

Acoustic Properties of FeCl₃ in Water at different Temperatures

B.R. ARBAD,* C.S. PATIL and A.G. SHANKARWAR

*Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University
Aurangabad-431 004, India*

Apparent molar volume (ϕ_v) and compressibility study of FeCl₃ in water, in the concentration range of 0.04 to 0.2 M at different temperatures have been computed from measured sound velocities and densities. The limiting values of ϕ_v (ϕ_{v0}), ϕ_k (ϕ_{k0}) and their concentration variations are explained on the basis of solute-solvent interactions.

INTRODUCTION

Ferric chloride is used for the manufacture of salts, pigments, pharmaceuticals, dyes, as an etching agent for photoengraving, in photography and printed circuitry, an oxidising chlorinating condensing and styptic agent, in water purification, waste water and sewage treatment. Taking into consideration all these wide applications of FeCl₃ in various fields, we decided to explore the different thermodynamic properties of FeCl₃ in aqueous solutions.

Secondly a large number of physico-chemical investigations of simple inorganic salts have been made in water under different conditions of temperature and ionic strength. The interaction studies of the inorganic salts of variable oxidation states like iron are still lacking.

In the present work, therefore, we report viscosity, density and ultrasonic study of aqueous binary systems comprising FeCl₃ in H₂O at different temperatures for predicting the solution properties in terms of different apparent molar properties as well as to investigate the effect of factors like ionic concentration and size. The measurement of ultrasonic velocity, viscosity and density were carried out and the experimental data were used to deduce apparent molar parameters such as β_s , ϕ_{ks} , ϕ_v , B, S_n, Z, R_A and L_f. These were used to study the structural interactions occurring in aqueous solutions. The study of (ϕ_v), (ϕ_k) and B coefficient can furnish useful information on the nature of solute-solvent and ion-solvent interactions respectively.¹

EXPERIMENTAL

Ferric chloride of AnalaR grade is used as such, provided all necessary precautions were taken during weighing. Water used was double distilled and had

a conductance less than 1.0 μmhos . A Mettler balance which can read up to 5th place of decimal was used for weighing. All weighings were done within ± 0.01 mg. The necessary buoyancy correction was applied. Densities of different solutions were determined from the mathematical equation given by Venenty *et al.* Viscosity measurements were performed by using Schott Gerate AVS 350 (made in Germany) viscosity measuring system equipped with a series of Ubbelohde viscometers. In all the determinations the kinetic energy corrections have been taken into account, according to the method suggested by Hagenbach (AVS 350, Viscosity Measuring System Instruction Manual, Schott Gerate Hofheim IS Germany, 1983). Experiments were generally performed at least on five replicates for each solution and at each temperature, and the results were averaged. The experimental reproducibility of the viscosity measurements, at each temperature of solution was $\pm 0.2\%$.

The speed of sound waves was obtained by using variable path, single crystal interferometer (Mittal Enterprises, New Delhi, Model MX-4). In the present work, a steel cell fitted with a quartz crystal of variable frequency was employed. The instrument was calibrated by measuring ultrasonic velocity of water at 25°C (our value 1497.05 m s^{-1} is in good agreement with literature value 1496.69 m s^{-1})³.

The maximum error limit in the measurement of ultrasonic velocity was estimated to be around 0.15%.

The temperatures were maintained by circulating water through an ultrathermostat (Julabo F-25, made in Germany) which has an accuracy $\pm 0.02^\circ\text{C}$.

RESULTS AND DISCUSSION

Various physical parameters were calculated using the following formulae:

(i) Partial Molar volume (ϕ_{v_0})

The apparent molar volume (ϕ_v) of ferric chloride was calculated from equation (1):

$$\phi_v = \frac{1000(d_0 - d)}{C \cdot d_0 \cdot d} + \frac{M}{d} \quad (1)$$

where d and d_0 are the densities of solution and solvent at concentration C of a solute of molecular weight M .

The partial molar volume ϕ_{v_0} was derived from equation (2):

$$\phi_v = \phi_{v_0} + S_v C \quad (2)$$

where S_v is experimental slope.

(ii) Viscosity B coefficient

Relative viscosity n_r is obtained from equation (3):

$$n_r = \frac{d \cdot t}{d_0 \cdot t_0} \quad (3)$$

where d and t are the density and time flow of ferric chloride solution, while d_0 and t_0 are corresponding values for water. The viscosity B-coefficient was derived from Jones-Dole equation (4) ($C > 0.1$ M):

$$n_r = 1 + BC \quad (4)$$

(iii) Partial molar compressibility (ϕ_{k_0})

Adiabatic compressibility coefficient β was derived from the relation

$$\beta = \frac{100}{u^2 \times d} \quad (5)$$

where 'u' is the ultrasonic velocity and 'd' is the density of solution.

The apparent molar adiabatic compressibility ϕ_k of liquid solution was calculated from equation (6).

$$\phi_k = \frac{1000(\beta \cdot d_0 - \beta_0 \cdot d)}{C \cdot d_0 \cdot d} + \frac{\beta \cdot M}{d} \quad (6)$$

where β and β_0 are the adiabatic compressibility of the solution and solvent respectively. ϕ_{k_0} was obtained by the expression

$$\phi_k = \phi_{k_0} + S_k C \quad (7)$$

The other parameters which speak about the solute-solvent interaction are intramolecular free length (L_f), specific acoustic impedance (Z) and relative association (R_A). These are obtained through the equations (8), (9) and (10):

$$L_f = K\sqrt{\beta} \quad (8)$$

$$Z = u \times d \quad (9)$$

$$R_A = \frac{d}{d_0} \times \left(\frac{u_0}{u} \right)^{1/3} \quad (10)$$

where 'K' is Jacobson's constant and other symbols have usual meaning. The values of $K \times 10^{-4}$ are taken as 6.31, 6.36, 6.42, 6.47 and 6.52 at 303.15, 308.15, 313.15, 318.15 and 323.15 K respectively⁵.

The experimental values of density, ultrasonic velocity, apparent molar volume and apparent molar compressibility as a representative data at 30°C are presented in Table-1. The apparent molar volume increases with increase in concentration and decreases with temperature. The variation of ϕ_k between 30 to 50°C in the concentration range investigated is almost equal. The solute-solvent interaction is guessed from the magnitude of partial molar volume at infinite dilution. It is derived from the equation (2) and presented in Table-2.

Viscosity B-coefficient (Table-3), originally introduced as an empirical term has been found to depend upon solvent-solute interactions and on the relative size of the solute and solvent molecules. The interpretations of the sign and magnitude of B-coefficient are well known in literature. The B-parameter which measures the structure making/breaking capacity of an electrolyte in a solution also contains a contribution from structural effects, and is responsible for solute-solvent interactions in a solvent^{6,7}. The salt ferric chloride is water-structure making due to positive B-coefficient. In the present study the B-coefficient increases with temperature.

TABLE-1
DENSITY, ULTRASONIC VELOCITY, APPARENT MOLAR VOLUME AND
APPARENT MOLAR ISENTROPIC COMPRESSIBILITY AT 30°C

Conc.	d (g/cm ³)	u (m s ⁻¹)	ϕ_v (cm ³ /mole)	ϕ_k (cm ³ /dyne/mol)
0.00	0.99563	1510.00	—	—
0.04	1.00150	1514.39	14.793	-1.220×10^{-2}
0.08	1.00726	1518.69	16.080	-1.193×10^{-2}
0.12	1.01294	1522.99	17.105	-1.172×10^{-2}
0.16	1.01856	1527.25	17.935	-1.154×10^{-2}
0.20	1.02412	1531.59	18.684	-1.139×10^{-2}

TABLE-2
PARTIAL MOLAR VOLUME AND PARTIAL MOLAR ISENTROPIC
COMPRESSIBILITY AT DIFFERENT TEMPERATURES

Temp. (°C)	ϕ_{v_0} (cm ³ /mole)	ϕ_k^0 (cm ³ /dyne/mole)
30	13.755	-1.229×10^{-2}
35	13.104	-1.208×10^{-2}
40	12.757	-1.148×10^{-2}
45	12.901	-1.140×10^{-2}
50	13.406	-1.133×10^{-2}

TABLE-3
VISCOSITY B-COEFFICIENT AND B/ ϕ_{v_0} AT DIFFERENT TEMPERATURES

Temp. (°C)	B (lit. mol ⁻¹)	B/ ϕ_{v_0} (lit. mol ⁻³)
30	0.5803	4.219
35	0.6166	4.705
40	0.6578	5.156
45	0.7665	5.941
50	0.7149	5.332

TABLE-4
DIFFERENT ACOUSTIC PROPERTIES AT 30°C

Conc.	L _f (Å)	Z (g/cm ² /sec)	R _A
0.04	4.16357×10^{-6}	1516.661	1.0049
0.08	4.13989×10^{-6}	1528.715	1.0097
0.12	4.11661×10^{-6}	1542.697	1.0144
0.16	4.09378×10^{-6}	1555.595	1.0191
0.20	4.07109×10^{-6}	1568.532	1.0237

The effect of solute size on the B-coefficient is apparent from hydrodynamic theories applicable to particles in a liquid continuum. In these theories the increase in viscosity due to presence of particles arises from the fact that they lie across the fluid stream lines and are subject to torsional force^{8,9}. They tend to rotate and absorb energy. This energy absorption corresponds to an increased viscosity for the solution.

The solvation of any solute can be judged from the magnitude of B/ϕ_{v_0} . These values are important indicators¹⁰ as to whether a particular solute is solvated or unsolvated since a value between 0–2.5 points to unsolvated species and any higher values to solvated ones. In the present study the values of B/ϕ_{v_0} are larger than 2.5, showing a distinct hydration. B/ϕ_{v_0} (Table-3) increases with temperature.

The values of ultrasonic velocity, u , increases with concentration of the ferric chloride. u values increase with temperature and the increment $\Delta u = (u_0 - u)$ for 0.12 M solution from 30 to 50°C is 12.99, 12.72, 11.72, 11.81 and 11.81 m s⁻¹ respectively. Adiabatic compressibility, β , decreased with concentration and temperature. It is well known that for electrolytic solution the compressibility β of solution decreases with increasing concentration¹¹. This is because, as the concentration of electrolyte increases, a larger portion of the water molecules are electrostricted and the amount of bulk water decreases causing the compressibility to decrease. In the present study $d\beta/dc$ is negative which indicates the electrostriction of water molecules.

A linear relation between ϕ_k and C holds throughout the concentration range studied. S_k parameter, which speaks about the solute-solute interaction, is positive and decreases with the increasing temperature.

It is well known that solutes causing electrostriction lead to decrease in the compressibility of the solution. This is reflected by the negative values of ϕ_k . Hydrophilic solutes often show negative compressibilities as well, due to the ordering that is induced by them in water-like structure^{12,13}.

The variation in ultrasonic velocity depends on the intermolecular free length on mixing¹⁴. In the present investigation, it has been observed that the intermolecular free length decreases with the concentration of ferric chloride at all temperatures.

The acoustic properties L_f , Z and R_A are given in Table-3. It is observed that the value of acoustic impedance (Z) varies with increase in solute concentration^{15,16}. The trend observed as regards the variation in U with temperature is in line with the reported values¹⁴.

The property which can be studied to understand the interaction is the relative association R_A .¹⁷ It is influenced by two factors:

- (i) Breaking up of the associated solvent molecules on addition of solute in it and
- (ii) The solvation of solute molecules.

The former leads to the decrease and latter to the increase of relative association. In the present study, R_A increases with increase in the solute concentration and nearly constant at higher temperatures.

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