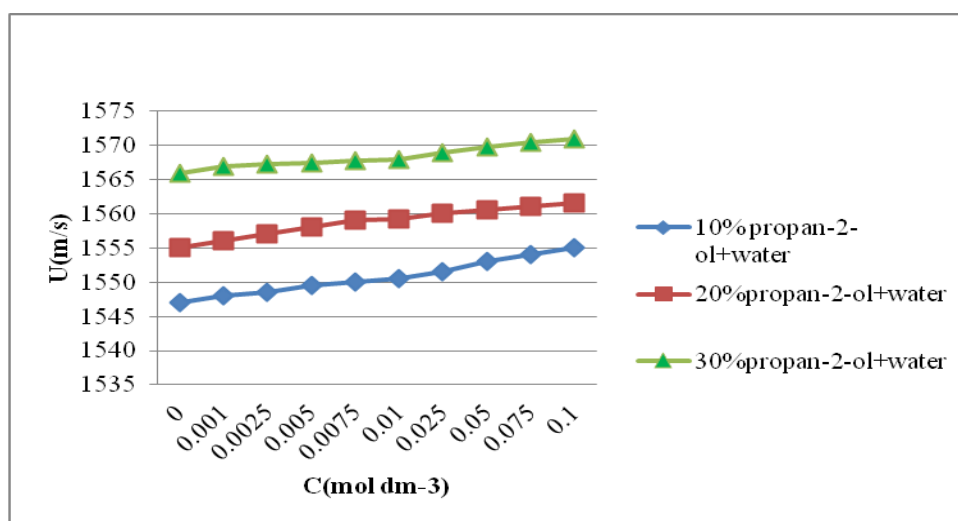

Figure 2. Plot of η_r -1/$\sqrt{C}$ vs $\sqrt{C}$ of potassium sulfate at 303.15 K for 10% propan-2-ol +water, 20% propan-2-ol +water and 30% propan-2-ol +water

The ultrasonic velocity measurement [12-18] shows that the velocity increases with increase in concentration of the solution in all the cases (**Figure 3**). The isentropic compressibility (β_s) values of the solution go on decreasing with increase in concentration of the solution. We know that the internal pressure increases with concentration which lowers the values of β_s in K_2SO_4. This suggests that, at higher concentration, the primary effect of dissolving a solute lowers the compressibility of the solvent.

The intermolecular free length (L_f) decreases with increasing concentration of the solute in the solutions (**Figure 4**). The decrease of L_f with concentration suggests the strong solute solvent interactions. It is observed that the limiting apparent molar compressibility (φ^o_k) is negative for maximum number of solutions studies, which indicates the higher incompressibility. The slope (S_k) of the plot of φ_k vs $C^{1/2}$ in the equation (6) is positive in all the solution. This agrees with our earlier findings that all the solutions contain electrolytes. The molar sound velocity (R) decreases

linearly with increase in the concentration as shown in **Figure 5**. This decreasing order of molar sound velocity with concentration shows that the relative association in the solution decreases with the increase in concentration. The molar compressibility (W) decreases with the increase in solute concentration and acoustic impedance (Z) increases with increase in solute concentration in almost linear manner as shown in **Figure 6**. The increasing order of Z with concentration can be explained on the basis of the decreasing number of free solvent molecules. As most of the solvent molecules are engaged in interaction with the solute, addition of more solute to the solvent leads to the acceleration of the process of breaking of aggregates of solvent molecules. This process leads to the inhibition of propagation of sound waves due to large sized solute molecules acting as structure promoters. The variation in molar sound velocity is identical to that of ultrasonic velocity in the bulk. As the value of (βs) decreases, ultrasonic velocity increases. From this, we can conclude that the formation of more clusters of the solute and solvent molecules with increasing hydrodynamic volume increases the isothermal compressibility [19] while the density increases marginally over the solvent, the value thereby causing increased sound velocity.
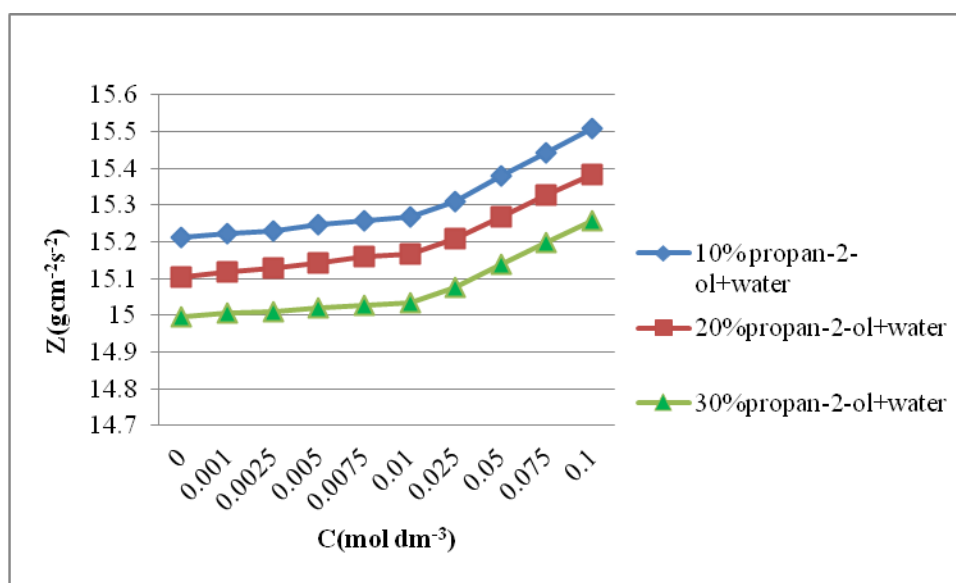

Figure 3. Plot of Ultrasonic Velocity (U) vs C of potassium sulfate at 303.15K for 10% propan-2-ol+water , 20% propan-2-ol+water and 30% propan-2-ol+water
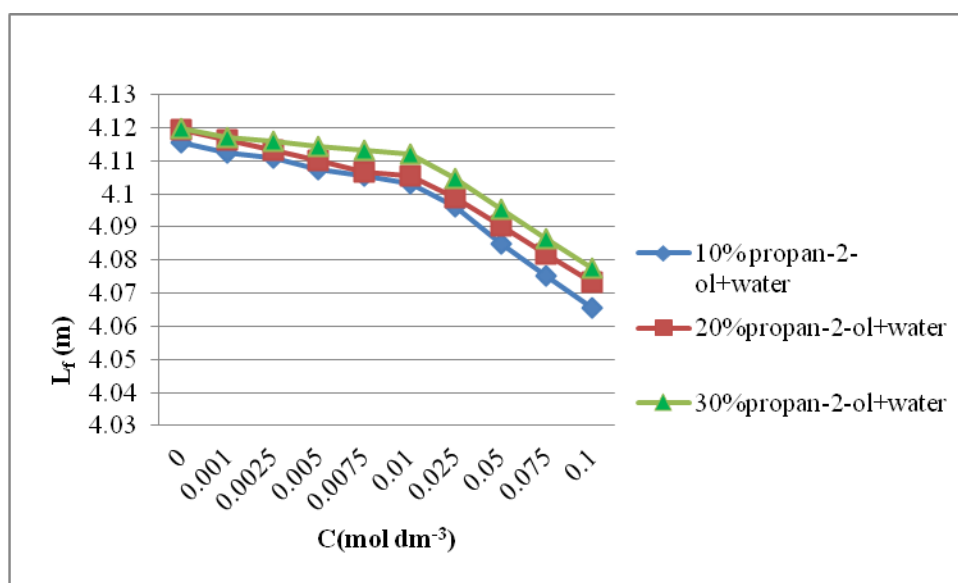
Figure 4. Plot of Intermolecular free length (L_f) vs C of potassium sulfate at 303.15K for 10% propan-2-ol+water, 20% propan-2-ol+water and 30% propan-2-ol+water
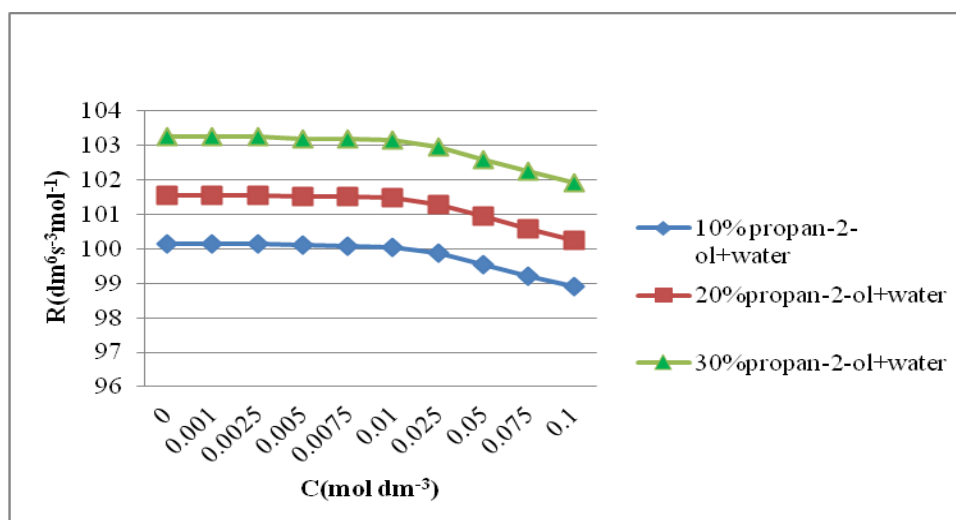
Figure 5. Plot of Molar sound Velocity(R) vs C of potassium sulfate at 303.15K for 10% propan-2-ol+water , 20% propan-2-ol+water and 30% propan-2-ol+water

Figure 6. Plot of Acoustic impendence (Z) vs C of potassium sulfate at 303.15K for 10% propan-2-ol+water, 20% propan-2-ol+water and 30% propan-2-ol+water

Conclusions

Acoustical and volumetric properties of potassium sulfate in various compositions of propan-2-ol and water at 303.15K was studied. From the experimental and derived parameters, the solute-solute and solute-solvent interactions of electrolyte in the mixed binary solvent were correlated and found that the electrolyte is 3D-structue breaker in the given aquo-organic solvent mixture.

Acknowledgement

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