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ULTRASONIC INVESTIGATION OF KBr AND KI AT DIFFERENT TEMPERATURE AND CONCENTRATIONS

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ABSTRACT: The present experimental investigation was carried out in order to explore the possible molecular interionic interactions of aqueous alkali metal halides namely potassium bromide (KBr) and potassium iodide (KI) at 35°C, 40°C, 45°C. Experimental values of density and ultrasonic velocities were carried out on the liquid mixtures of water + alkali metal halides was prepared under molality (m) basis say, at five fixed molalities (0.2, 0.4, 0.6, 0.8 and 1.0 mol.kg⁻¹). The related and relevant parameters correlated to our present study such as adiabatic compressibility (β), change in adiabatic compressibility ($\Delta\beta$), relative change in adiabatic compressibility ($\Delta\beta/\beta^0$), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), limiting apparent molal compressibility (ϕ_k^0), limiting apparent molal volume (ϕ_v^0) and their associated constants (S_k, S_v) were determined

Index Terms - Ultrasonic, interionic interactions, alkali metal halides.

INTRODUCTION

Ultrasonic studies provide a wealth of information about the state of liquid mixtures and provide extensive application in characterizing the thermodynamic and physico-chemical behaviour of liquid mixtures. The study of propagation of ultrasonic waves in pure liquids, liquid mixtures is well established for determining the nature of intermolecular interactions. Molecular interactions determine the properties and the structure of matter. Molecular interactions are also of prime importance in deciding the structure and properties of biological systems as well as energy transfer in enzymes, phase transitions, etc. In the last few years one has been able to observe fascinating progress in the study of molecular interactions. The field of ultrasonics has grown enormously in the last few decades. It provides much insight into the problems of basic physics, and finds large number of industrial, biological and medical applications by characterizing thermodynamic and physico-chemical behaviour of liquid mixtures. The measurement of ultrasonic velocity enables the accurate determination of some useful acoustical parameters which are highly sensitive to the study of molecular interactions. These acoustical parameters provide qualitative information about the physical nature and strength of the molecular interactions in the liquid mixtures. Acoustical and thermodynamic parameters have been used to understand different kinds of association, the molecular packing, molecular motion and their respective strength influenced by the size in pure components and in the mixtures.

Ultrasonic velocity together with density and viscosity data furnish sufficient information about the sum of total interactions between ions, dipoles, H-bonding, multi-polar dispersion forces and elastic forces (Rastogi *et al.*, 2002; Acharya *et al.*, 2003). Hence, this technique seems to be complementary to spectroscopic (Hyder *et al.*, 2000; Sati *et al.*, 2000; Baluja and Karia 2000; Ali *et al.*, 2002; Deshmukh *et al.*, 2003) and dielectric methods. The study of molecular interaction plays an important role in the development of molecular sciences.

The intermolecular distance in liquids and liquid mixtures are so small and the effects of the intermolecular forces are correspondingly so large because of the strongest ionic bonds. The study of intermolecular forces which are responsible for molecular interaction is of considerable importance in the formation of simple to complex liquids and liquid mixtures.

In liquid mixtures, the interactions occur between like molecules and unlike molecules. From a theoretical point of view it is convenient to classify molecular interactions into long and short range interactions. The long range interaction leads to the existence of vander Waal's force between the molecules in a liquid and the behaviour of the liquid mainly depends on this force. This force arises when the interacting molecules come close together without the overlap of their electron clouds. The hydrogen bond and electron donor-acceptor (charge transfer) interactions arise from short range interaction. This can be augmented by the fact that the hydrogen bond distance is smaller than the vander Waal's radii. Short range interactions are due to dipole-dipole, dipole-induced dipole, charge transfer, complex formation and hydrogen bonding interactions.

These forces arise when two molecules come close enough together causing a significant overlap of electron clouds and are often highly directional.

In recent years, there has been considerable advancement in the experimental investigation of excess thermodynamic of properties of liquid mixtures. These properties have been adequately employed in understanding the nature of molecular interactions in binary liquid mixtures. In chemical industry, knowledge of the thermodynamic properties of non-electrolyte solutions is essential in the design involving chemical separation, heat transfer, mass transfer, and fluid flow. Furthermore, thermodynamic properties of binary mixtures containing components capable of undergoing specific interactions exhibit significant deviations from ideality arising not only from differences in molecular size and shape but also due to structural changes (Radhamma *et al.*, 2008).

Ultrasonic investigation of binary liquid mixture has revolutionaries the world of medical petrochemical and pharmaceutical industries to a great extent (Ali and Nain 2002; Comeli *et al.*, 2002). The ultrasonic measurements have been widely used to study the molecular structure and molecular interaction mechanism of the matter.

MATERIALS AND METHODS

The experimental techniques used to measure the ultrasonic velocities and densities are furnished in detail. The basic theory involved in calculating the acoustical parameters has also been outlined.

Temperature Control

An electronically operated constant temperature bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is $\pm 0.1\text{K}$.

Preparation of Solution

All the chemicals used in this present research work are laboratory reagent (LR) grade and of minimum assay of 99.9% obtained. Fresh water is used for preparing the solutions at different concentrations. Aqueous solutions were prepared and used on the day they were prepared. The binary solution of water + alkali metal halide (KBr and KI) was prepared under molality (m) basis. The required quantity of alkali metal halide

(KBr and KI) for a given molality was added as solutes separately in the solvent (water) and similar procedure was adapted for different molalities.

Measurement of Density

Density is one of the prime parameters characterising many physical properties of a liquid medium. The density of pure liquids, liquid mixtures and amino acids are determined using a specific gravity bottle by relative measurement method. A specific gravity bottle with 25ml capacity is cleaned well and dried and filled with reference liquid (water) and then suspended in a temperature controlled water bath. The temperature of the bath can be maintained at any desired value. The bottle with water is allowed to attain the temperature at which density is to be measured and the weight is determined as W_w with an accuracy of $\pm 0.1g$. After standardising the specific gravity bottle with water, the liquid whose density to be determined is filled in the bottle and is weighed as W_s . By using the following relation, the density of the unknown mixture at any temperature can be determined.

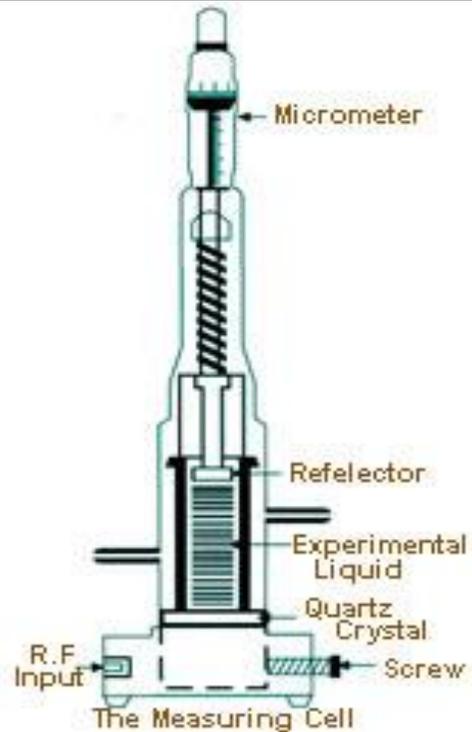
$$\rho_s = \frac{W_s}{W_w} \times \rho_w$$

... (1)

The density of water (ρ_w) at different temperatures are taken from literature.

Ultrasonic Interferometer

The ultrasonic interferometer is a versatile instrument for the measurement of ultrasonic velocity in liquids. An ultrasonic interferometer (Model: F80) supplied by M/s. Mittal Enterprises, New Delhi, having the frequency 2MHz with an overall accuracy of $\pm 2 \text{ ms}^{-1}$ has been used for velocity measurement. The main parts of the assembly of an interferometer are (a) high frequency generator (b) the cell and measuring assembly.



Cross-section of the liquid cell

Working Principle

Ultrasonic waves of known frequency are produced by an X-cut quartz crystal which is fitted at the bottom of the measuring cell. These waves travel through the liquid and they are reflected back by a movable metallic plate kept parallel to the crystal. When the distance between the transducer and reflector plate is an integral multiple of half wave length, standing waves are setup in the medium. The reflected waves arriving back at the crystal surface are out of phase. The resulting decrease in the amplitude of crystal oscillations is accompanied by alternating current through the crystal. The driving oscillator is loosely coupled to an LC circuit with a quartz crystal in parallel with the capacitor and the same is tuned to the resonating frequency of the crystal and the current through the crystal is measured. When the position of the reflector is changed, there is a variation in crystal current. The distance between successive minima and maxima is half the wavelength in the medium. Knowing the crystal frequency and wavelength, the velocity of sound in the medium can be calculated.

An X-cut quartz crystal is the transducer that is excited by the a-c energy from an RF oscillator. This transducer is a circular plate of 1cm diameter and is fitted at the bottom of the measuring cell. The measuring cell is specially designed double walled cylindrical vessel and has a

capacity to hold approximately 12ml. of liquid. Water can be circulated through the annular space between the two walls for maintaining the temperature of the liquid in the cell. Inner wall of the cell is corrugated to prevent wall reflections. A vertical electrode coming from a solid base makes the electrical contact to the lower face of the crystal. The side screw makes the fitting of the cell in solid base. The reflector is connected with the cylindrical plunger. The upper end of the plunger is connected to the lower end of the screw by means of locking ring. A fine micrometer screw, having a least count of 0.001mm is employed for the motion of the reflector. Hence, the position of the reflector can be accurately measured. The distance of 25mm is available for the movement of the micrometer screw.

The quartz crystal in the measuring cell is connected to the RF generator, through a shielded cable. The cell is filled with the experimental liquid. On exciting the crystal, the ultrasonic waves travelling through the liquid are reflected back from the reflector and so standing waves are formed between the crystal and reflector. The micrometer screw is moved upward until the anode current in the micro ammeter showed maximum deflection. Initial reading of the micrometer screw is carefully noted. Screw is then rotated slowly in the same direction of successive maxima are allowed to pass till the tenth maxima. For this tenth maxima reading on the micrometer are again noted. The total distance 'd' through which the reflector shifted is thus found out for 'n' maxima. Then the wavelength 'λ' is calculated using the relation,

$$\lambda = \frac{2d}{n} \quad \dots(2)$$

Knowing the values of 'λ' and the frequency 'f' of the quartz crystal (2MHz) used, velocity of sound 'U' is calculated using the relation

$$U = \lambda f \quad \dots(3)$$

Adiabatic Compressibility (β)

The electrostatic field produced by the interacting atoms in the solution influences the structural arrangement of the molecules, which in turn has pronounced effect on compressibility. When acoustical wave passes through a medium, adiabatic compression and rarefaction takes place. This results in a change in pressure (δP) and a corresponding change in volume (δV).

Hence, the adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. These changes are related to the compressibility of the medium by the thermodynamic relation [Rowbinson *et. al.* (1982)].

$$\beta = \frac{1}{V} \left(\frac{\delta V}{\delta P} \right) \quad \dots(4)$$

It can also be calculated from the speed of sound (U) and the density of the medium (ρ) using the equation of Newton and Laplace as

$$\beta = \frac{1}{U^2 \rho} \quad \dots(5)$$

Change in Adiabatic Compressibility ($\Delta\beta$)

The change in adiabatic compressibility was calculated by the relation

$$\Delta\beta = \beta - \beta_0 \quad \dots (6)$$

where β and β_0 are the adiabatic compressibility of the solution and solvent respectively.

Relative Change in Adiabatic Compressibility ($\Delta\beta/\beta_0$)

The relative change in adiabatic compressibility were determined by

$$\frac{\Delta\beta}{\beta_0} \quad \dots (7)$$

Apparent Molal Compressibility (φ_K)

When an electrolyte is dissolved in a solvent, it decomposes partly or completely into ions. In solutions the molar volumes of solute and solvent differ from their molar volumes in pure form. This change in volume and hence change in pressure leads to partial molar compressibility for the solvent and solute. Thus, the apparent molal compressibility of the solute is the compressibility of an amount of solution of one mole of solute minus the compressibility of the solvent and is given by the relation,

$$\varphi_K = \frac{1000}{m\varphi_0} (\rho_0\beta - \rho\beta_0) + \left(\frac{\beta_0 M}{\rho_0} \right) \quad \dots(8)$$

where β , ρ and β_0 , ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, m is the molal concentration of the solute and M the molecular mass of the solute. φ_K is the function of 'm' as obtained by [Guckar (1933)] from Debye Huckel theory [Debye *et. al.*, (1923)] and is given by

$$\varphi_K = \varphi_K^0 + S_K m^{1/2} \quad \dots(9)$$

where φ_K^0 is the limiting apparent molal compressibility at infinite dilution and S_K is a constant. φ_K^0 and S_K were obtained by least square method.

Apparent Molal Volume (φ_V)

The apparent molal volume φ_V of the solute is the volume of the amount of solution containing one mole of the solute minus the volume of solvent present in the solution.

The apparent molal volume of a solute is related to the density, molar compressibility etc. of the solution. The volume change may be due to

- i) the contraction of volume as the dissolved salt may absorb solvent and
- ii) the ability of the solute to cause electrostriction [Jerry March *et. al.*, (1984); Volkenshtein *et. al.*, (1983)]. The apparent molal volume may be obtained as

$$\varphi_V = \frac{1000}{m\rho_0}(\rho_0 - \rho) + \left(\frac{M}{\rho_0}\right) \quad \dots(10)$$

The apparent molal volume has been found to differ with concentration according to Masson's empirical relation [Mason *et. al.*, (1929)] as

$$\varphi_V = \varphi_V^0 + S_V m^{1/2} \quad \dots(11)$$

where φ_V^0 is the limiting apparent molal volume at infinite solution and S_V is a constant and these values were determined by least square method.

Acoustical parameter such as adiabatic compressibility (β), change in adiabatic compressibility ($\Delta\beta$), relative change in adiabatic compressibility ($\Delta\beta/\beta_0$), apparent molal compressibility (ϕ_K), apparent molal volume (ϕ_V), limiting apparent molal compressibility (ϕ_K^0), limiting apparent molal volume (ϕ_V^0) and the constants (S_K , S_V) were calculated using the observed values of density (ρ) and velocity (U).

RESULTS AND DISCUSSION

The experimental values of density and ultrasonic velocity for different molal composition of aqueous potassium bromide and potassium iodide solution at different temperatures of 35°C, 40°C and 45°C which are shown in Tables 1-2, the values of adiabatic compressibility, change and relative change in adiabatic compressibility, apparent molal compressibility, apparent molal volume, limiting apparent molal compressibility, limiting apparent molal volume and the constants S_K and S_V are given in Tables 3-7.

In alkali metal halide systems from Tables 1-2, the values of density and ultrasonic velocity increases with increase of molal concentration of alkali metal halides. And the same, except density, decreases with rise in temperature.

The ultrasonic velocity (U) from Table 1-2, increases with increase in the concentration of the solute as well as rise temperature. Such an increase in ultrasonic velocity (U) clearly shows that there is molecular association is being taking place in these liquid mixtures. The factors apparently responsible for such behaviour may be the presence of interactions caused by the reactions of alkali metal halide and hydrophilic nature of aqueous potassium bromide and potassium iodide [Banipal et. al., (2007)]

Density (ρ) is a measure of solvent-solvent and ion-solvent interactions. Increase of density with concentration indicates the increase in solvent-solvent and solute-solvent interactions, where as decrease in density indicates the lesser magnitude of solute-solvent and solvent-solvent interactions. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, the increase in density may be interpreted to the structure-maker of the solvent due to the added solute. Similarly, the decrease in density with concentration indicates structure-breaker of the solvent. It may also be true that solvent-solvent interactions bring about a bonding, probably hydrogen bonding between them. So, size of the resultant molecule increases and hence there will be decrease in density.

Usually the values of density of any system vary with increase in concentration of solutions. The change in structure of solvent or solutions as a result of hydrogen bond formation or dissociation or hydrophobic (structure-breaking) or hydrophilic (structure-forming) character of solute. That is hydrogen bond forming or dissociating properties can thus be correlated with change in density

The increase in ultrasonic velocity (U) in these solutions may be attributed to the cohesion brought about by the ionic hydration. When the alkali metal halides are dissolved in the molecules are attracted to the ions strongly by the electrostatic forces, which introduce a greater cohesion in the solution. Thus, cohesion increases with increase of alkali metal halide concentration in the solutions. The increased associations obtained in these solutions may also be due to water enhancement brought by the increase in electrostriction in the presence of potassium bromide and potassium iodide.

Table 1 Density (ρ) and velocity (U) of aqueous potassium bromide

Molality m (mol.Kg ⁻¹)	DENSITY ρ /(kg/m ³)			VELOCITY U/(ms ⁻¹)		
	Temperature (°C)					
	35	40	45	35	40	45
0.00	1007.03	1006.38	1005.12	1542.06	1544.76	1560.70
0.02	1007.96	1007.86	1007.01	1548.75	1556.70	1560.84
0.04	1008.12	1008.05	1007.04	1555.08	1561.05	1566.60
0.06	1008.99	1008.88	1007.30	1556.55	1564.80	1569.24
0.08	1009.43	1009.06	1008.96	1561.44	1566.96	1571.10
0.10	1009.68	1009.32	1009.18	1564.50	1569.30	1572.90

Table 2 Density (ρ) and velocity (U) of aqueous potassium iodide

Molality m (mol.Kg ⁻¹)	DENSITY $\rho(\text{kg/m}^3)$			VELOCITY U(ms ⁻¹)		
	Temperature (°C)					
	35	40	45	35	40	45
0.00	1007.03	1006.38	1005.12	1542.06	1544.76	1560.70
0.02	1008.26	1008.32	1007.48	1551.15	1556.28	1560.84
0.04	1008.62	1008.50	1008.03	1552.20	1557.66	1561.20
0.06	1008.90	1008.73	1008.36	1554.15	1560.30	1562.85
0.08	1009.58	1009.00	1008.74	1559.10	1562.25	1564.95
0.10	1009.81	1009.61	1009.42	1561.05	1565.04	1566.60

Table 3-4, show the variation of adiabatic compressibility (β) with molal concentration of alkali metal halides. The values of β in all the systems show a decreasing trend. The adiabatic compressibility's values are larger in **potassium bromide** system than that of potassium iodide. This shows that the molecular association is greater in **potassium bromide**. The increasing electrostrictive compression of water around the molecules results in a larger decrease in the compressibility of the solutions.

Tables 3-4, show the values of change in adiabatic compressibility ($\Delta\beta$) and relative change in adiabatic compressibility ($\Delta\beta/\beta^0$) of aqueous potassium iodide and potassium bromide solution at varying temperatures. The negative values of ($\Delta\beta$) increases with increasing molality of the solute in all the systems.

The β , $\Delta\beta$ and ($\Delta\beta/\beta^0$) vary non-linearly with rise in temperature, which are shown in the Tables 3-4, such a behaviour lends further support to the contention of having apparently ideal systems caused by solute-solvent interactions.

The value of apparent molal compressibility (ϕ_k) are all negative over the entire range of molality, which are furnished in the Tables 5-6. No systematic variation between the ϕ_k and the solute over the entire range of composition as well as rise in temperature is observed. The maximum value of ϕ_k is obtained for **potassium bromide** system irrespective of molality and temperature indicates electrostriction and hydrophilic interactions accruing in these systems, thereby indicating solute-solvent interaction. The limiting apparent molal compressibility(ϕ_k^0) and the related constant S_k from the alkali metal halides have been tabulated in Table 7. The limiting apparent molal compressibility(ϕ_k^0) provides information regarding solute-solvent interaction and the related constant S_k that of solute-solute interaction in the solution. From Table 7, one can observe that all ϕ_k^0 values are negative in all the systems. Appreciable negative values of (ϕ_k^0) for all the systems reinforce the view that the existence of solute-solvent interaction in the present systems. From the Table 7, the values are non-linear over the elevation of temperature.

Table 3 Adiabatic compressibility (β), Change in adiabatic compressibility ($\Delta\beta$) and Relative change in adiabatic compressibility ($\Delta\beta/\beta^0$) of aqueous potassium bromide

Molality m (mol.Kg ⁻¹)	Adiabatic Compressibility β ($\times 10^{-10} \text{ m}^2 \text{ N}^{-1}$)			Change in Adiabatic Compressibility $-\Delta\beta(\times 10^{-12} \text{ m}^2 \text{ N}^{-1})$			Relative change in Adiabatic Compressibility $\Delta\beta/\beta^0(\times 10^{-2} \text{ m}^2 \text{ N}^{-1})$		
	Temperature ($^{\circ}\text{C}$)								
	35	40	45	35	40	45	35	40	45
0.00	4.176	4.164	4.084	-	-	-	-	-	-
0.02	4.136	4.094	4.076	3.9827	6.9621	0.7351	0.9537	1.6720	0.1800
0.04	4.102	4.071	4.046	7.4108	9.3207	3.7417	1.7746	2.2384	0.9163
0.06	4.091	4.048	4.031	8.5382	11.6028	5.2049	2.0446	2.7864	1.2746
0.08	4.063	4.036	4.015	11.2742	12.7869	6.8191	2.6998	3.0708	1.6699
0.10	4.046	4.023	4.005	12.9586	14.0968	7.8253	3.1031	3.3854	1.9163

Table 4 Adiabatic compressibility (β), Change in adiabatic compressibility ($\Delta\beta$) and Relative change in adiabatic compressibility ($\Delta\beta/\beta^0$) of aqueous potassium iodide

Molality m (mol.Kg ⁻¹)	Adiabatic Compressibility β ($\times 10^{-10} \text{ m}^2 \text{ N}^{-1}$)			Change in Adiabatic Compressibility $-\Delta\beta(\times 10^{-12} \text{ m}^2 \text{ N}^{-1})$			Relative change in Adiabatic Compressibility $\Delta\beta/\beta^0(\times 10^{-2} \text{ m}^2 \text{ N}^{-1})$		
	Temperature ($^{\circ}\text{C}$)								
	35	40	45	35	40	45	35	40	45
0.00	4.176	4.164	4.084	-	-	-	-	-	-
0.02	4.122	4.095	4.074	5.3844	6.9296	0.9248	1.2894	1.6641	0.2265
0.04	4.115	4.087	4.070	6.0894	7.7269	1.3341	1.4582	1.8556	0.3267
0.06	4.104	4.072	4.060	7.2357	9.2040	2.3284	1.7327	2.2104	0.5702
0.08	4.075	4.061	4.048	10.1130	10.3250	3.5679	2.4217	2.4796	0.8737
0.10	4.064	4.044	4.035	11.2220	12.0164	4.8980	2.6873	2.8858	1.1995

Table 5 Apparent molal compressibility (ϕ_k) and Apparent molal volume (ϕ_v) of aqueous potassium bromide

Molality m (mol.Kg ⁻¹)	Apparent molal compressibility - ϕ_k ($\times 10^{-8} \text{ m}^2 \text{ N}^{-1}$)			Apparent molal Volume - ϕ_v ($\times \text{m}^3 \text{ mol}^{-1}$)		
	Temperature ($^{\circ}\text{C}$)					
	35	40	45	35	40	45
0.02	21.8509	37.8605	7.5194	46.1586	73.0167	93.9023
0.04	19.6706	25.0342	11.3156	27.1516	41.3688	47.8020
0.06	15.5956	21.0669	10.1585	32.4597	41.2859	36.0981
0.08	15.3468	17.3704	10.4787	29.7978	33.0717	47.6390
0.10	14.0627	15.3185	9.4800	26.2072	29.1053	40.2878

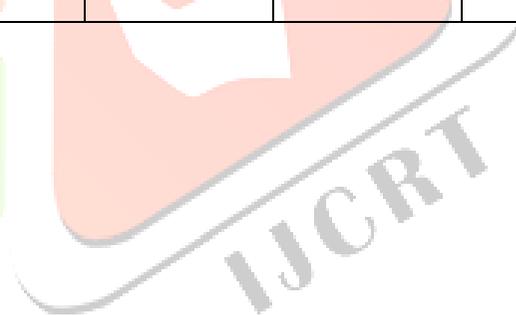
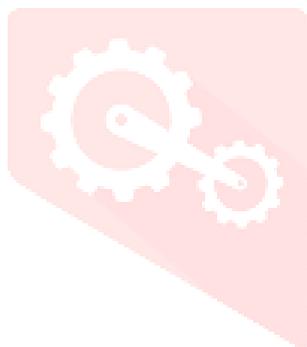


Table 6 Apparent molal compressibility (ϕ_k) and Apparent molal volume (ϕ_v) of aqueous potassium iodide

Molality m (mol.Kg^{-1})	Apparent molal compressibility - ϕ_k ($\times 10^{-8} \text{ m}^2 \text{ N}^{-1}$)			Apparent molal Volume - ϕ_v ($\times \text{m}^3 \text{ mol}^{-1}$)		
	Temperature ($^{\circ}\text{C}$)					
	35	40	45	35	40	45
0.02	29.4818	38.6578	9.4208	61.0665	96.0715	117.2349
0.04	16.8803	21.5088	6.2925	39.4468	52.4003	72.1904
0.06	13.3600	16.9653	6.0812	30.9112	38.8038	53.6602
0.08	13.9715	14.2614	6.3019	31.6272	32.3161	44.8802
0.10	12.3815	13.3543	6.8580	27.5382	31.9012	47.7695

Table 7 Limiting apparent molal compressibility (ϕ_k^0), Limiting apparent molal volume (ϕ_v^0), and the constants S_k and S_v of Alkali metal halides

Alkali metal halides	Limiting apparent molal compressibility ϕ_k^0 ($\times 10^{-8} \text{ m}^2 \text{ N}^{-1}$)			Constant S_k ($\times 10^{-8} \text{ N}^{-1} \text{ m}^{-1} \text{ mol}^{-1}$)			Limiting apparent molal volume ϕ_v^0 ($\times \text{m}^3 \text{ mol}^{-1}$)			Constant S_v ($\text{N}^{-1} \text{ m}^{-1} \text{ mol}^{-1}$)		
	35	40	45	35	40	45	35	40	45	35	40	45
Potassium bromide	-34.66	-46.73	-19.60	72.95	98.36	41.25	-64.71	-87.14	-106.29	136.47	183.77	224.16
Potassium iodide	-34.48	-41.96	-13.99	72.57	88.32	29.45	-76.24	-100.60	-87.40	160.78	212.15	184.32

The value of S_k exhibits positive values and also it is non-linear with increase of temperature in all the systems. This behaviour indicates the existence of ion-ion/solute-solute interaction with increase in temperature. It is well known that solutes causing electrostriction led to decrease in compressibility of the solution, which is reflected by the negative values of (ϕ_k) of the alkali metal halides.

The perusal of Tables 5-6, represent the value of apparent molal volume (ϕ_v) which are all negative over the entire range of molality. No systematic variation has been found in (ϕ_v) values with increase of molality of the solute as well as temperature. The maximum value of apparent molal volume (ϕ_v) obtained for **potassium bromide**. These observations clearly suggest that the negative values of (ϕ_v) in all the systems indicate the presence of solute-solvent interaction. The negative values of (ϕ_v) indicates electrostrictive solvation of ions [Dhanalakshmi and Vasantharani (1999)]. From Tables 5-6, the value of (ϕ_v) in all the systems are negative and vary irregularly. This enhances/reduces the electrostriction of water molecules. Thus, it can be concluded that the strong molecular association is found in **potassium bromide** system than potassium iodide and hence **potassium bromide** is acting as effective structure- maker.

It is clear from the Table 7, the values of the limiting apparent volume (ϕ_v^0) in all the systems and it is non-linear with rise in temperature. This enhances the electrostriction of water molecules. The negative value of (ϕ_v^0) indicates solute-solvent interaction present in these systems. The maximum value of (ϕ_v^0) is observed for **potassium bromide**.

It is evident from Table 7, that the constant S_v exhibits positive values in all the systems suggesting the presence of ion-ion interactions. Usually the negative values of S_v indicate weak ion-ion interaction whereas the positive values of S_v predict strong solute-solvent interactions in the systems, which clearly confirm that potassium bromide is acting as an effective structure-maker. From the magnitudes of all

the relevant parameters, it can be concluded that the molecular interaction between the alkali metal halides are of the order **Potassium bromide (KBr) > Potassium iodide (KI)**.

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