



Ultrasonic Analysis of Molecular Interactions of Lithium Salts in Aqueous Medium

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Abstract

In present study an attempt has been made to report the ultrasonic speed (u) and density (ρ) of the various compositions of liquid mixture of aqueous solutions (1N) of Lithium chloride and Lithium sulphate. The density and ultrasonic velocity for all binary mixtures were measured experimentally. Other acoustical parameters like adiabatic compressibility (β) and acoustic impedance (z) are also determined. The variations of these parameters with mole fraction have been shown through graphs.

Keywords: Ultrasonic, compressibility, acoustic impedance.

Introduction

Ultrasonic investigation techniques find extensive applications in characterizing various aspects of thermodynamic and physiochemical behavior of various liquids and liquid mixtures. The measurement of ultrasonic speed and some allied parameters derived from it, has been used in understanding the nature of intermolecular interactions in liquid mixtures by many workers¹⁻⁸. Liquid mixtures rather than single pure liquids are of utmost practical importance in most chemical and industrial processes as they provide the wide range of mixtures of two or more components in varying proportions so as to permit continuous adjustment of the derived properties of the medium. Lithium salts like, Lithium chloride (LiCl) and Lithium sulphate (Li_2SO_4) have significant importance in industrial as well as medicinal applications.

In present study an attempt has been made to report the ultrasonic speed (u) and density (ρ) of the various compositions of liquid mixture of aqueous solutions (1N) of Lithium chloride and Lithium sulphate. Using these some derived acoustical parameters like adiabatic compressibility (β) and acoustic impedance (z) are also determined. The variation of these parameters with mole fraction was found useful in understanding the nature of interactions between the components of binary liquid mixtures.

Material and Methods

Aqueous solution (1N) of LiCl and Li_2SO_4 were prepared with double distilled water. The chemicals used were of analytical grade (Merk>99%). The solutions were left for sufficient time to allow them to have complete ionization. The binary mixtures of desired compositions were prepared by mixing known volumes of two prepared solutions. The ultrasonic velocities were measured at 2MHz with a single crystal variable path

interferometer (F-81 D Mittal make) with an accuracy of 0.01%. The densities of aqueous solutions and mixtures were measured with a pycnometer of bulb volume 10cc.

Results and Discussion

The density and ultrasonic velocity for all binary mixtures were measured experimentally. Various acoustic parameters like, adiabatic compressibility (β) and specific acoustic impedance (z) were evaluated from the measured values of ultrasonic velocity (u) and density (ρ) using following relations⁹

$$U = \lambda F \quad (1)$$

$$\beta_{ad} = \frac{1}{U^2 \rho} \quad (2)$$

$$z = U \rho \quad (3)$$

where λ is wave length, F is the frequency (2MHz) of ultrasonic wave, and ρ is the density of solution.

The values of density (ρ), ultrasonic speed (U), adiabatic compressibility (β) and specific acoustic impedance (z) for various mole fractions are shown in table-1, 2, 3 and 4 respectively. The density of solution (binary mixture) increases with increasing mole fraction of Li_2SO_4 in solution. Figure-1 shows that the variation of density with mole fraction of Li_2SO_4 is almost linear. The density increases due to existence of ions in the solution¹⁰.

The ultrasonic velocity as indicated in figure-2 is found increasing non-linearly with increasing mole fraction of Li_2SO_4 indicating that the ultrasonic velocity increases with density of solution but at the specific mole fraction (0.7) of Li_2SO_4 the ultrasonic velocity decreases, probably at this mole fraction, a complex is formed that does not allow the ultrasonic wave to travel freely in the solution and hence the ultrasonic velocity

decreases^{11,12}. On further increasing the mole fraction of Li_2SO_4 (above 0.7) the velocity again increases nonlinearly. The dip in the velocity at this specific mole fraction shows some significant interaction between the solute and solvent molecules. The similar behavior has earlier been reported by some other workers^{13,14}.

Table-1
Density (gm/cm³) for the binary mixture of LiCl and Li_2SO_4 with varying mole fraction

Mole Fraction of		Temperature K			
LiCl	Li_2SO_4	303K	308K	313K	318K
1.0	0.0	1.01773	1.01608	1.01422	1.01215
0.9	0.1	1.02092	1.01926	1.01739	1.01531
0.8	0.2	1.02403	1.02237	1.02049	1.01840
0.7	0.3	1.02542	1.02375	1.02187	1.01978
0.6	0.4	1.02698	1.02531	1.02343	1.02134
0.5	0.5	1.02820	1.02553	1.02294	1.02054
0.4	0.6	1.03155	1.02987	1.02798	1.02588
0.3	0.7	1.03475	1.03307	1.03117	1.02906
0.2	0.8	1.03714	1.03545	1.03355	1.03144
0.1	0.9	1.03881	1.03692	1.03482	1.03299
0.0	1.0	1.04111	1.03942	1.03751	1.03539

Table-2
Ultrasonic Velocity (m/s) for the binary mixture of LiCl and Li_2SO_4 with varying mole fraction

Mole Fraction of		Temperature K			
LiCl	Li_2SO_4	303K	308K	313K	318K
1.0	0.0	1557.701	1566.474	1573.656	1581.636
0.9	0.1	1558.595	1567.075	1574.247	1583.232
0.8	0.2	1559.292	1570.065	1577.247	1585.626
0.7	0.3	1561.686	1571.676	1579.641	1587.110
0.6	0.4	1561.686	1572.267	1580.242	1589.419
0.5	0.5	1562.883	1575.257	1582.642	1592.409
0.4	0.6	1567.272	1577.247	1584.230	1594.701
0.3	0.7	1564.878	1576.050	1582.434	1592.409
0.2	0.8	1570.863	1581.636	1586.025	1594.192
0.1	0.9	1572.459	1583.232	1588.419	1596.404
0.0	1.0	1575.651	1585.626	1592.808	1598.394

Table-3
Adiabatic Compressibility ($\times 10^{-10} \text{ Kg}^{-1} \text{ ms}^2$) for the binary mixture of LiCl and Li_2SO_4 with varying mole fraction

Mole Fraction of		Temperature K			
LiCl	Li_2SO_4	303K	308K	313K	318K
1.0	0.0	4049	4011	3983	3949
0.9	0.1	4031	3996	3966	3929
0.8	0.2	4017	3968	3940	3906
0.7	0.3	3999	3955	3922	3893
0.6	0.4	3993	3945	3913	3876
0.5	0.5	3982	3930	3903	3864
0.4	0.6	3947	3903	3876	3833
0.3	0.7	3961	3912	3887	3846
0.2	0.8	3908	3861	3846	3815
0.1	0.9	3893	3837	3830	3798
0.0	1.0	3869	3826	3799	3781

Table-4
Acoustic Impedance ($\times 10^3$ kg/m²/sec.) for the binary mixture of LiCl and Li₂SO₄ with varying mole fraction

Mole Fraction of		Temperature K			
LiCl	Li ₂ SO ₄	303K	308K	313K	318K
1.0	0.0	1585.27	1591.46	1595.94	1600.73
0.9	0.1	1591.07	1597.08	1601.43	1607.42
0.8	0.2	1596.62	1605.01	1609.37	1614.77
0.7	0.3	1601.24	1608.84	1614.03	1618.36
0.6	0.4	1603.60	1611.97	1617.17	1623.25
0.5	0.5	1606.87	1615.36	1618.84	1625.04
0.4	0.6	1616.56	1624.20	1628.39	1635.84
0.3	0.7	1613.30	1621.70	1626.54	1633.48
0.2	0.8	1629.07	1637.58	1639.13	1644.15
0.1	0.9	1633.40	1645.89	1643.67	1648.92
0.0	1.0	1640.35	1648.04	1652.53	1654.71

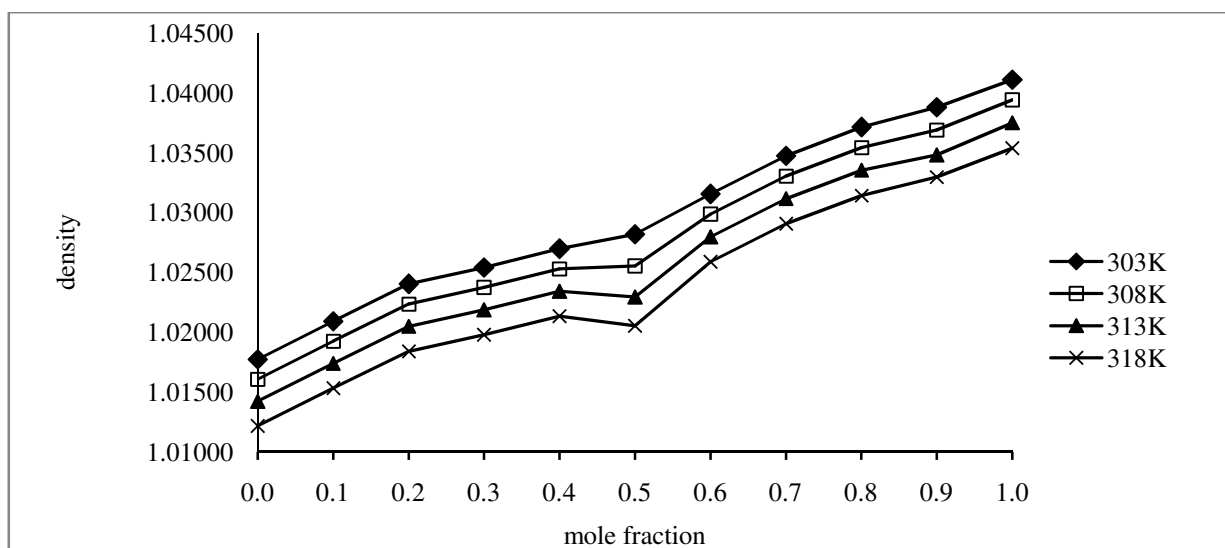


Figure-1
Variation of Density (gm/cm³) for the binary mixture of LiCl and Li₂SO₄ with varying mole fraction

The adiabatic compressibility (β_{ad}) is a measure of inter molecular association or repulsion due to the presence of unlike molecules in the solution. The variation of adiabatic compressibility with mole fraction of Li₂SO₄ is shown in figure-3. The compressibility decreases with increasing mole fraction of Li₂SO₄ in the solution and attains a sudden increase at 0.7 mole fraction of Li₂SO₄. On further increasing the mole fraction it again starts decreasing. The reverse behavior of compressibility occurs because of the structural changes present in the mixtures, that bring the molecules to a close packing^{15,16}. The presence of velocity maxima and compressibility minima at same mole fraction of Li₂SO₄ supports the existence of complex formation through hydrogen bonding at this mole fraction.

When ultrasonic wave travels through a solution certain part of it travels through the solution and rest gets reflected by the ions^{17,18}. The characteristic that determine the backward movement (or restrictions) of wave is known as acoustic impedance (z). As shown in figure-4 the acoustic impedance is found to increase with increasing mole fraction of Li₂SO₄ in solution. The higher impedance indicates the presence of bulkier solvated (Li₂SO₄) ions, due ion-solvent interaction that restricts the free flow of ultrasonic wave. The variation of acoustic impedance (z) further proves the formation of complex at (0.7) mole fraction of Li₂SO₄.

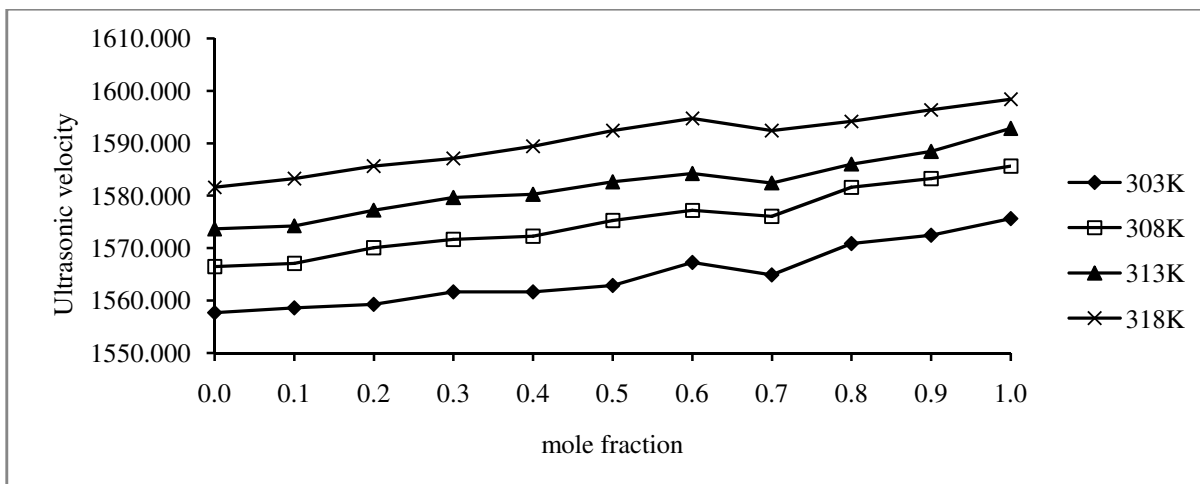


Figure-2

Variation of Ultrasonic Velocity (m/s) for the binary mixture of LiCl and Li₂SO₄ with varying mole fraction

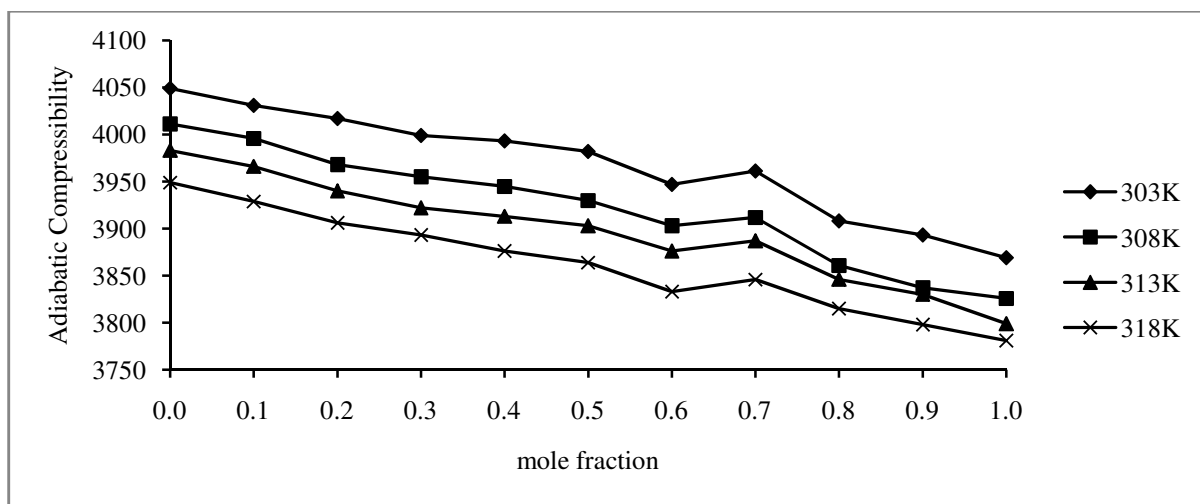


Figure-3

Variation of Adiabatic Compressibility ($\times 10^{-10} \text{ Kg}^{-1} \text{ ms}^2$) for the binary mixture of LiCl and Li₂SO₄ with varying mole fraction

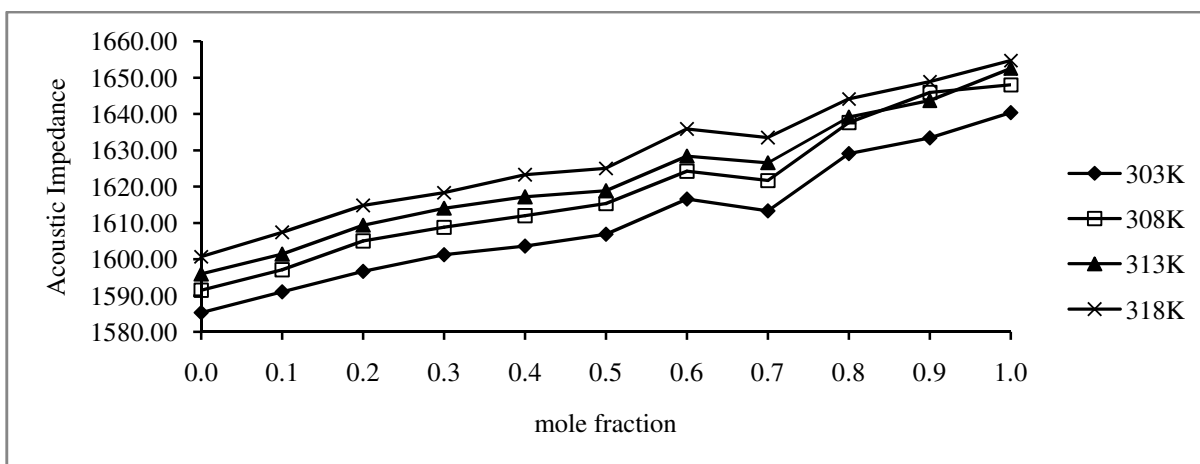


Figure-4

Variation of Acoustic Impedance ($\times 10^3 \text{ kg/m}^2/\text{sec.}$) for the binary mixture of LiCl and Li₂SO₄ with varying mole fraction

Conclusion

The present study concludes that in the binary mixture under investigation a strong interaction is present between solute and solvent molecules that form a complex at specific composition. Further this specific mole fraction at which the complex is formed does not shift even on increasing the temperature of the mixture above room temperature. This suggests that the structural changes occurring in the binary mixture are of stable nature.

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