

Studies in acoustic properties, partial molar volumes, viscosity, *B*-coefficients of lithium chloride in aqueous medium at five temperatures

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Thermodynamic properties like partial molar volume (ϕ_v^0), *B*-Coefficients and partial molar compressibility (ϕ_k^0) of aqueous lithium chloride solutions has been determined at 30, 35, 40, 45 and 50°C in an aqueous medium. The apparent molar volume (ϕ_v^0), viscosity *B*-coefficient, and apparent molar compressibility (ϕ_k^0) values were determined from density, time flow and ultrasonic velocity of lithium chloride in an aqueous solution ϕ_v and ϕ_k decreased with increase in concentration and temperature. The values of ϕ_v and ϕ_k were obtained from the linear plots of ϕ_v and ϕ_k versus *C*. The other parameters, like intermolecular free length decreases with increase in concentration and temperature, and specific acoustic impedance, relative association are almost constant with increase in temperature and gradually increases with concentration of solute. All these parameters reveal the importance of hydrophilic part of the solute.

1 Introduction

Water at ordinary temperature has a quasi-crystalline structure¹. A dynamic equilibrium, seems to exist between the three dimensional hydrogen bonded clusters and the denser monomers.



Electrolytes dissolving in water has been classified as structure makers or breakers, depending on whether the above equilibrium shifts to the left or to the right. It has been reported that ions with a low charge density are net structure breakers, on the other hand ions with a high charge density show an opposite behaviour and are net structure makers. Hence it is an interesting field to explore particularly of the ionic processes accompanying the solutions of strong electrolytes. In the present work, volumetric, viscometric, and ultrasonic velocity measurements of lithium chloride in aqueous medium at 30, 35, 40, 45 and 50°C have been carried out and the results are reported herein.

2 Experimental Details

Lithium chloride of AnalaR grade is used as such. Water used was double distilled and had a conductance less than 1.0 μ mhos. A mettler balance which can read up to 5th place of decimal, was used for weighing. All weighings were done to within \pm

0.01 mg. The necessary buoyancy correction was applied. Density of different solutions were determined from mathematical equation given in².

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 has 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 and solution was $\pm 0.2\%$.

The speed of sound waves were 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 the literature value is 1496.69 $m s^{-1}$) [Ref. 3]. The values of speed of sound were reproducible to within $\pm 1.0 m s^{-1}$. The

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

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

3 Results and Discussion

Various physical parameters were calculated at 30, 35, 40, 45 and 50°C using the following formulae.

i) *Partial molar volume* (ϕ_v^0) — The apparent molar volume (ϕ_v) of lithium chloride were calculated from Eq. (1).

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

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

The partial molar volume ϕ_v^0 was derived from Eq. (2)

$$\phi_v = \phi_v^0 + S_v C \quad \dots(2)$$

where S_v is experimental slope.

ii) *Viscosity B-coefficient* — Relative viscosity n_r is obtained from Eq. (3).

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

where d and t are the density and time flow of lithium chloride solution, while d_0 and t_0 are corresponding values for water. The viscosity B -coefficient was derived from Jones-Dole equation⁴ ($C > 0.1\text{ M}$).

$$n_r = 1 + B \cdot C \quad \dots(4)$$

iii) *Partial Molar compressibility* (ϕ_k^0) — Adiabatic compressibility coefficient β , was derived from the relation:

$$\beta = \frac{100}{U^2 \cdot d} \quad \dots(5)$$

where U is the ultrasonic velocity and d is the density of solution.

The apparent adiabatic compressibility, ϕ_k , of liquid solution was calculated from Eq. (6).

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

where β and β_0 are the adiabatic compressibility of the solution and solvent respectively ϕ_k was obtained by the expression.

$$\phi_k = \phi_k^0 + S_k C \quad \dots(7)$$

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

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

$$Z = U \cdot d \quad \dots(9)$$

$$R_\Lambda = \frac{d}{d_0} \left(\frac{U_0}{U} \right)^{1/3} \quad \dots(10)$$

where K is the Jacobsons 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 30, 35, 40, 45, and 50°C ⁵.

The experimental values of density, ultrasonic velocity, apparent molar volume and apparent molar compressibility as a representative data at 30°C presented in Table 1. The apparent molar volume (Fig. 1) decreases with increase in concentration and 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 ϕ_v^0 , which is apparent molar volume at infinite dilution. It is derived from the Eq. (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. B -coefficient values of lithium chloride are positive and lesser than B -coefficient value of carbohydrates and other organic compounds which may be due to the size effect⁶, larger B values indicate structure making capacity of a solute. The B -coefficient values slightly decrease with increasing temperatures^{7,8}. In the present study the B -coefficient decreases with temperature. The same trends are shown in ϕ_v^0 . The effect of solute size on the B -coefficient is apparent from hydrodynamic

Table 1 — Density, ultrasonic velocity, apparent molar volume and apparent molar compressibility at 30°C

Conc	$d(\text{g}/\text{cm}^3)$	$U(\text{ms}^{-1})$	ϕ_v (cm^3/mole)	ϕ_k $\text{cm}^2/\text{dyne}/\text{mole}$
0	0.99563	1510.0		
0.2	1.00036	1520.8	18.644	-3.354×10^{-3}
0.4	1.00510	1531.4	18.535	-3.241×10^{-3}
0.6	1.00984	1541.4	18.432	-3.181×10^{-3}
0.8	1.01458	1551.5	18.332	-3.146×10^{-3}
1.0	1.01933	1562.1	18.235	-2.957×10^{-3}

Table 2 — Partial molar volume & partial molar adiabatic compressibility at five different temperatures

Temp ($^{\circ}\text{C}$)	ϕ_v^0 (cm^3/mole)	ϕ_k^0 $\text{cm}^2/\text{dyne}/\text{mole}$
30	18.738	-3.303
35	18.718	-3.085
40	18.668	-3.045
45	18.563	-2.972
50	18.425	-2.940

Table 3 — Viscosity B -coefficients & B/ϕ_v^0 at five different temperatures

Temp ($^{\circ}\text{C}$)	B	B/ϕ_v^0
30	0.1427	7.615
35	0.1431	7.645
40	0.1429	7.655
45	0.1427	7.687
50	0.1421	7.712

Table 4 — Different acoustic properties at 30°C

Conc	$L_t(\text{A}^0)$	$Z \text{ gm}/\text{cm}^2/\text{sec.}$	R_A
0.2	4.14838×10^{-6}	1521.347	1.0023
0.4	4.11101×10^{-6}	1539.201	1.0047
0.6	4.07479×10^{-6}	1556.567	1.0073
0.8	4.03769×10^{-6}	1574.120	1.0098
1.0	4.0009×10^{-6}	1592.295	1.0123

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^{9,10}. 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 indicators¹¹ 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 value of B/ϕ_v^0 are larger than 2.5, showing a distinct hydration. B/ϕ_v^0 Table 3 decrease with temperature. The trend is similar to the trend shown by B -coefficient and ϕ_v^0 , at high temperatures. dB/dt is negative emphasising the greater hydration at higher temperature⁷. dB/dt reveals the structure making capacity of solute.

The values of ultrasonic velocity, U , (Fig. 2) increases with concentration of the lithium chloride. U values increase with temperature and the increment $\Delta U = (U_0 - U)$ for 0.6 M solution from 30°C to 50°C is 31.4, 30.7, 30.5, 30.2 and 29.4 m s^{-1} respectively. Adiabatic compressibility, β , decreased with concentration. It is known that for electrolytic solution the compressibility β of solutions decrease with increasing concentration¹². 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.

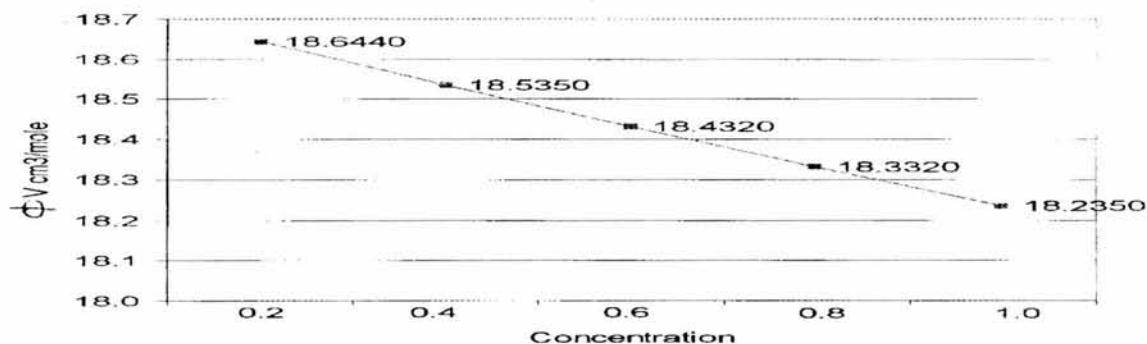


Fig. 1 — Plot of apparent molar volume versus concentration of aqueous LiCl in water at 30°C

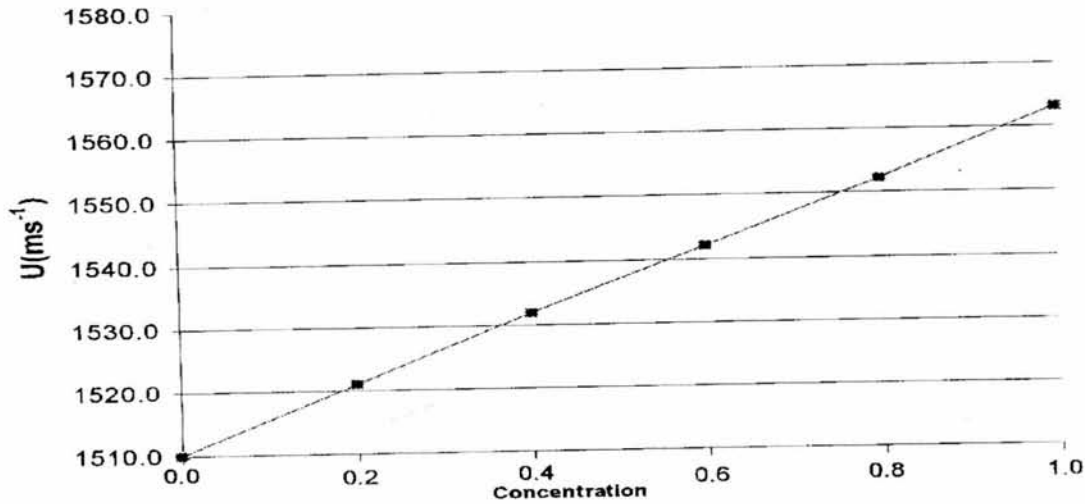


Fig. 2—Plot of ultrasonic velocity versus concentration of LiCl in water at 30°C

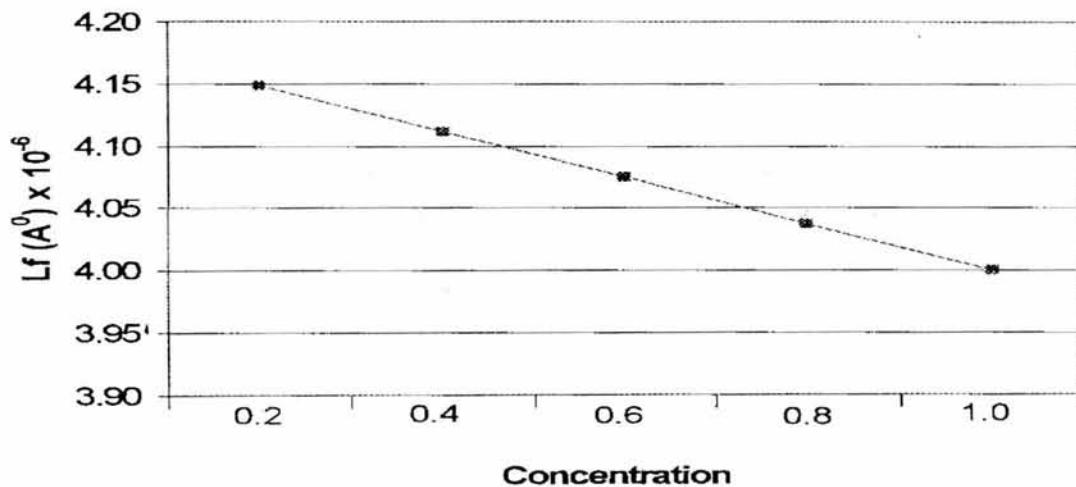


Fig. 3—Plot of intermolecular free length versus concentration of LiCl in water at 30°C

A linear relation between ϕ_k and c hold throughout the concentration range studied. S_k parameter, which speaks about the solute-solute interaction, is positive and decrease 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 of electrolytic solution. Hydrophilic solutes often show negative compressibilities as well, due to the ordering that is induced by them in water structure^{13, 14}.

The variation in ultrasonic velocity depends on the intermolecular free length on mixing¹⁵. In the present investigation, it has been observed that the intermolecular free length (Fig. 3) decreases with the concentration of lithium chloride at all temperatures.

It is observed that the values of acoustic impedance (Z) (Fig. 4) varies with increase in solute concentration^{16, 17}. The trend observed as regards the variation in U with temperature is in line with the reported values¹⁵.

The property which can be studied to understand the interaction is the relative association R_A ¹⁸. It is influenced by two factors:

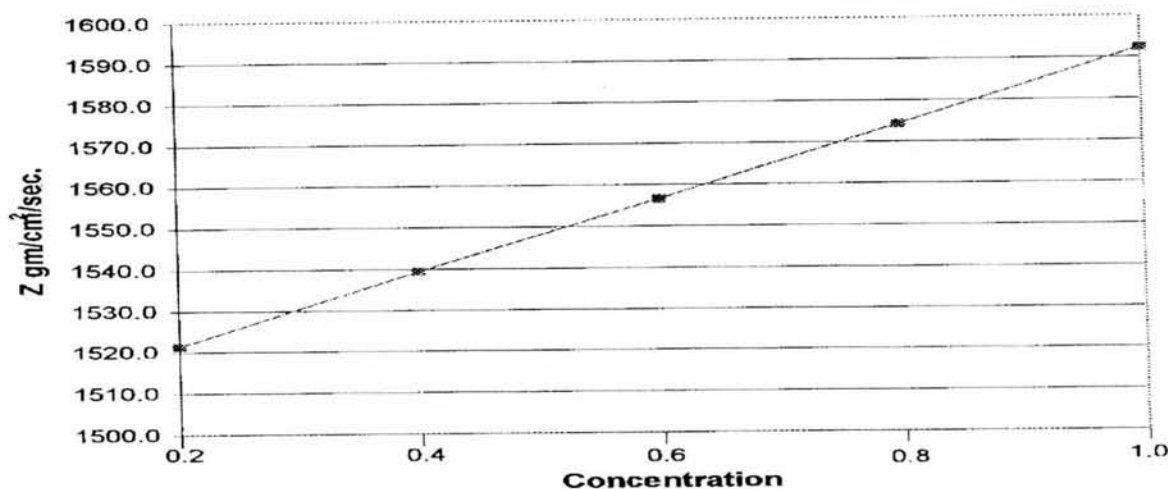


Fig. 4—Plot of acoustic impedance versus concentration of LiCl in water at 30°C

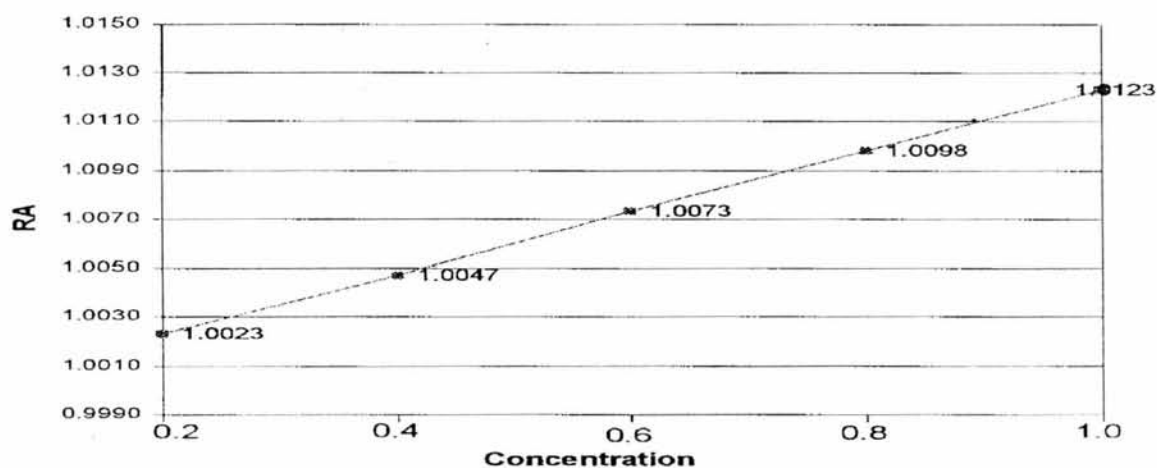


Fig. 5—Plot of relative association versus concentration of LiCl in water at 30°C

(i) Breaking up of the associated solvent molecules on addition of solute in it and

(ii) The solvation of solute molecule. The former leads to the decrease and later to the increase of relative association. In the present study, R_A increases with increase in the solute concentration (Fig. 5) of lithium chloride. The acoustic properties v , Z and R_A are given in Table 3.

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