

Study of Ultrasonic Velocity Parameters of Multi-Charged Electrolytes (Potassium Ferri and Ferro Cyanide) in Aqueous Dextrose Solutions at 298.15 K

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Abstract: The experimental ultrasonic velocity values have been utilized to compute specific acoustic impedance (Z), molar sound velocity (R), molar compressibility (W), free volume (V_f), isentropic compressibility (K_s), internal pressure (π_i) and relative association (R_A) for the solutions of potassium ferri and ferrocyanide in aqueous dextrose solutions at 298.15 K. The results have been discussed considering all the parameters in terms of solute-solvent and solute-solute interactions and various structural effects.

Keywords: Ultrasonic velocity, Dextrose, Density, Potassium ferri and ferrocyanide

Introduction

Dextrose is a water soluble sugar and acts as a source of instant energy to human system. It is available in the world market in different brand names. Pure aqueous dextrose solution is generally used in saline, ORS-Electrokind packets and used to conduct the blood sugar test. Dextrose is a big deal for many researchers to study the ion solvent interactions in its mixed solvents because of its extensive pharmaceutical, biomedical and industrial applications. The present investigation has been carried out to study the interactions of multi-charged electrolytes (potassium ferricyanide and ferrocyanide) with aqueous dextrose (5, 10 and 15 wt%) solutions at 298.15 K and at atmospheric pressure by means of ultrasonic velocity measurements. In continuation of our earlier work in dextrose solution¹, we aims at studying various important ultrasonic parameters like acoustic impedance (Z), molar sound velocity (R), molar compressibility (W), free volume (V_f), isentropic compressibility (K_s) and internal pressure (π_i) for both the electrolytes. The results have been analyzed considering the structural effects of the solute and solvent in solutions and in the light of ion-ion and ion-solvent interactions.

Experimental

All chemicals used were of G.R., B.D.H. or AnalaR grades. Conductivity water (Sp. cond. $\sim 10^{-6}$ S cm⁻¹) was used for preparing water + dextrose (5, 10 and 15%,(w/w)) mixtures.

The dextrose content in the mixed solvents was accurate to within $\pm 0.01\%$. The electrolyte solutions were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression² using the density values of the solutions determined at 298.15 K. Solutions were kept for 2 h in a water thermostat maintained at the required temperature accurate to within ± 0.05 K before use for density measurements. Density measurements were done using a specific gravity bottle of 25 mL capacity. At least five observations were taken and differences in any two readings did not exceed $\pm 0.02\%$. Ultrasonic velocity measurements on the solutions of both the electrolytes were made by using an Ultrasonic Interferometer (Mittal Enterprises, New Delhi, India) at a frequency of 2 MHz at 298.15 K only. The accuracy of the ultrasonic velocity measurement is within ± 0.5 m/s. The electrolyte content of the solutions varied over a concentration range of 1.0×10^{-2} to 1.0×10^{-1} mol dm⁻³ for all these measurements.

Theory

From the ultrasonic velocity and density data, the values of isentropic compressibility, K_s , apparent isentropic compressibility, $K_{s,\phi}$, acoustic impedance (Z) and relative association (R_A) have been calculated by using equations (1)–(4), respectively³⁻⁶.

$$K_s = (1/U^2 d) \quad (1)$$

where, U = ultrasonic velocity of the solution
 d = density of the solution

$$K_{s,\phi} = 1000 K_s c^{-1} - K_s^0 d_0^{-1} (1000 c^{-1} d - M) \quad (2)$$

$$Z = Ud \quad (3)$$

$$R_A = (\rho/\rho_0) \times (U_0/U)^{1/3} \quad (4)$$

The molar sound velocity (R), free volume (V_f), molar compressibility (W) and the increase in internal pressure (π_i) due to electrostatic field of the ion have also been calculated by using the following equations, respectively⁷⁻¹¹,

$$R = \overline{M} d^{-1} U^{1/3} \quad (5)$$

$$V_f = V_m - b \quad (6)$$

$$W = K_s^{-1/7} \overline{M} d^{-1} \quad (7)$$

and

$$\pi_i = (K_s^0 - K_s) \quad (8)$$

$$\text{Where, } \overline{M} = \frac{\sum n_i m_i}{\sum n_i}, \quad V_m = \frac{\overline{M}}{d}$$

$$b = \frac{\overline{M}}{d} \left[1 - \left(\frac{RT}{\overline{M} U^2} \right) \left\{ \left(1 + \frac{\overline{M} U^2}{3RT} \right)^{1/2} - 1 \right\} \right] \quad (9)$$

Results and Discussion

The measured value of ultrasonic velocity (U) has been presented in Table 1. As observed, ultrasonic velocity (U) values tend to increase with the increase of dextrose content in water

and of concentration of potassium ferri and ferrocyanide in various solvent systems. This suggests that disruption of water structure is enhanced with the addition of dextrose and the solutes. This result is in agreement with the earlier studies³⁻⁶ made in various mixed solvents.

Table 1. Ultrasonic velocity U (m/s) and density ρ (kg/m³) of potassium ferri and ferrocyanide in water+ dextrose mixtures at 298.15 K

C mol/dm ³	5.0 wt% Dextrose		10.0 wt% Dextrose		15.0 wt% Dextrose	
	U	ρ	U	ρ	U	ρ
Potassium Ferricyanide						
0.01	1518.8	1017.2	1532.0	1036.8	1544.4	1057.3
0.02	1520.4	1019.7	1537.6	1039.4	1552.0	1059.8
0.04	1530.0	1022.8	1546.0	1042.9	1556.0	1062.6
0.06	1536.8	1026.0	1552.0	1045.4	1560.0	1064.9
0.08	1538.4	1029.7	1553.2	1049.4	1564.0	1069.1
0.1	1549.6	1033.1	1559.2	1052.7	1580.0	1072.1
Potassium Ferrocyanide						
0.01	1524.0	1019.8	1538.8	1039.1	1545.6	1060.8
0.02	1528.0	1023.8	1549.2	1042.8	1556.8	1063.5
0.04	1532.0	1027.1	1552.4	1046.5	1570.0	1067.3
0.06	1540.0	1031.7	1554.0	1050.4	1575.2	1070.6
0.08	1542.8	1037.0	1560.0	1055.8	1588.0	1076.1
0.1	1552.0	1040.6	1576.0	1059.5	1602.4	1079.8

The specific acoustic impedance (Z) values have been calculated in aqueous solutions of 5, 10 and 15 wt% dextrose at 298.15 K. It is found that the values of Z increase with increase in dextrose content in water as well as with increase in solute concentration in all the mixed solvents. This is in agreement with the theoretical requirements as both U and density (ρ) increase with increase in concentration of solute. Typical plots of Z versus c of the solutions of potassium ferri and ferrocyanide are shown in Figure 1 for different wt% of dextrose solution.

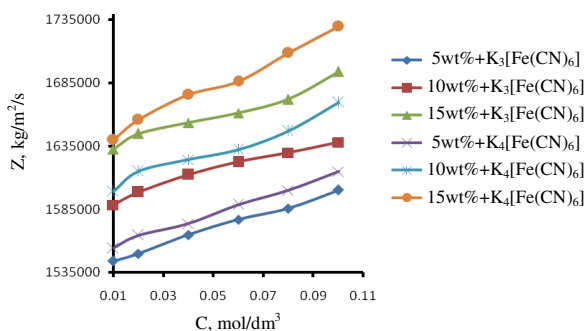


Figure 1. Plot of Z versus c of the solution of potassium ferri and ferro cyanide in different wt% of dextrose solutions

The increase in Z values with solute concentration can be attributed to the effective solute-solvent interactions. A similar type of behavior has been obtained for various salts studied in different solvent systems. Since the acoustic impedance is a measure of the resistance offered by the liquid medium to the sound wave and is a function of the elastic property of the medium, *i.e.*, the bulk modulus of elasticity, which depends on the structural changes of the solution, the higher Z values of potassium ferrocyanide in the aqueous

dextrose solutions as than that of ferricyanide and increasingly higher values with increase in the solute concentration and also with increase in dextrose content in water point to the fact that the solution medium in each case starts gaining its elastic property. The lower Z values of ferricyanide solutions than that of solutions of ferrocyanide may be due to its lower molecular mass for which the solutions of potassium ferricyanide start losing the elastic property.

The variation of the molar sound velocity (R) with solute concentrations in different wt% of dextrose solutions is shown in Figure 2. As observed, the molar sound velocity increases with increase in wt% of dextrose solutions for both electrolytes in all the solvents.

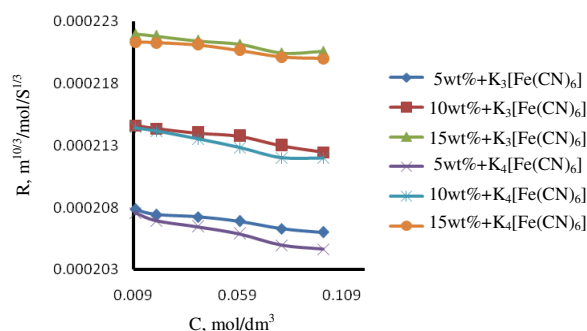


Figure 2. Plot of R versus c of the solutions of potassium ferri and ferrocyanide in different wt% of dextrose solutions

It is a well known fact that when a solute dissolves in a solvent some of the solvent molecules are attached to the ions (produced from the solute) because of ion-solvent interactions. Since the solvent molecules are oriented in the ionic field (*i.e.*, electrostatic fields of ions) the solvent molecules are more compactly packed in the primary solvation shell as compared to the solvent structure in the absence of the ions. This is the reason why the solvent is compressed by the introduction of ions. Thus, the electrostatic field of the ion causes compression of the medium giving rise to a phenomenon called electrostriction. Since the solvent molecules are compressed they do not respond to any further application of pressure. So the solution becomes harder to compress, *i.e.*, the compressibility decreases and internal pressure increases. Hence, isentropic compressibility as well as internal pressure describe the molecular arrangement in the liquid medium.

The increase in internal pressure, π_i due to electrostatic field of ions is given by the following equation:

$$\pi_i = (K_s^0 - K_s)$$

Where K_s^0 and K_s are the isentropic compressibility of the solvent and the solution respectively. Positive values of π_i indicate the presence of some specific interactions between unlike molecules in the components. Typical plot of π_i versus c is shown in Figure 3 for solutions of potassium ferri and ferrocyanide in different wt% of dextrose solutions.

Free volume, V_f , is the effective volume accessible to the centre of a molecule in a liquid. The structure of a liquid is determined by strong repulsive forces in the liquid with the relatively weak attractive forces providing the internal pressure which holds the liquid molecules together. The free volume seems to be conditional by repulsive forces whereas the internal pressure is more sensitive to attractive forces. These two factors together uniquely determine the entropy of the system. Thus, the internal pressure, free volume and temperature seem to be the thermodynamic variables that describe the liquid system of fixed

composition. It is seen that the free volume, V_f increases with solute concentration in all the solvents with slight deviation in 10 wt% dextrose solution but increases with dextrose content in the mixed solvents. Typical plots are shown in Figure 4.

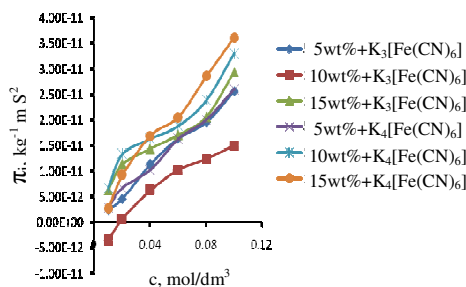


Figure 3. Plot of π_i vs. c of the solutions of potassium ferri and ferrocyanide in different wt% of dextrose solutions

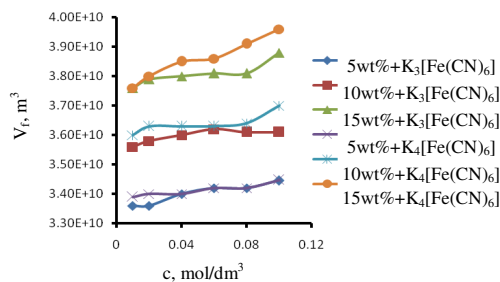


Figure 4. Plot of V_f vs. c of the solutions of potassium ferri and ferrocyanide in different wt% of dextrose solutions

As observed, the relative association, R_A is a function of ultrasonic velocity. The relative association is influenced by two factors: (i) the breaking-up of the solvent structures on addition of solutes to it and (ii) the solvation of solutes. The former results decreases and the latter results increases in R_A . The increase in R_A with concentration suggests that the solvation of the electrolytes predominates over the breaking-up of the solvent structure. As observed, R_A increases exponentially with concentration for both the electrolytes. Typical plots are shown in Figure 5.

Figure 6 shows the variation of molar compressibility (W) for both potassium ferri and ferrocyanide solutions in different wt% of dextrose solutions. As observed, the values of W increase with increase in the dextrose content in water but decrease with increase in the solute concentrations. The decrease in molar compressibility implies that there is enhanced molecular associations in these systems on increase in solute content, as the new entities formed due to molecular association, become compact and less compressible, satisfying the phenomenon of electrostriction.

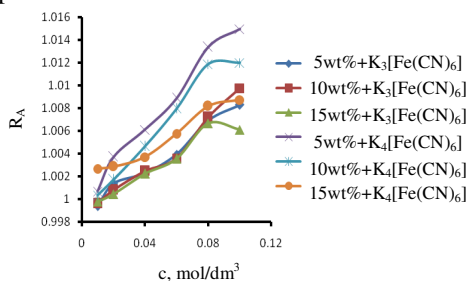


Figure 5. Plot of R_A versus c of the solutions of potassium ferri and ferrocyanide in different wt% of dextrose solutions

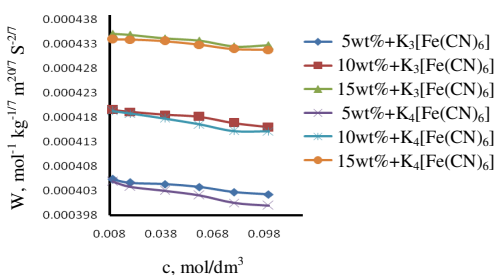


Figure 6. Plot of W versus c of the solutions of potassium ferri and ferrocyanide in different wt% of dextrose solutions

Conclusion

From the ultrasonic velocity and density data, various important acoustic parameters like specific acoustic impedance (Z), molar sound velocity (R), molar compressibility (W), free

volume (V_f), isentropic compressibility (K_s), internal pressure (π_i) and relative association (R_A) for the solutions of potassium ferri and ferrocyanide in aqueous dextrose solutions at 298.15 K have been calculated. The results reveal that the specific ion-ion, ion-solvent and solvent-solvent interactions play an important role for explaining various acoustic parameters. However, any deviation from the usual behavior is probably due to characteristic structural changes in the respective system.

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