

## Evaluation of Acoustic Parameters of Halides of Alkali Metals and Ammonium in Aqueous and Aqueous Dextran Solutions at 298.15 K

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**Abstract:** The acoustic behavior of halides of alkali metals and ammonium in aqueous and aqueous dextran solutions has been studied at 298.15 K. The structural arrangement of molecules of the solvent has been discussed with reference to the electrostatic field of ion in the solution. The qualitative intermolecular elastic forces between the solute and solvent molecules are explained in terms of compressibility.

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**Keywords:** aqueous dextran solutions; alkali metal halides; apparent molar volumes; isentropic compressibility

### 1. Introduction

Dextran, a water soluble polymer, is a -D-1, 6-glucose-linked glucan with side chains 1-3 linked to the backbone units of polymer. It has occupied a separate area of investigations by researchers because of its versatile pharmaceutical, biomedical and industrial applications. It is of interest to study the physicochemical properties such as partial molar and thermal expansibility properties, apparent molar isentropic compressibility, intermolecular attractive forces, transport properties of simple and multi-charged electrolytes in aqueous solutions of dextran. Since the ultrasonic method is a versatile technique for studying the physical properties that provide a lot of information about ion-solvent interactions in various solutions (Owen, 1957; Owen, 1961; Kauglud, 1975; Prakash, 1960; Kauglud 1988; Chottopadhyay, 1982; Dash, 1994; Dash, 1997; Dash, 2004; Ogawa, 1987; Fumio, 1983; Palani, 2008; Sonar, 2010), in the present investigation, we have studied important ultrasonic parameters like acoustic impedance ( $Z$ ), molar sound velocity ( $R$ ), molar compressibility ( $W$ ), free volume ( $V_f$ ), isentropic compressibility ( $K_s$ ) and internal pressure ( $P_i$ ) for the solutions of halides of alkali metals and ammonium in water and water +0.1%, +0.5% and +1.0% dextran mixtures at 298.15 K. The results are discussed in the light of ion-ion and ion-solvent interactions and of the structural effects of the solute and solvent in solutions.

### 2. 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.  $\sim 10^{-6}$  S  $\text{cm}^{-1}$ ) was used for preparing water + dextran (0.1, 0.5 and 1.0 % (w/v) ) mixtures. The dextran content in the mixed solvents was accurate to within  $\pm 0.01\%$ . The salt solutions were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression (Robinson, 1955) using the density values of the solutions determined at 298.15K. Solutions were kept for 2 hours in a water thermostat maintained at the required temperature accurate to within  $\pm 0.1\text{K}$  before use for density measurements. Density measurements were done using a specific gravity bottle (25 ml capacity) as described elsewhere (Dash, 1992). At least five observations were taken and differences in any two readings did not exceed  $\pm 0.02\%$ . Ultrasonic velocity measurements on the solutions of the salts were made by using an Ultrasonic Interferometer (Mittal Enterprise, New Delhi, India) at a frequency of 2 MHz at 298.15K only.

The precision of the ultrasonic velocity measurements was within  $\pm 0.5\text{m/s}$ . The salt content The precision of the ultrasonic velocity measurements was within  $\pm 0.5\text{m/s}$ . The salt content

of the solutions varied over a concentration range of  $4.0 \times 10^{-3}$  to  $8.0 \times 10^{-2}$  mol dm<sup>-3</sup> for all these

### 3. Theoretical

From the ultrasonic velocity and density data, the values of isentropic compressibility ( $K_s$ ), apparent isentropic compressibility ( $K_{s,0}$ ) and acoustic impedance ( $Z$ ) have been calculated by using Eqns. (1) – (3), respectively (Dash, 2004; Wanchoo, 1986).

$$K_s = U^{-2} d^{-1} \quad (1)$$

where,  $U$  = ultrasonic velocity of the solution

$d$  = density of the solution

$$K_{s,0} = 1000 K_s c^{-1} - K_s^0 (1000 c^{-1} d - M) \quad (2)$$

$$Z = Ud \quad (3)$$

The molar sound velocity ( $R$ ), free volume ( $V_f$ ), molar compressibility ( $W$ ) and the increase in internal pressure ( $i$ ) due to electrostatic field of the ion have also been calculated by using the following equations, respectively (Artigas, 2001).

measurements.

$$R = \bar{M} d^{-1} U^{1/2} \quad (4)$$

$$V_f = V_m - b \quad (5)$$

$$W = K_s^{-2/3} \bar{M} d^{-1} \quad (6)$$

$$i = (K_s^0 - K_s) \quad (7)$$

$$\text{where, } \bar{M} = \frac{\sum n_i m_i}{\sum n_i}$$

$$V_m = \frac{M}{d} \quad \text{and}$$

$$b = \frac{M}{d} \left[ 1 - \left( \frac{RT}{MU^2} \right) \left\{ \left( 1 + \frac{MU^2}{3RT} \right)^{1/2} - 1 \right\} \right] \quad (8)$$

### 4. Results and Discussion

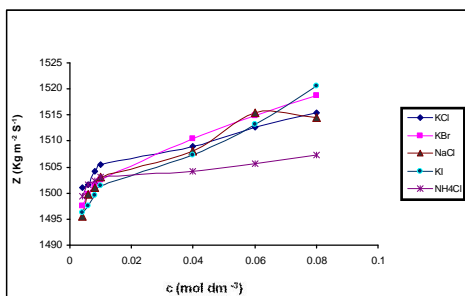
The measured values of ultrasonic velocity ( $U$ ) and density ( $d$ ) have been presented in Table 1. As observed, ultrasonic velocity ( $U$ ) values tend to increase with the increase of dextran content in water and also of solutes (halides of alkali metals and ammonium) concentrations in various solvent systems. This suggests that disruption of water structure is enhanced with the addition of dextran and the solutes. This result is in agreement with the earlier studies made in various mixed solvents (Dash, 1994; Dash, 1997; dash, 2004; Dash, 1992).

The specific acoustic impedance ( $Z$ ) values have been calculated in aqueous and aqueous solutions of 0.1, 0.5 and 1.0% dextran at 298.15 K. It is found that the values of  $Z$  increase with increase in dextran content in water as well as with increase in solute concentration in all the studied composition range.

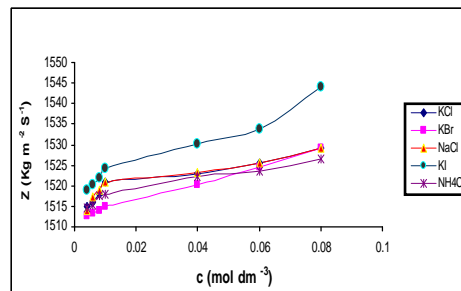
This is in agreement with the theoretical requirements as both  $U$  and density ( $d$ ) increase with increase in concentration of solute. Typical plots of  $Z$  versus  $c$  of the solutions of halides of alkali metals and ammonium are shown in Figure 1 for aqueous and aqueous 0.1 % dextran solution.

Table1. Ultrasonic velocity  $U$  ( $\text{ms}^{-1}$ ) and density  $d$  ( $\text{kg m}^{-3}$ ) of salt solutions in water and water + dextran mixtures at 298.15K

c/mol $\text{dm}^{-3}$	water		0.1% D		0.5% D		1.0% D	
	U	d	U	d	U	d	U	d
<b>NaCl</b>								
0.004	1498.90	997.00	1503.55	997.33	1508.00	998.67	1513.00	1000.63
0.006	1502.50	997.20	1506.00	997.48	1511.00	999.30	1516.00	1000.86
0.008	1503.20	997.34	1509.33	997.58	1512.36	998.88	1517.00	1001.27
0.010	1504.97	997.45	1510.40	997.60	1514.66	999.14	1518.80	1001.42
0.040	1509.00	998.20	1511.11	998.81	1515.50	999.90	1519.90	1002.22
0.060	1511.00	998.76	1512.72	999.42	1520.00	1001.25	1521.00	1002.94
0.080	1512.00	999.90	1514.90	999.95	1521.33	1001.87	1523.00	1004.08
<b>NH<sub>4</sub>Cl</b>								
0.004	1503.00	997.00	1505.23	997.60	1509.77	999.20	1512.40	1001.39
0.006	1504.00	997.62	1508.28	997.98	1512.36	999.30	1513.50	1001.20
0.008	1504.80	997.70	1510.60	997.78	1514.80	999.49	1515.40	1001.46
0.010	1505.40	997.84	1512.80	997.94	1515.20	999.53	1516.20	1001.23
0.040	1506.40	998.53	1514.20	998.60	1517.22	1000.59	1519.20	1002.00
0.060	1507.00	998.80	1516.00	999.00	1519.63	1000.30	1520.40	1002.00
0.080	1507.80	999.10	1517.80	999.26	1520.50	1000.55	1522.77	1002.37
<b>KCl</b>								
0.004	1503.00	997.50	1503.81	998.00	1507.33	999.20	1512.40	1001.70
0.006	1504.80	997.60	1505.00	997.70	1508.40	999.23	1514.90	1000.76
0.008	1506.54	997.70	1507.60	996.90	1510.80	998.96	1515.11	1001.77
0.010	1507.20	998.00	1509.88	996.80	1512.00	999.40	1519.11	1001.10
0.040	1510.00	999.00	1511.40	999.20	1514.66	1000.90	1519.54	1002.30
0.060	1511.63	1001.00	1513.07	1000.36	1515.20	1001.43	1520.00	1003.66
0.080	1512.80	1001.70	1518.40	1000.30	1520.44	1003.47	1522.18	1004.69
<b>KBr</b>								
0.004	1500.00	993.66	1506.22	995.65	1507.63	999.34	1512.80	999.80
0.006	1501.60	994.10	1507.45	995.90	1508.44	998.99	1513.60	999.91
0.008	1503.00	995.30	1508.67	996.16	1508.80	1000.14	1514.00	1000.02
0.010	1504.00	996.74	1509.22	997.26	1509.33	1000.14	1514.80	1000.17
0.040	1508.00	998.76	1510.00	999.62	1511.00	1002.60	1515.90	1002.90
0.060	1510.00	1000.30	1511.27	1001.47	1512.00	1004.50	1517.60	1004.52
0.080	1511.20	1000.59	1512.86	1003.00	1514.54	1006.00	1519.50	1006.29
<b>KI</b>								
0.004	1498.40	997.20	1504.60	997.56	1513.00	999.29	1517.00	1001.24
0.006	1499.60	998.50	1505.90	998.92	1517.00	1000.37	1518.54	1001.20
0.008	1501.00	998.70	1506.80	999.00	1517.33	1000.97	1519.55	1001.60
0.010	1502.00	999.00	1509.70	999.00	1517.33	1001.27	1520.00	1002.68
0.040	1503.00	1002.56	1510.00	1002.70	1519.00	1003.00	1521.77	1005.60
0.060	1505.00	1004.50	1512.40	1005.00	1521.60	1005.90	1522.50	1007.50
0.080	1508.60	1007.90	1514.40	1006.70	1522.30	1007.95	1527.11	1011.00



(a)



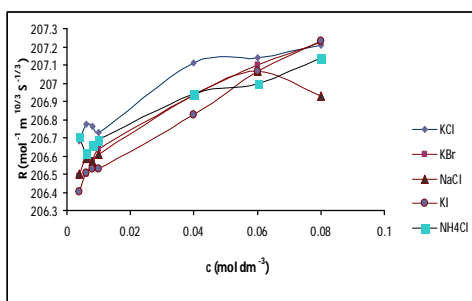
(b)

Figure 1. Plot of  $Z$  versus  $c$  of the solutions of halides of alkali metals and ammonium (a) in water and (b) in water + 0.1 % dextran.

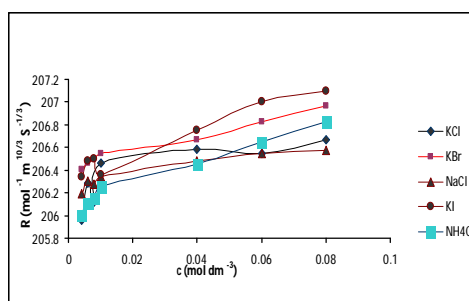
The increase in  $Z$  values with solute concentration can be attributed to the effective solute – solvent interactions. A similar type of behavior has been obtained for various salts studied in different solvent systems ( Dash, 2004; Dash, 2003). Since the acoustic impedance is a measure of the resistance offered by the liquid medium to the sound wave, and is a function of the elastic property of the medium, i.e. the bulk modulus of elasticity, which depend on the structural changes of the solution, the higher  $Z$  values in the aqueous dextran solutions as compared to that in water and increasingly higher values with increase in the solute concentration and also with increase in dextran content in water point to the fact that the solution medium in each case starts gaining its elastic

property. A comparison of the  $Z$  values of ammonium chloride solutions in aqueous and aqueous dextran media with that of solutions of alkali metal halides shows that the  $Z$  values are lower for the ammonium chloride solutions which may be due to its lower molecular mass, as a result, the solutions of ammonium chloride start losing the elastic property.

The variation of the molar sound velocity ( $R$ ) with solute concentrations in water and 0.1% dextran solution is shown in Figure 2. As observed, the molar sound velocity increases with increase in concentration of the solutions for all the halides in all the solvents. This type of behavior is similar to that observed earlier (Dash,2004).



(a)

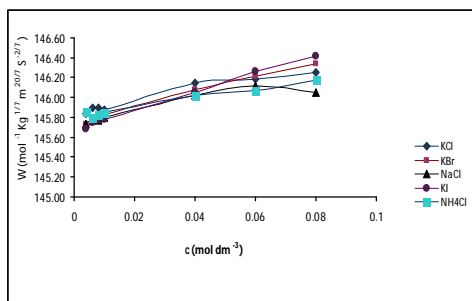


(b)

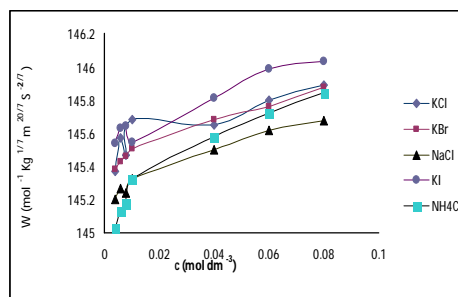
Figure 2. Plot of  $R$  versus  $c$  of the solutions of halides of alkali metals and ammonium (a) in water and (b) water + 1% dextran

Figure 3 shows the variation of molar compressibility ( $W$ ) for the halide solutions in water and water + 0.5% dextran. As observed, the values of

$W$  increase with concentration in all solvents for all the salts studied.



(a)



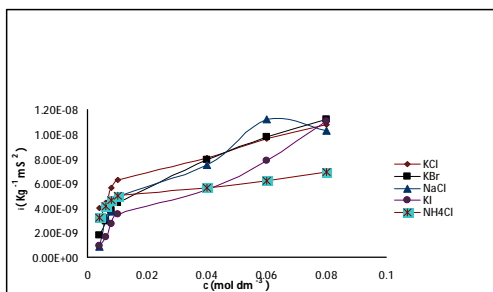
(b)

Figure 3. Plot of  $W$  versus  $c$  of the solutions of halides of alkali metals and ammonium (a) in water and (b) in water + 1% dextran

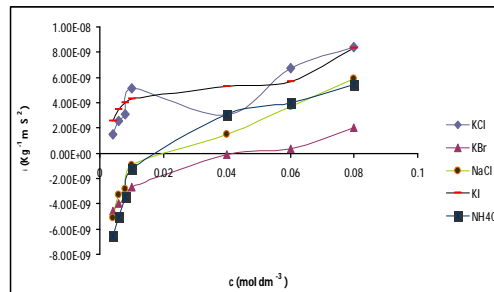
It is a well-known fact that when a solute dissolves in a solvent some of the solvent molecules are attached to the ions (produced from the solute) because of ion-solvent interactions. Since the solvent molecules are oriented in the ionic field (i.e., electrostatic fields of ions) the solvent molecules are more compactly packed in the primary solvation shell as compared to the packing in the absence of the ions. This is the reason why the solvent is compressed by the introduction of ions. Thus, the electrostatic field of the ion causes compression of the medium giving rise to a phenomenon called electrostriction. Since the solvent molecules are compressed they do not respond to any further application of pressure. So the solution becomes harder to compress, i.e., the compressibility decreases and internal pressure

increases. Hence isentropic compressibility as well as internal pressure describes the molecular arrangement in the liquid medium. The increase in internal pressure,  $i$  due to electrostatic field of ions is given by equation 7. T.W Richards (1925) pointed out the importance of internal pressure and its potentiality in understanding the liquid properties.

Suryanarayan et al. (1991) showed that the free energy of activation,  $G$  is almost equal to the cohesive energy,  $iV_m$ . The result indicates that  $G$  increases with concentration, and dextran content in the mixed solvent. Positive values of  $i$  indicate the presence of some specific interactions between unlike molecules in the components. Typical plots of  $i$  versus  $c$  are shown in Figure 4 for halide solutions in water and water + 1% dextran solution.



(a)



(b)

Figure 4. Plot of  $i$  versus  $c$  of the solutions of halides of alkali metals and ammonium (a) in water and (b) in water + 1% dextran

Free volume ( $V_f$ ) is the effective volume accessible to the centre of a molecule in a liquid. The structure of a liquid is determined by strong repulsive forces in the liquid with the relatively weak attractive forces providing the internal pressure which held the liquid molecules together. The free volume seems to be conditional by repulsive forces whereas the internal pressure is more sensitive to attractive forces. These two factors together uniquely determine the

entropy of the system. Thus, the internal pressure, free volume and temperature seem to be the thermodynamic variables that describe the liquid system of fixed composition.

It is seen that the free volume ( $V_f$ ) decreases with solute concentration in all the solvents but increases with dextran content in the mixed solvent. Typical plots are shown in Figure 5.

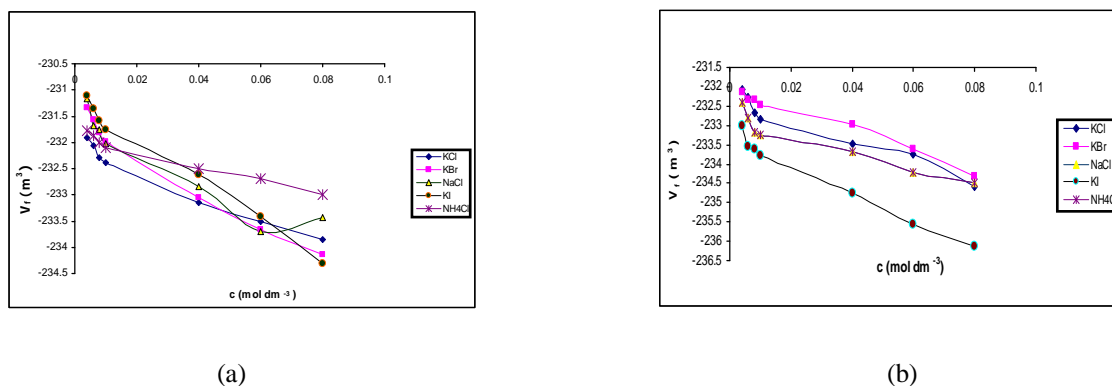


Figure 5. Plot of  $V_f$  versus  $c$  of the solutions of halides of alkali metals and ammonium in (a) water and (b) water + 0.5 % dextran

Internal pressure changes in a manner opposite to that of free volume. The decrease of  $V_f$  (or increase of  $\rho$ ) indicates the formation of hard and/ or tight solvation layer around the ion. The fractional free volume ( $V_f/V$ ) is a measure of disorderliness due to increased mobility of the molecules in a liquid. It is observed that mobility/disorderliness decreases with concentration and dextran content. This implies that

the frictional force exerted by different layers of liquid increases with concentration and dextran content. As the frictional force increases, ultrasonic absorption increases. In the present case, ultrasonic absorption or attenuation increases with concentration and dextran content. Typical plots are shown in Figure 6.

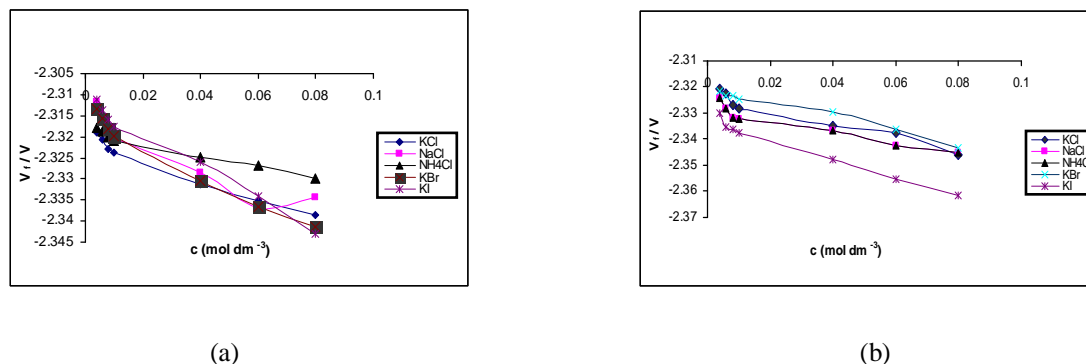


Figure 6. Plot of ( $V_f/V$ ) versus  $c$  of the solutions of halides of alkali metals and ammonium (a) in water and (b) in water + 0.5 % dextran

## Conclusions

From the ultrasonic velocity and density values of the solutions of halides of alkali metals and ammonium in water and water+0.1%,+0.5% and 1.0% dextran, the acoustic parameters like isentropic compressibility, acoustic impedance, molar sound velocity, free volume, molar compressibility and internal pressure have been calculated at 298.15K. The results show that the specific ion-ion, ion-solvent and solvent-solvent interactions play an important role for explaining acoustic parameters. However, any deviation from the usual behavior is probably due to characteristic structural changes in the respective system.

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## References

- [1] Owen BB, Simon HL. J. Phys. Chem. 1957; 61: 479.
- [2] Owen BB, Kronick PL, J. Phys. Chem. 1961; 65: 84.
- [3] Kauglud MV, Patel KJ. Indian J. Pure and Applied Phys 1975;13: 32.
- [4] Prakash O, Singh S, Prakash A, Singh SK, Kumar A. Indian J. Pure and Applied Phys. 1960;18: 92.
- [5] Kaulgud MV, Rao KSM. Indian J. Chem. 1988; 27A: 12.
- [6] Chottopadhyay AK, Lahiri SC. Electrochim Acta. 1982; 27: 269.
- [7] Dash UN, Sahu R. Acoustic Letters 1994; 17: 157.
- [8] Dash UN, Pasupalak NN. Indian Journal of Chemistry 1997; 36A: 834.
- [9] Dash UN, Roy GS, Mohanty S. Indian Journal of Chemical Technology 2004; 11: 178.
- [10] Ogawa H, Murukami SJ. J. Solution Chemistry 1987; 16: 315.
- [11] Fumio K, Katsuyuki M, Hiroyasu N. J. Phys. Chem. 1983; 87(16): 3161.
- [12] Palani R, Saravanan S. Res. J. Phys. 2008; 2(1): 13.
- [13] Sonar AN, Pawar NS. E.J. Chem. 2010;7(3): 789.
- [14] Robinson RA, Stokes RH. Electrolyte Solutions. London: Butterworth's: 1955: 30.
- [15] Dash UN, Supkar S. Acoustic Letters 1992; 16: 135.
- [16] Wanchoo RK, Rattan VK, Singh S, Sethi BPS. Acoustica 1986; 62:172.
- [17] Artigas H, Lafuente C, Lopez MC, Royo FM, Urieta JS. Zeit. Phys. Chem. 2001; 215: 933.
- [18] Dash UN, Roy GS, Mohanty S. Ultrascience 2003; 15(1): 1.
- [19] Richards TW. Chemical Reviews 1925; 2: 315.
- [20] Suryanarayan CV, Arun P, Natarajan SL. Indian Journal of Technology 1991; 29: 327.

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