



**ACOUSTICAL AND THERMODYNAMICAL PROPERTIES OF
POTASSIUM FERRICYANIDE AND POTASSIUM FERROCYANIDE
IN CHITOSAN SOLUTIONS AT 298.15K**

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ABSTRACT

The nature and relative strength of the intermolecular interaction between the components of the liquid mixtures have been successfully investigated by the ultrasonic velocity (U), density (d) and viscosity (η) measurements for potassium ferricyanide and potassium ferrocyanide in chitosan solutions in different concentrations at 298.15K. Experimental data have been used to estimate the isentropic compressibility (K_s), apparent molar volume (V_ϕ), limiting apparent molar isentropic compressibility ($K_{s,\phi}$), and acoustic impedance. The variation of these parameters has been discussed in the light of solute-solvent and solute-solute interactions. The viscosity data have been analysed on the basis of Jones-Dole equation to interpret the ion-solvent interaction for which Jones-Dole coefficients, A_F and B_J have also been determined.

KEYWORDS: Chitosan solution, potassium ferricyanide, potassium ferrocyanide, apparent molar volume, isentropic compressibility and molecular interaction.



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INTRODUCTION

Solvation dynamics¹⁻² has been the focus of intense research activities for the past few years. The study of propagation of ultrasonic waves in liquid system is established as an important tool in determining the nature of interactions between molecules in liquids and solutions. The ultrasonic parameters are directly related to a number of thermodynamic parameters and different state theories are based on thermodynamic considerations. Measurements of bulk properties like viscosity (η), density (d) and ultrasonic velocity (U) provide insight into the intermolecular arrangements of the components in solutions and help to understand the thermodynamic and acoustic properties of the solutions³⁻⁴. Evaluation of partial molar quantities is of importance as they provide a lot of informations regarding ion-solvent interactions in various solutions. Since these quantities cannot be directly measured from the experiment, it is difficult to study the molecular interaction in ternary mixtures. However, ultrasonic is a versatile non-destructive technique and highly useful for investigation of various physico-chemical properties, such as adiabatic compressibility which gives the information about structural dynamics. In continuation of our work in the solutions of chitosan⁵, the present investigation aim at determining the values of η , d , U and related acoustic parameters and to study the possible ion-ion and ion-solvent interactions for the solutions of $K_3[Fe(CN_6)]$ and $K_4[Fe(CN_6)]$ in 0.01, 0.05, and 0.1% (w/v) chitosan in 0.1 molar HCl solution. Chitosan is derived from chitin a polysaccharide, which is also a cellulose like polymer consisting mainly straight chains of N-acetyl-D-glucosamine. Since chitosan finds wide applications in agriculture, horticulture, water filtration process, biomedical and industrial materials, the present work aims at determining the physico-chemical properties of the halides in chitosan solutions.

MATERIALS AND METHODS

All chemicals used were of G.R. or B.D.H., AnalaR grades. Alkali metal halides were heated at 120°C for 4 hours and kept along with ammonium chloride in vacuum desiccator over anhydrous calcium chloride until required. Conductivity water (Sp.cond.~ 10^{-6} S cm^{-1}) was used for preparing 0.1 molar HCl solution. Since chitosan was not soluble in water the solution was prepared in 0.1 molar HCl solution and three different compositions of chitosan, e.g., 0.1, 0.5 and 1.0 % (w/v) were prepared. The chitosan content in the mixed solvents was accurate to within $\pm 0.01\%$. The salt solutions were prepared on the molar basis and conversion of molality to molarity was done by using the standard expression⁶ considering the density data at the corresponding temperature. Solutions were kept for 2h in a water thermostat maintained at the required temperature accurate to within $\pm 0.05K$ before use for density measurements. Density measurements were done using a specific gravity bottle (25 ml. capacity) as described earlier⁷. At least five observations were taken and differences in any two readings did not exceed $\pm 0.02\%$. Viscosity measurements were made by using an Ostwald Viscometer as described elsewhere⁷. The viscosity values of water at the experimental temperatures were obtained from literature⁶. Ultrasonic velocity measurements on the solutions of the salts were made by using an Ultrasonic Interferometer (Mittal Enterprise, New Delhi, India) at frequency of 2MHz at 298.15K only. The accuracy of the ultrasonic velocity measurement is within $\pm 0.5m/s$. The salt content of the solutions varied over a concentration range of 4.0×10^{-3} to 8.0×10^{-2} M for all these measurements.⁵

THEORY

The apparent molar volume V_ϕ , was calculated from the density data by the standard equation (1)⁸

$$V_\phi = 1000(cd_0)^{-1} (d_0 - d) + Md_0^{-1} \quad (1)$$

where c is the molar concentration, d_0 is the density of the solvent, d is the density of the solution and M is the molar mass of the solute. The V_ϕ data were fitted to the Masson equation⁹ by least squares method and the limiting apparent volume, V_ϕ^0 was determined by the equation (2),

$$V_\phi = V_\phi^0 + S_v c^{1/2} \quad (2)$$

where S_v is the slope of the V_ϕ versus $c^{1/2}$ plot.

c = molar concentration of the salt

d_0 = density of pure solvent (solutions of chitosan)

d = density of the salt solution in chitosan

M = Molecular mass of the salt concerned

The values of adiabatic compressibility (K_s) apparent isentropic compressibility ($K_{s,\phi}$), solvation number (S_n) of the solute have been calculated from the sound velocity data using the following relations², respectively.

$$K_s = (1/U^2 d) \quad (3)$$

$$K_{s,\phi} = 1000 K_s c^{-1} - K_s^0 d_0^{-1} (1000 c^{-1} d - M) \quad (4)$$

$K_{s,\phi}$ is a function of c as obtained by Gucker¹⁰ and is given by

$$K_{s,\phi} = K_{s,\phi}^0 + S_k c^{1/2} \quad (5)$$

and

$$S_n = n_1 n_2^{-1} [1 - K_s K_s^0] \quad (6)$$

where n_2 = number of moles of the solute

V_1^0 = molar volume of the solvent,

n_1 = number of moles of the solvent

K_s^0 = the adiabatic compressibility of solvent

The viscosity data of the solutions have been analyzed by the Jones-Dole equation¹¹

$$\frac{\eta}{\eta_0} = 1 + A_F C^{\frac{1}{2}} + B_J C \quad (7)$$

where η = viscosity of the solution
 η_0 = viscosity of the solvent
 A_F = Falken-Hagen constant¹² characteristic of the solute
 B_J = Jone-Dole co-efficient

RESULTS

- The experimental values of density (d), viscosity (η) and ultrasonic velocity (U) for different molar concentrations of potassium ferricyanide and potassium ferrocyanide in 0.01, 0.05 and 0.1% (w/v) chitosan in 0.1 M HCl solution.

Table 1

Values of density(d), ultrasonic velocity(U),viscosity(η),adiabatic compressibility(K_s), solvation number(S_n), apparent molal compressibility($K_{s,\phi}$),and apparent molal volume(V_ϕ) of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ in chitosan solutions at 298.15K

c mol dm ⁻³	d Kg m ⁻³	U m s ⁻¹	10 ⁴ η Pa Sec	10 ¹¹ K_s Pa ⁻¹	10 ¹³ $K_{s,\phi}$ m ³ mol ⁻¹ Pa ⁻¹	10 ⁶ V_ϕ m ³ mol ⁻¹	S_n
0.1 M HCl							
Potassium Ferricyanide							
0	998.01	1492.0	8.950	45.01			
0.004	1005.04	1506.2	8.987	43.86	-35.28	-1424.34	350.71
0.006	1005.45	1508.6	8.996	43.7	-25.95	-907.12	268.67
0.008	1006.04	1509.4	9.029	43.63	-20.32	-671.47	212.56
0.01	1006.59	1510.7	9.089	43.53	-17.20	-526.38	182.22
0.04	1012.05	1514.5	9.234	43.08	-4.93	-20.32	59.45
0.06	1015.25	1516.8	9.421	42.81	-3.48	43.08	45.09
0.08	1018.31	1518.4	9.605	42.59	-2.68	76.60	37.18
Potassium Ferrocyanide							
0	998.01	1492.0	8.950	45.01			
0.004	1005.78	1507.3	9.078	43.76	-38.10	-1515.15	384.27
0.006	1006.04	1509.0	9.182	43.65	-26.79	-911.94	278.67
0.008	1006.40	1511.6	9.326	43.49	-21.90	-624.18	234.52
0.01	1006.96	1513.8	9.432	43.34	-18.89	-469.88	206.08
0.04	1012.89	1517.6	9.708	42.87	-5.14	51.85	65.96
0.06	1016.73	1520.3	9.834	42.55	-3.60	111.87	50.39
0.08	1020.82	1523.0	9.956	42.23	-2.85	138.65	42.72
0.01 wt. % chitosan							
Potassium Ferricyanide							
0	998.68	1493.5	9.088	44.89			
0.004	1006.04	1508.8	9.184	43.66	-37.47	-1507.13	378.42
0.006	1006.29	1510.6	9.193	43.55	-26.60	-937.80	275.95
0.008	1006.44	1513.4	9.238	43.38	-21.75	-639.28	232.76
0.01	1006.81	1515.6	9.409	43.24	-18.69	-482.34	203.68
0.04	1012.27	1519.5	9.737	42.79	-5.31	-9.57	64.87
0.06	1015.55	1523.6	9.896	42.42	-3.90	48.91	50.82
0.08	1018.76	1526.2	10.156	42.14	-3.09	79.06	42.39

Potassium Ferrocyanide

0	998.68	1493.5	9.088	44.89			
0.004	1005.92	1510.2	9.382	43.59	-38.83	-1386.16	401.88
0.006	1006.40	1512.3	9.467	43.45	-27.97	-863.02	297.05
0.008	1006.85	1514.0	9.572	43.33	-22.21	-596.70	240.75
0.01	1005.78	1515.6	9.683	43.28	-17.36	-286.01	198.21
0.04	1012.27	1519.4	9.819	42.79	-4.88	83.70	64.73
0.06	1017.91	1522.0	9.943	42.41	-3.68	102.89	51.01
0.08	1022.04	1525.0	10.142	42.07	-2.94	131.36	43.46

0.05 wt. % chitosan

Potassium Ferricyanide

0	998.78	1498.6	9.411	44.58			
0.004	1006.29	1512.4	9.820	43.45	-35.33	-1545.81	352.9
0.006	1006.77	1514.2	9.998	43.32	-25.48	-1000.39	260.9
0.008	1007.07	1516.8	10.060	43.16	-20.92	-704.71	220.68
0.01	1007.14	1518.6	10.231	43.05	-17.53	-505.23	189.63
0.04	1012.71	1522.8	10.602	42.58	-5.08	-18.07	62.08
0.06	1017.72	1526.6	10.710	42.16	-3.97	14.35	50.09
0.08	1019.90	1528.4	10.924	41.97	-2.97	66.02	40.5

Potassium Ferrocyanide

0	998.78	1498.6	9.411	44.58			
0.004	1006.18	1514.0	9.998	43.36	-36.97	-1424.84	379.91
0.006	1006.51	1515.6	10.025	43.25	-26.03	-864.19	275.17
0.008	1007.55	1517.2	10.146	43.12	-21.32	-671.26	227.39
0.01	1007.51	1519.4	10.273	42.99	-17.89	-448.83	197.22
0.04	1013.96	1524.0	10.765	42.46	-5.11	43.87	65.79
0.06	1018.17	1526.2	10.893	42.17	-3.58	100.25	50.01
0.08	1022.15	1528.0	10.998	41.90	-2.77	131.20	41.59

0.1 wt. % chitosan

Potassium Ferricyanide

0	999.19	1504.0	9.919	44.24			
0.004	1006.66	1516.6	10.381	43.19	-33.19	-1537.47	330.1
0.006	1007.03	1518.8	10.401	43.05	-24.26	-976.42	249.43
0.008	1007.18	1520.4	10.521	42.95	-19.12	-668.42	202.23
0.01	1007.95	1522.8	10.607	42.78	-17.03	-546.17	182.83
0.04	1013.34	1526.6	11.260	42.34	-4.86	-23.87	59.44
0.06	1018.13	1528.4	11.983	42.05	-3.60	14.11	45.85
0.08	1020.60	1531.2	12.436	41.79	-2.79	62.11	38.38

Potassium Ferrocyanide

0	999.19	1504.0	9.919	44.24			
0.004	1006.59	1517.4	10.510	43.15	-33.76	-1425.76	343.36
0.006	1007.03	1519.6	10.628	43.00	-24.60	-883.21	258.88
0.008	1007.14	1521.8	10.739	42.87	-19.66	-570.59	214.34
0.01	1007.55	1524.0	10.857	42.73	-16.94	-412.39	189.1
0.04	1014.40	1528.0	11.431	42.22	-4.87	42.64	63.26
0.06	1018.94	1530.6	12.037	41.89	-3.51	93.82	49.07
0.08	1023.00	1534.0	12.547	41.54	-2.83	125.39	42.29

The values of apparent molar volume (V_{ϕ}^0), limiting apparent isentropic compressibility ($K_{s,\phi}^0$) and their constants (S_V and S_K) and the values of A_F and B_J coefficients of Jones-Dole equation.

Table 2

Values of limiting apparent molal compressibility ($K_{s,\phi}^0$), limiting apparent molal volume (V_{ϕ}^0), constants S_k and S_v and A_F and B_J coefficients of Jones - Dole equation for $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ in chitosan solutions at 298.15K

	$K_{s,\phi}^0$	S_k	V_{ϕ}^0	S_v	A_F	B_J
	$m^3 mol^{-1} Pa^{-1}$	$m^3 mol^{-1} Pa^{-1}$	$cm^3 mol^{-1}$	$mol^{-3/2} cm^3 lt^{1/2}$	$dm^{3/2} mol^{-1/2}$	$dm^{3/2} mol^{-1}$
0.1M HCl						
P.Ferricyanide	-35.248	4.092	-1349.17	5684.85	0.0279	0.0432
P.Ferrocyanide	-37.715	4.386	-1383.97	6114.74	0.3681	0.4538
0.01 wt. % Chi						
P.Ferricyanide	-37.165	4.285	-1372.8	5824.00	0.1241	0.1656
P.Ferrocyanide	-38.08	4.444	-1243.56	5568.38	0.6422	0.6344
0.05 wt. % Chi						
P.Ferricyanide	-35.244	4.048	-1432.59	5987.04	0.8676	0.8895
P.Ferrocyanide	-36.486	4.237	-1333.86	5863.474	1.0334	0.9668
0.1 wt. % Chi						
P.Ferricyanide	-33.236	3.82	-1419.12	5914.98	0.6035	0.5509
P.Ferrocyanide	-33.759	3.89	-1293.84	5696.75	0.9447	0.8867

DISCUSSION

As observed, in all the two systems, the values of density, viscosity and ultrasonic velocity (Table 1.) increase with increase in concentration of the salt solutions as well as with the concentrations of chitosan in HCl solution. This increasing behaviour suggests that the solute tends to attract the solvent molecules. The increase in ultrasonic velocity in these solutions is due to molecular association arising from the cohesion brought about by the ionic solvation. The values of V_{ϕ} are negative in all solutions excepting at higher concentrations of the solute, and increase with increase in concentration of the solute in all the two systems. The negative values of V_{ϕ} indicate electrostrictive solvation of ions. However, electrostrictive solvation seems to be absent in higher concentration of the solute in all compositions of chitosan. From the magnitude of V_{ϕ} , it can be concluded that strong molecular

association is found in potassium ferrocyanide in 0.1M HCl solution while in potassium ferricyanide in all compositions of chitosan in 0.1M HCl solution, and hence potassium ferricyanide is a more effective structure maker than potassium ferrocyanide in chitosan medium. The values of V_{ϕ}^0 for the two systems are found to be negative (Table 2), which indicate weak solute solvent interaction and also provide for the evidence of electrostriction¹³⁻¹⁴. The positive and large values of S_v in all solutions of chitosan indicate the presence of strong solute-solute interaction varying with chitosan content in water. The values of $K_{s,\phi}$ (Table 1) and $K_{s,\phi}^0$ (Table 2) are negative. The negative $K_{s,\phi}^0$ values can be explained in terms of loss of compressibility¹⁵ of surrounding solvent molecules due to strong electrostrictive¹⁶ forces in the vicinity of ions causing electrostrictive solvation of ions. As

observed, the $K_{s,\phi}^0$ value increases with an increased proportion of chitosan in water. This indicates that electrostrictive solvation of ions decreases as the chitosan content increases. A perusal of Table 1 shows that the solvation numbers are positive for the two systems in all solvents indicating appreciable solvation of the solutes. This is an added support for the structure intensifying property of the solutes as well as for the presence of appreciable dipole-dipole interaction between the solute and water molecules in chitosan in 0.1M HCl solution. This also points to the fact that the compressibility of the solution will be less than that of solvent. As a result, the solutes will gain mobility and have more probability of contacting solvent molecules, thereby enhancing the interaction between solute and solvent molecules¹⁷. As observed, the values of S_n decrease with increasing chitosan content in 0.1M HCl solution. But, the S_n values are higher in 0.01 wt % chitosan in 0.1M HCl solution than in 0.1M HCl solution. This shows that the solvation effect is more in the presence of 0.01 wt% chitosan but decreases with increase of the chitosan content in 0.1M HCl solution. From Table 1 it is found that viscosity values increase with increase in concentration of chitosan in 0.1M HCl solution, and also with increase in solution concentration. This increasing trend indicates the existence of molecular interaction

occurring in these systems. Table 2 shows that the values of A_F and B_J are positive in all systems studied. Since A_F is a measure of ionic interaction, it is evident that there is solute-solute interaction in the solutions. B_J coefficient is also known as a measure of order and disorder introduced by the solute into the solvent¹⁸. It is also a measure of solute-solvent interaction and relative size of solute and solvent molecules. The larger values of B_J as compared to that of A_F points to the fact that the solute-solvent interaction dominates over solute-solute interaction and the solutes possess structure intensifying property in the chitosan solutions.

CONCLUSION

From the present study, it may be concluded that the ionic solvation and electrostrictive solvation of ions exist in the system. Derived acoustical and thermodynamical parameters indicate that strong interactions exist between the chitosan and the potassium salts in acid medium. The solute-solvent interactions dominate over the solute-solute interaction. Any deviation from the usual behaviour is probably due to characteristic structural changes in the respective system.

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