



Densities, refractive indices and apparent molar volumes of potassium hexacyanoferrate(II) trihydrate in acidic media at 35⁰C

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ABSTRACT

Densities (ρ) and refractive indices (n_D) of potassium hexacyanoferrate(II) trihydrate of different molal concentrations ($m=0.010-0.102 \text{ mol}\cdot\text{kg}^{-1}$) in aqueous 0.1 M HCl solutions were measured at 35⁰C. Specific refractions (R_D) were calculated from refractive index and density of solutions. Apparent molar volumes (φ_v) were calculated from density data and partial molar volumes were evaluated by Masson's relation. Physicochemical behavior of experimental solutions has been studied in terms of ion-ion and ion-solvent interactions.

Keywords: Potassium hexacyanoferrate(II), Partial molar volume, Density, Refractive index

INTRODUCTION

Potassium hexacyanoferrate(II) trihydrate is inorganic compound having formula $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ and it is a potassium salt of $[\text{Fe}(\text{CN})_6]^{4-}$ ion. It is used for separation of copper from molybdenum ores, purification of tin and as anti-caking agents for road salt and table salt. Potassium ferrocyanide is used for the production of citric acid and wine. Density of solution is an important key thermodynamic property. Using density data of solution the partial molar volumes are calculated. Many workers have carried out molecular interaction studies in solution [1-3] and ion-ion and ion-solvent interactions in electrolyte solutions from partial molar volumes [4-6]. Partial molar volumes of hexaamminecobalt(III) nitrate in proteated and deuterated water has been studied by A. Zanella et al [7]. Studies over the transport properties of tris(hydroxymethyl)aminomethane hydrochloride in 20% (v/v) acetone-water were carried out by A. Dixit [8]. Ion-solvent interactions in ionic solutions of alkali metal chlorides in tetrahydrofuran + water mixture at different temperatures [9], atmospherically important electrolyte solutions [10], magnesium sulphate in formamide + ethylene glycol mixed solvents [11], aqueous solutions of sodium acetate at different temperatures [12], salts of transition metal and magnesium sulphates at different temperatures [13] studies carried out. Density, viscosity, and refraction index of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ in DMSO have been studied by A. K. Mamyrbekova [14].

In aqueous media, $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ complex produce $[\text{Fe}(\text{CN})_6]^{4-}$ complex ions and K^+ ions. In aqueous 0.1 M HCl solution, H^+ and Cl^- ions will be formed as HCl is strong acid. Study of solvation of $[\text{Fe}(\text{CN})_6]^{4-}$ and other ions by water molecules due to ion-solvent interactions is interesting, therefore, in continuation with our interest to study physicochemical properties of solutions [15-19], herein we report changes in density, refractive index and apparent molar volume of 0.010-0.102 $\text{mol}\cdot\text{kg}^{-1}$ aqueous solutions of potassium hexacyanoferrate(II) trihydrate in 0.1 M HCl at 35⁰C.

EXPERIMENTAL SECTION

Aqueous solution of HCl (0.1 M) was prepared in calibrated volumetric flask (500 cm^3) using double distilled water. Experimental solutions of potassium hexacyanoferrate(II) trihydrate ($M=422.39 \text{ g/mol}$) having different molal concentrations ($m=0.010-0.102 \text{ mol}\cdot\text{kg}^{-1}$) were prepared by dissolving required quantities of solid complex in 0.1 M

stock solution of HCl in calibrated volumetric flask (50 cm³). Densities of different solutions were measured using single capillary pycnometer of 10 cm³ capacity. The pycnometer was calibrated using distilled water at 35 °C. Weighing was done on electronic balance (Anamed, e=0.0001g). Pycnometer with experimental solution was immersed in the water bath for 10 min to attain thermal equilibrium and it was then removed and outer walls were cleaned and weighed. Abbes refractometer (Rico Sci. Ind., New Delhi India, RSR-F1; Sr. No.-515-2-09; range 1.3000-1.7000; ±0.001) was used for the refractive index measurements at experimental temperature. Constant temperature water bath was used for maintaining desired temperature of solutions. Temperature was maintained constant in Abbes refractometer by passing water at desired temperature through the water jacket provided with refractometer.

RESULTS AND DISCUSSION

Experimental data of density, refractive index and calculated apparent molar volumes and specific refractions are reported in Table 1. Variation in density and refractive index with concentration of experimental solutions is presented in Figure 1 and 2.

Table 1: Densities (ρ), refractive indices (n_D), apparent molar volumes (ϕ_v) and specific refractions (R_D) of aqueous K₄[Fe(CN)₆]·3H₂O in 0.1 M HCl solutions at 35°C

$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{\sqrt{m}}{\text{mol}^{1/2}\cdot\text{kg}^{-1/2}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	n_D	$\frac{\phi_v}{\text{cm}^3\cdot\text{mol}^{-1}}$	$\frac{n_D^2-1}{n_D^2+2}$	$\frac{R_D}{\text{cm}^3\cdot\text{mol}^{-1}}$
0.010	0.100	0.99584	1.3325	424.24	0.2054	0.2063
0.020	0.141	1.00125	1.3342	421.64	0.2064	0.2061
0.030	0.173	1.00305	1.3355	420.90	0.2071	0.2065
0.040	0.200	1.00576	1.3360	419.74	0.2074	0.2062
0.051	0.226	1.00756	1.3366	419.00	0.2077	0.2062
0.061	0.247	1.01027	1.3370	417.87	0.2079	0.2058
0.071	0.266	1.01388	1.3378	416.36	0.2084	0.2055
0.081	0.285	1.01568	1.3389	415.63	0.2090	0.2058
0.092	0.303	1.01929	1.3399	414.14	0.2096	0.2056
0.102	0.319	1.02200	1.3405	413.04	0.2099	0.2054

It can be seen that overall densities and refractive indices of aqueous potassium hexacyanoferrate(II) trihydrate in 0.1 M HCl solutions increased with increase in concentration of complex which is attributed to presence of strong ion-solvent interactions.

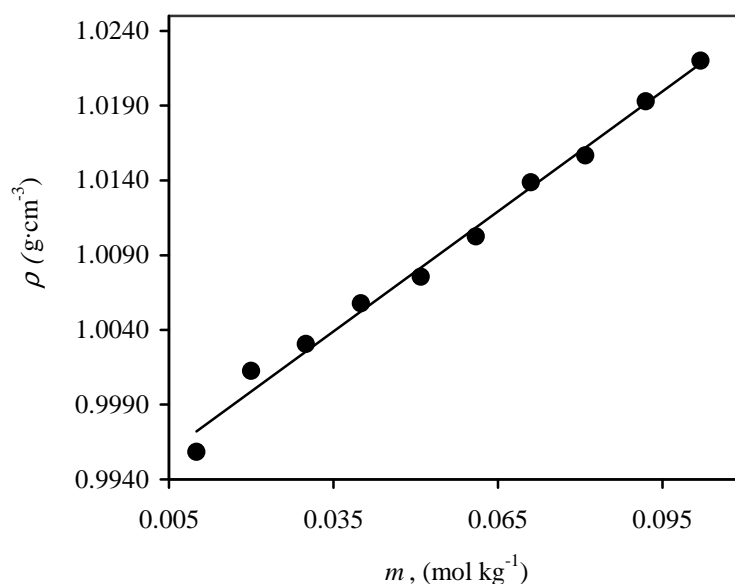


Fig. 1. Variation in density (ρ) with concentration (c) of experimental solutions

Specific refraction (R_D) which is electronic polarizability parameter was calculated by using experimental refractive indices (n_D) and density of solutions (ρ) in Lorentz and Lorenz [20] Eq. 1.

$$R_D = \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \times \frac{1}{\rho} \quad (1)$$

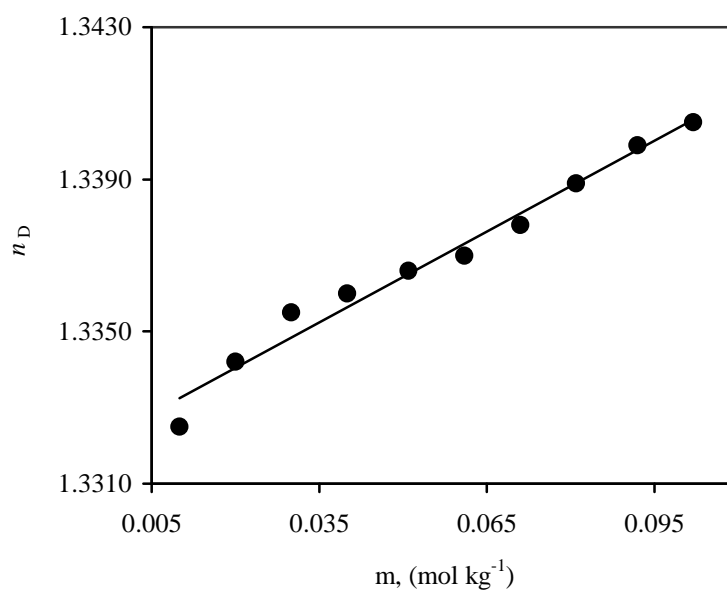


Fig. 2. Variation in refractive index (n_D) with concentration (c) of experimental solutions

Calculated specific refractions are reported in Table 1. The R_D values roughly decrease with increase in concentration of complex due to change in the electronic polarizability of system.

Apparent molar volume (φ_v) of different solutions was calculated from density data [21] using following Eq. 2.

$$\varphi_v = \frac{M}{\rho} - \frac{\rho - \rho_0}{m\rho\rho_0} \quad (2)$$

Where; ρ_0 = density of aqueous 0.1 M HCl solutions; ρ =density of potassium hexacyanoferrate(II) trihydrate in 0.1 M HCl solutions; M = molar mass of complex; m =molal concentration of complex solution.

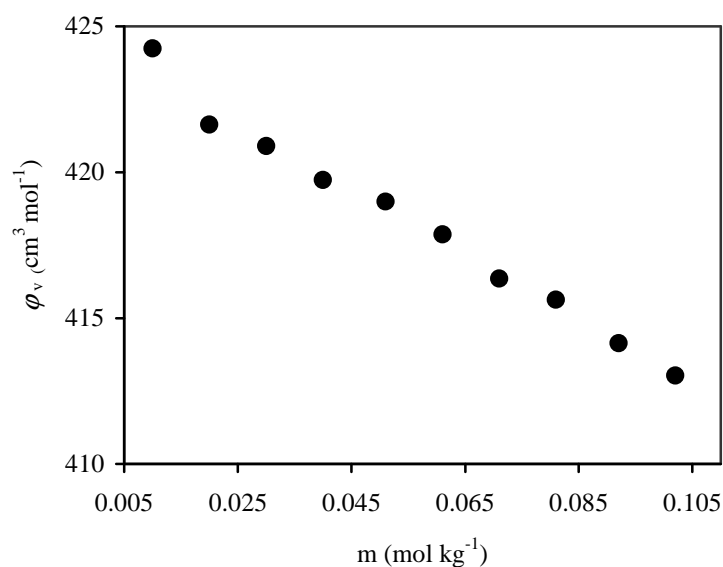


Fig. 3. Variation in apparent molar volume (φ_v) with concentration (c) of solutions

It is seen from Figure 3 that the ϕ_v values decreased with increase concentration of complex which suggests strengthening of ion-solvent interactions in solution. Upon addition of the solute, resultant change in volume of becomes less due to strong approach of solvent to solute molecules.

The ϕ_v values were fitted to Masson's relation [22-23] Eq. 3, Fig 4:

$$\phi_v = \phi_v^0 + S_v \sqrt{m} \quad (3)$$

From Figure 4, S_v (ion-ion interaction parameter) and ϕ_v^0 (ion-solvent interaction parameter) were determined as slope and intercept of the plot between ϕ_v and \sqrt{m} .

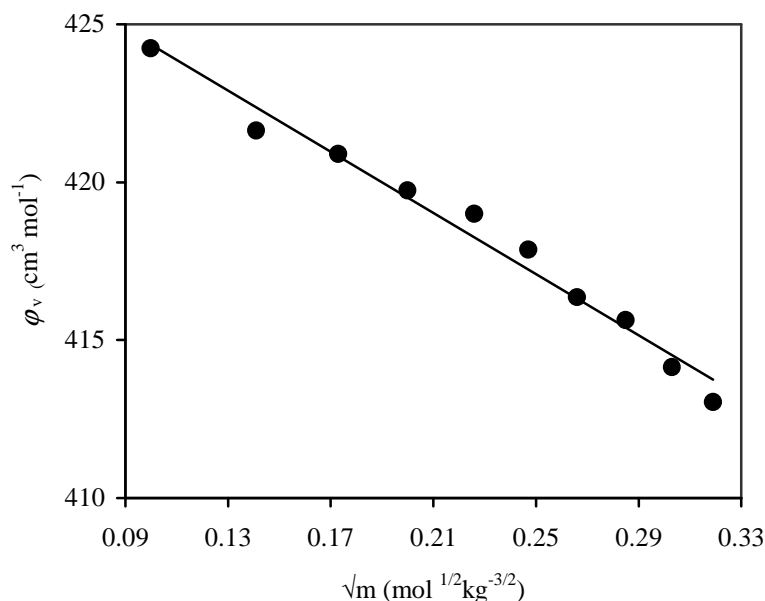


Fig. 4. Graphical determination of ϕ_v^0 and S_v from ϕ_v vs. \sqrt{m} plot using Masson's relation

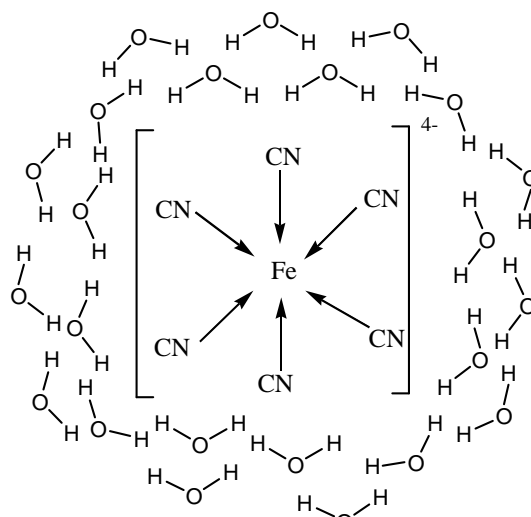


Fig. 5. Imaginary snapshot of $[\text{Fe}(\text{CN})_6]^{4-}$ ion in aqueous media

The ϕ_v^0 value is measure of ion-solvent interaction [24] in ionic solutions and it gives information regarding structure of solute in solution [25]. Graphical value of ϕ_v^0 was found to be 429.20 cm³·mol⁻¹; which is larger than ϕ_v values for any experimental concentration of solution. This indicates that the apparent molar volume at infinite dilution is larger than for other concentrated solutions which may be due to absence of some ion-ion interactions in infinitely diluted solution. This also implies that presence of ions in solution causes contraction in volume due to ion-solvent interactions. The ϕ_v^0 value is positive and large which indicates existence of strong positive ion-solvent

interactions in solution [24, 26]. Ion-solvent interactions between $[\text{Fe}(\text{CN})_6]^{4-}$ ions and polar water molecules are shown in Figure 5. Polar water molecules surround highly charged $[\text{Fe}(\text{CN})_6]^{4-}$ ions as a result of this volume contraction occurs. Other ions such as K^+ from complex and H^+ and Cl^- ions in aqueous HCl solution will also shows ion-solvent interactions.

Graphical value of S_v is found to be $-48.44 \text{ cm}^3 \cdot \text{kg}^{3/2} \cdot \text{mol}^{-3/2}$. Negative value of S_v indicates weak ion-ion interactions and structure promoting effect of complex. It is seen from magnitude of ϕ_v^0 and S_v values that ion-solvent interactions dominate over ion-ion interactions.

CONCLUSION

Densities and refractive indices of aqueous solutions of potassium hexacyanoferrate(II) trihydrate in 0.1 M HCl were measured at 35 °C. Specific refractions and apparent molar volumes for solutions were calculated. It can be concluded from variations in the experimental and derived physicochemical properties that strong ion-solvent interactions dominating over the ion-ion interactions are present in solutions.

Acknowledgement

Authors are thankful to the Director, School of Chemical Sciences, S. R. T. M. University Nanded (MS) India for providing facilities for carrying out present work.

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