



Ultrasonic studies of KCL in dioxan and water solvent mixture at 303.15K

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Abstract

Various acoustic parameters like isentropic compressibility (β_s), intermolecular free length (L_f), apparent molar volume (ϕ), apparent molar compressibility (ϕ_k), molar compressibility (w), molar sound velocity (R), acoustic impedance (Z) of KCl in 10%, 20%, 30% and dioxan and water solvent mixture 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 in dioxan and water mixture when the solute is added to it.

Keywords: Ultrasonic, viscosity, molar concentration, KCL solution, dioxan and water solvent mixture at 303.15k

Introduction

The dissolution of electrolyte in various solvents is responsible for structure maker or structure breaker [1]. Viscosity and density data leads an insight to the state of association of the solute and the extent of interaction of the solute with the solvent. The present work mainly deals with the reflects the ion-ion, ion-solvent and solvent-solvent interaction KCl solution in 10%,20% and 30% in dioxan and water mixture

Materials and methods

The solvents used were purified by appropriate method. Dioxan was used in AR grade, sample and water was triple distilled. Purity was about 99.9% which was in good

agreement with the standard values of density, viscosity etc. The solvents of different Dioxan content were prepared by taking required volume of dioxan in distilled water, For the preparation of different concentration of solution, the required amount of KCl was weighed and dissolved in a 250 ml measuring flask. In the present work the ultrasonic velocity of the solution was measured by a commercially available ultrasonic interferometer of frequency 5 MHz manufactured by Mital enterprisers.

Results and discussion

The experimental data of density (ρ) and relative viscosity (η_r) for the solute in different concentration of the dioxan and water solvent mixture at 303.15 K are given in Table-1.

Table 1: Physical properties of KCl of different concentration in 10%,20% and 30% dioxan and water solvent mixture at 303.15K

Concentration	η_r	Pgm ml ⁻¹	ϕ Gm ³ ml ⁻¹
i) 10% dioxan+water			
0.1000	1003.982	1.013519	17.66050
0.0750	1003.289	1.012106	17.61220
0.0500	1002.385	1.010690	17.55491
0.0250	1001.479	1.009271	17.48025
0.0100	1000.832	1.008419	17.41400
0.0075	1000.693	1.008277	17.39873
0.0050	1000.529	1.008134	17.38061
0.0025	1000.359	1.007992	17.35700
0.0010	1000.218	1.007906	17.33605
0.0000	1000.011	1.007849	-
ii) 20% dioxan+water			
0.1000	1005.718	1.021753	17.37947
0.0750	1004.547	1.020335	17.32863
0.0500	1003.317	1.018616	17.26833
0.0250	1001.978	1.017494	17.18974
0.0100	1000.832	1.008419	17.41400
0.0075	1000.872	1.016497	17.10392
0.0050	1000.684	1.016354	17.08485
0.0025	1000.437	1.016211	17.06000
0.0010	1000.258	1.01626	17.3795
0.0000	1000.019	1.016069	-
iii) 30% dioxan+water			
0.1000	1007.338	1.028706	16.44272
0.0750	1005.784	1.027269	16.38341
0.0500	1004.172	1.025829	16.31305
0.0250	1002.439	1.024386	16.22136
0.0100	1001.263	1.023518	16.14000

0.0100	1001.032	1.023373	16.12124
0.0075	1000.789	1.023229	16.09899
0.0050	1000.506	1.023084	16.07000
0.0025	1000.294	1.022996	16.04427
0.0010	1000.098	1.022938	-
0.0000			

From the result it is clear that the relative viscosity (η_r)^[2] increases with the increase in volume percentage of dioxan. Such characteristics indicate the more extent of H-bonding of O(CH₂)₄O. With H₂O with the increase in volume percentage of O(CH₂)₄O. With the increase in concentration of the solute the relative viscosity increases which is in good agreement^[3]. With Widemann and coworkers. The apparent molar volume (\bar{V}) were determined from the equations

$$\bar{V} = \frac{M(r-r_0)}{\rho_0 \rho c} \text{ and are given in Table - 1}$$

Where M is the molecular wt. of the solute, ρ_0 is the density of the solvent, ρ is the density of the solutions, c is the molar concentration of the solution. The data obtained have been found to agree with the Masson's equation^[4] as the plot of

$$\bar{V} \text{ vs } c^{1/2} \text{ is linear - } \bar{V} = \bar{V}_0 + S_v c^{1/2}$$

The value of the limiting apparent molar value \bar{V}_0 obtained from the extrapolation of the above plot to zero concentration. The limiting slope S_v is a constant dependent on charge and salt type and can be related ion-ion interaction. The value of \bar{V}_0 and S_v are listed in Table-2.

Table 2: Limiting apparent molar volume (\bar{V}_0), limiting slope (S_v) A and B for KCl in 10%, 20%, 30%, dioxan and water solvent mixture at 304.15 K.

Parametre	10%	20%	30%
\bar{V}_0 (cm ³ mol ⁻¹)	17.3	17.0	16.0
S_v (cm ^{9/2} mol ^{-3/2})	1.14	1.20	1.40
Ax 10 ⁻² (cm ^{1/2} It ^{1/2})	6.16	6.33	5.50
B (mol ⁻¹ It)	10.0	12.2	16.0

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Table - 3: Variation of U, B_s, W, R, Z, L and \bar{V}_k with concentration of KCl in 10%, 20%, and 30% dioxan and water solvent mixture at 303.15K.

Conc. Mole dm ⁻³	U m/sec	$\beta_s \times 10^{-2}$ cm ² Dync ⁻¹	W	R	Zx 10 ⁻⁵ cm ² Dync ⁻¹	L _f x 10 ⁻⁶ m	\bar{V}_k
10% dioxan + water							
0.1000	1546	41.2809	2240.6361	851.09249	1.56690	6.42502	-1.41953
0.0750	1543	41.4995	2242.0720	851.72906	1.56167	6.44201	-1.62686
0.0500	1540	41.7197	2229.8157	85236923	1.55646	6.45908	-2.03801
0.0250	1538	41.8870	2245.3866	853.19796	1.55226	6.47202	-3.482254
0.0100	1536	42.0317	2246.1769	853.54851	1.54893	6.48319	-737267
0.0075	1531	42.3126	2244.3566	852.74143	1.54367	6.50481	-6.37267
0.0050	1528	42.4849	2243.3722	852.30496	1.54043	6.51804	-5.75605
0.0025	1526	42.6024	2242.8031	852.05295	1.53820	6.52705	-6.88765
0.0100	1525	42.6619	2242.5473	851.93948	1.53706	6.53161	11.3790
0.0000	15423	42.7764	2241.8156	851.61504	1.53495	6.54037	---
20% dioxan + water							
0.1000	1567	39.8581	2233.7439	848.03915	1.60109	6.31333	-1.62207
0.0750	1563	40.1180	2234.7723	848.49450	1.59478	6.33398	-1.84053
0.0500	1560	40.3285	2236.2121	849.13220	1.58951	6.35047	-2.37628
0.0250	1557	40.5407	2237.6591	849.77348	1.58429	6.36716	-3.97623
0.0100	1555	40.6792	2238.4479	850.12299	1.58087	6.37802	-0.66395
0.0075	1551	40.8950	2237.0713	849.51292	1.57659	6.39492	-8.69831
0.0050	1546	41.1125	2235.6913	848.90142	1.57230	6.41190	-8.73305
0.0025	1543	41.3318	2234.3072	848.28849	1.56801	6.42898	-8.76526
0.0100	1541	41.4426	2233.6397	847.99275	1.56586	6.43759	-10.9432
0.0000	1539	41.5528	2232.9177	847.67329	1.56373	6.44615	---
30% dioxan + water							
0.1000	1582	38.8415	2226.8501	844.98639	1.62741	6.23229	-1.35609
	1578	30.0933	2227.9075	845.45463	1.62103	6.25246	-1.50681

The limiting slope (S_v) is positive suggestion ion-ion interaction. This increases with the increases in non-aqueous solvent. The increase in \bar{V}_0 with increase in O(CH₂)₄O content may be attributed to low surface charges. density as a result of which the electrostatic attraction is more in a medium of low dielectric constant and hence ion-solvent interaction would also be more. The plot of $(\eta_r-1)/c^{1/2}$ is linear, which is in good agreement with the Jones-Dole equation.^[5]

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

$$\frac{\eta_r - 1}{c^{1/2}} = A + Bc^{1/2}$$

The values of A and B are obtained from the graph and are recorded in Table-2. The result reveals that the value of A increases in O(CH₂)₄O content, which also supports the increase in electrostatics attraction in a medium of low dielectric constant and also the increase in ion solvent interaction. The increase in B values with increase in O(CH₂)₄O content is due to large size of the solvent molecule and also the strong association between water and organic solvent through H-bonding.

The ultrasonic velocity (V ^[6, 7]), isentropic compressibility (β_s)^[8], Molar compressibility (w), Molar sound velocity (R), Acoustic impedance (Z)^[9], inter molecular free length (L_f) and Apparent molar compressibility (\bar{V}_k) of KCl in 10%, 20% and 30% O(CH₂)₄O + h₂O at 303.15K are recorded in Table-3.

0.0750	1575	39.2974	2229.3759	456.10457	1.61568	6.26876	-1.88548
0.0500	1571	39.5534	2230.4463	846.57853	1.60931	6.28915	-2.81342
0.0250	1569	39.6879	2231.2556	846.93677	1.60590	6.29983	-5.78736
0.0100	1565	39.8967	2229.8995	846.33633	1.60158	6.31636	-4.95426
0.0075	1563	40.0046	2229.3530	846.09471	1.59931	6.32592	-5.30686
0.0050	1561	40.1128	2228.8088	845.85353	1.59703	6.33347	-6.35107
0.0025	1560	40.1677	2228.8029	845.74562	1.59588	6.33543	-13.4818
0.0100	1558	40.2732	2227.8564	845.43196	1.59374	6.34612	
0.0000							

The values of U , W , R , & ϕ_k increases and β_s , Z , L_f decreases in $O(CH_2)_4O$ content in the solvent, suggest the powerful interaction between $O(CH_2)_4O$ and water. The increase in value of U , Z , and decrease in values of β_s , w , R , L_f with the increase in concentration of the solute represents the decrease in cohesive force. The decrease in cohesive force is due to the structure breaking nature of the solute. The H-bond exists between dioxan and water is disrupted by the solute molecule and there by formation of new bonding between solute and solvent molecules has occurred.

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