ISSN 2348-1218 (print)
International Journal of Interdisciplinary Research and Innovations ISSN 2348-1226 (online)
Vol. 6, Issue 3, pp: (272-278), Month: July - September 2018, Available at: www.researchpublish.com

Comparative Study of Certain Acoustic and Thermodynamic Parameter of Aqueous Solution of NaCl and KCl

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Abstract: **Density, viscosity and velocity were measured for aqueous NaCl, aqueous KCl and aqueous NaCl + KCl solution at different concentration and at temperatures 288K, 298K, 308K. Surface tension, Gibb's function, internal pressure and free volume for these solutions were calculated at different temperatures and were compared to know the strength of molecular interaction.**

Keywords: **Ultrasonic velocity, Surface tension, Gibb's free energy, binding force between molecules, ionic hydration.**

I. INTRODUCTION

Ultrasonic velocity of sound waves in a medium is essentially related to the binding force between the molecules. Ultrasonic techniques have been effectively employed to understand the nature of molecular interaction in pure liquids [1], liquid mixtures [2],[3],[4],[5],[6],[7] and ionic interaction in electrolytic solutions [6],[7],[8],[9],[10],[11],[12]. aqueous

In the present paper we have compared parameters like density, viscosity, velocity, surface tension, Gibb's function, internal pressure, free volume for aqueous solution of NaCl, aqueous solution of KCl and aqueous solution of NaCl + KCl for different ratios of NaCl and KCl.

II. EXPERIMENTAL DETAILS

Fresh distilled water has been used as solvent for preparing all the three solutions of different concentrations [13]. The density, viscosity, and ultrasonic velocity were measured as a function of concentration of NaCl, KCl and aqueous solution of NaCl + KCl for different ratios of Na and K at temperatures 288 K, 298 K and 308 K. Ultrasonic velocity measurements were made using an ultrasonic interferometer (Model M-84, supplied by M/S Mittal Enterprises, New Delhi) with the accuracy of $\pm 0.1 m\cdot s^{-1}$. An electronically operated digital constant temperature bath (Model SSI-03 Spl., supplied by M/S Mittal Enterprises, New Delhi), operating in the temperature range of −10°C to 85°C with an accuracy of ±0.1°C has been used to circulate water through the outer jacket of the double-walled measuring cell containing the experimental liquid.

The densities of the mixture were measured using a 10 ml specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01\ kg\cdot m^{-3}$.

An Oswald viscometer (10 ml) with an accuracy of $\pm 0.001\ Ns\cdot m^{-2}$ was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of ±0.1s.

III. THEORY

1. **Gibb's free energy:** The Gibb's free energy is calculated by using the relation

$\Delta G = kT.Ln(kT\tau/h)$ --------- (7)

Where, 'τ' is the viscous relaxation time, 'T' is the absolute temperature, 'k' is the Boltzmann's constant and 'h' is the Planck's constant.

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2. **Internal Pressure:** The internal pressure is the cohesive force, which is a resultant o force of attraction and force of repulsion between the molecules. It is calculated by using the relation,

$\pi_i = b.R.T\ (k.\eta/U)^{1/2}\ (\rho^{2/3}/M^{7/6})$ ---------(5)

3. **Acoustic impedance:** Acoustic impedance (Z): The specific acoustic impedance is given by,

$Z = U.\rho$ ------------ (6)

Where 'U' is the velocity and 'ρ' is the density of the mixture.

4. **Free Volume:** Free volume can be calculated by using the relation

$$V = \left(\frac{M_{EFF}.U}{K.\eta} \right)^{\frac{3}{2}} \text{ ……… (4)}$$

Where 'M_{eff}' is the effective mass of the mixture, 'K' is a dimensionless constant independent of temperature and liquid. Its value is 4.281 x 10^9 and 'η' is the viscosity.

5. **Surface tension:** Surface tension can be calculated by using the relation

$S = 6.3 \times 10^{-4}.\ \rho.\ U^{3/2}$ ………. (3)

IV. RESULT AND ANALYSIS

The experimental values of density, viscosity and velocity of aqueous solution of NaCl, aqueous solution of KCl along with aqueous solution of NaCl and KCl taken together at different temperatures are represented in tables-1 (A), 1(B) and 1(C).

Table: I (A)-Experimental values of density, viscosity and ultrasonic velocity of NaCl+H_2o

Concentration of NaCl by %	Density (ρ) Kg.m^{-3}			Viscosity (η) (10^{-3} N.s.m^{-2})			Velocity (U) m.s^{-2}		
	288 K	298 K	308 K	288K	298K	308K	288 K	298 K	308 K
5 %	1044.1	1042.3	1036.2	1.38	1.053	0.846	1535.36	1560.36	1580.25
10 %	1078.2	1075.4	1071.4	1.44	1.097	0.877	1563.75	1590.30	1606.05
15 %	1120.1	1116.4	1111.1	1.52	1.139	0.899	1609.60	1624.50	1641.15
20 %	1163.4	1158.3	1153.2	1.58	1.18	0.93	1653.10	1665.12	1672.80
25 %	1200.3	1195.1	1190.1	1.64	1.25	0.98	1685.10	1695.80	1702.82

Table: I (B)-Experimental values of density, viscosity and ultrasonic velocity of KCl+H_2o

Concentration of KCl by %	Density (ρ) Kg.m^{-3}			Viscosity (η) (10^{-3} N.s.m^{-2})			Velocity (U) m.s^{-2}		
	288 K	298 K	308 K	288K	298K	308K	288 K	298 K	308 K
5 %	1007.6	1004.2	1000.5	1.41.2	1.074	0.748	1501.2	1506.2	1510.1
10 %	1010.5	1007.1	1003.8	1.443	1.098	0.7722	1513.1	1518.4	1523.6
15 %	1014.9	1011.5	1007.2	1.471	1.117	0.7858	1516.5	1521.8	1527.9
20 %	1018.8	1015.1	1011	1.501	1.142	0.7989	1521.8	1527.4	1532.1
25 %	1022.4	1019.2	1014.1	1.528	1.172	0.8129	1525.4	1530.4	1535.4

Table: I (C)-Experimental values of density, viscosity and ultrasonic velocity of NaCl+KCl+H_2o.

Na:K	Density (ρ) Kg.m^{-3}			Viscosity (η) (10^{-3} N.s.m^{-2})			Velocity (U) m.s^{-2}		
	288 K	298 K	308 K	288K	298K	308K	288 K	298 K	308 K
1:2	1035.25	1030.27	1027.68	0.895	0.723	0.692	1549.50	1568.30	1572.80
2:1	1039.91	1033.98	1030.47	0.915	0.736	0.705	1560.90	1577.40	1580.80
3:1	1048.30	1043.27	1040.68	0.955	0.762	0.722	1583.67	1593.00	1597.00
4:1	1065.07	1059.14	1055.53	1.011	0.801	0.746	1609.34	1616.00	1619.90
7:1	1102.34	1096.23	1093.25	1.114	0.890	0.845	1654.90	1665.90	1668.10

Temperature remaining constant, density, viscosity and velocity increase with increasing molar concentration of the salts. The same change is also observed where the ratio of sodium to potassium increases in the aqueous solution of NaCl + KCl. The above facts suggest a fairly strong interaction between solute and solvent molecules. However, concentration remaining constant, density and viscosity decreases, as temperature increases. This is because the interaction between solute and solvent molecules decrease due to thermal energy of the molecules. The compressibility decreases due to structural changes of the molecules leading to an increase in ultrasonic velocity. This happens in all the three above cases.

The Gibb's free energy (ΔG) for NaCl solution, KCl solution and NaCl + KCl solution are indicated in table-II(A), II(B), II(C). Increasing value of ΔG suggests closer approach of molecules indicating appreciable interaction between solute and solvent molecules and vice versa. Temperature remaining constant, ΔG increases slowly with increase in concentration of KCl solution whereas for NaCl solution it decreases slowly. Sodium ions are more solvated than potassium ions which results in low adiabatic compressibility of NaCl solution compared to KCl solution. As concentration of sodium ions increases, the adiabatic compressibility decreases, hence ΔG decreases slowly. Concentration remaining constant, ΔG decreases rapidly as temperature increases for KCl solution, where as it increases very slowly for NaCl solution. Since potassium ions are less hydrated than sodium ions, they move faster, increasing the distance between them. Hence ΔG decreases rapidly as temperature increases. Sodium ions being more hydrated, move much slower hence ΔG should decreases slowly, however it increases slowly. This may be due to the fact that strong electrostatic force between Na^+ ion and negative side of water molecule at high temperature prevents the motion of Na^+ ions thus reducing the distance between them.

Table: II (A)-Calculated values of ΔG, π_i and Z of NaCl+H_2o solution

Concentration of KCl by %	Gibb' free energy			Internal Pressure			Acoustic impedance		
	288 K	298 K	308 K	288K	298K	308K	288 K	298 K	308 K
5 %	0.597	0.508	0.437	11591.4	10380.7	9518.8	1.603	1.626	1.637
10 %	0.586	0.496	0.425	5343.2	4776.8	4381.7	1.686	1.710	1.721
15 %	0.570	0.479	0.401	3459.1	3077.3	2802.4	1.803	1.814	1.823
20 %	0.549	0.458	0.384	2551.0	2266.2	2068.5	1.923	1.929	1.929
25 %	0.536	0.454	0.378	2025.6	1818.7	1656.4	2.023	2.027	2.027

Table: II (B)-Calculated values of ΔG, π_i and Z of KCl+H_2o solution

Concentration of KCl by %	Gibb' free energy			Internal Pressure			Acoustic impedance		
	288 K	298 K	308 K	288K	298K	308K	288 K	298 K	308 K
5 %	0.638	0.560	0.439	3172.28	2851.54	2450.38	1.513	1.513	1.511
10 %	0.639	0.562	0.443	3073.42	2762.99	2385.22	1.529	1.529	1.529
15 %	0.643	0.565	0.446	2992.17	2687.21	2317.08	1.539	1.539	1.539
20 %	0.647	0.570	0.449	2917.65	2622.09	2255.86	1.550	1.550	1.549
25 %	0.651	0.577	0.454	2847.97	2571.24	2202.41	1.560	1.560	1.557

Table: II (C)-Calculated values of ΔG, π_i and Z of NaCl+KCl+H_2o solution.

Na:K	Gibb' free energy			Internal Pressure			Acoustic impedance		
	288 K	298 K	308 K	288K	298K	308K	288 K	298 K	308 K
1:2	0.4494	0.3796	0.3647	2665.5	2453.3	2408.2	1.604	1.616	1.616
2:1	0.4506	0.3807	0.3671	2632.5	2418.2	2374.1	1.623	1.631	1.629
3:1	0.4530	0.3833	0.3644	2645.0	2427.0	2370.9	1.660	1.662	1.662
4:1	0.4567	0.3859	0.3601	2689.4	2459.9	2381.1	1.714	1.712	1.710
7:1	0.4595	0.3902	0.3733	2733.8	2507.9	2453.5	1.824	1.826	1.824

There is slight deviation when one takes NaCl and KCl together with different ratios of NaCl and KCl. Temperature remaining constant ΔGincreases slowly as NaCl: KCl ratio increases. ΔGbecomes a minimum for the ratio NaCl: KCl = 4:1 in the temperature range 310 K~313 K, which is approximately the normal human body temperature.

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Minimum value of ΔG indicates a good flow of the mixture. For any particular ratio, ΔG decreases rapidly as temperature increases. Here although sodium proportion is more compared to potassium, but as temperature increases due to the high mobility of potassium ions ΔG decreases rapidly.

Table: III (A)-Calculated values of V_f, and S of $NaCl+H_2o$ solution

Concentration of NaCl by %	Free volume			Surface tension/$N.m^{-1}$		
	288 K	298 K	308 K	288K	298K	308K
5 %	0.0010	0.0016	0.0023	39573	40473	41008
10 %	0.0029	0.0044	0.0063	42004	42966	43444
15 %	0.0051	0.0079	0.0114	45570	46051	46539
20 %	0.0076	0.0120	0.0172	49258	49577	49706
25 %	0.0104	0.0158	0.0229	52744	52798	52683

Table: III (B)-Calculated values of V_f, and S of $KCl+H_2o$ solution

Concentration of KCl by %	Free volume			Surface tension/$N.m^{-1}$		
	288 K	298 K	308 K	288K	298K	308K
5 %	0.100	0.152	0.262	36922	36982	36988
10 %	0.103	0.156	0.266	37470	37540	37609
15 %	0.106	0.161	0.274	37760	37831	37896
20 %	0.108	0.164	0.281	38104	38175	38196
25 %	0.110	0.165	0.287	38374	38442	38487

Table: III (C)-Calculated values of V_f, and S of $NaCl+KCl+H_2o$ solution.

Na:K	Free volume			Surface tension/$N.m^{-1}$		
	288 K	298 K	308 K	288K	298K	308K
1:2	0.208	0.28	0.30	39781	40312	40380
2:1	0.201	0.278	0.297	40402	40810	40803
3:1	0.198	0.270	0.291	41622	41789	41842
4:1	0.190	0.265	0.285	43320	43347	43355
7:1	0.185	0.252	0.274	46753	46959	46924

The values of internal pressure are given in table-IV(A), IV(B), IV(C). Internal pressure decreases in all the cases as temperature increases which is obvious as the cohesion force decreases due to the increase in thermal energy, whereas internal pressure increases when concentration increase. However, for the ratio NaCl: KCl = 3:1 and about body temperature ~ 310 K the internal pressure becomes a minimum which indicates minimum cohesive force which is also observed while studying ΔG.

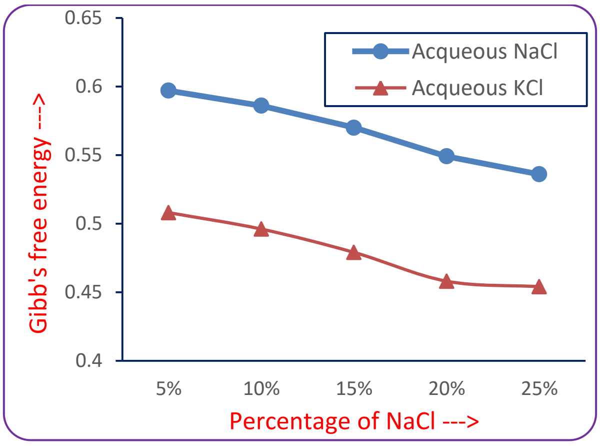

Fig 1: Variation of Gibb's free energy with % of NaCl or KCl

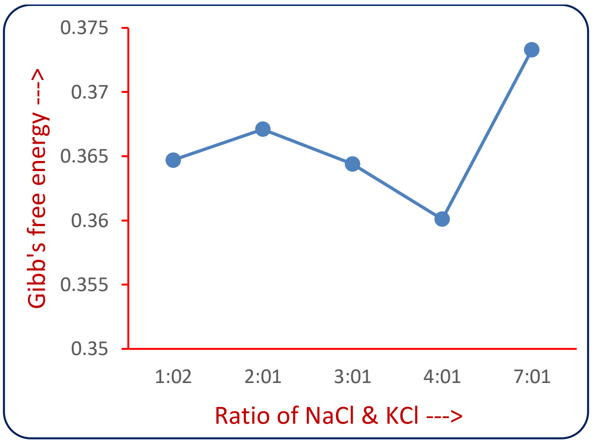

Fig 2: Variation of Gibb's free energy with ratio of NaCl & KCl

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The calculated values of acoustic impedance(Z) is represented in table II(A), II(B), II(C). Z is the product of ultrasonic velocity and the density of the given solution. For KCl solution as concentration increases, Z increases whereas for a particular concentration, when temperature increases, Z decreases. Decrease in acoustic impedance indicates weak interaction and vice versa. For NaCl solution, temperature remaining constant, when concentration increases, Z increases. However, when temperature increases, Z increases slowly. For the NaCl + KCl solution, Z increases as the ratio NaCl: KCl increases but remains practically constant when temperature increases for a particular ratio of sodium to potassium.

Free volume for different solutions have been represented in table-III(A), III(B), III(C). Free volume is the average volume in which the centre of a molecule can move due to the repulsion of the surrounding molecules. Effective free volume sometimes changes due to the transmission of collision effect through molecules. This is the reason why free volume increases sharply as temperature increases in all the three solutions whereas it increases slowly when concentration increases in case of KCl solution and NaCl solution. However free volume remains practically constant when ratio of NaCl: KCl increases initially but decreases finally when the ratio become too large. For larger ratios number of sodium ions increase. As electrostatic force between these ions and the water molecules becomes more hence the free volume decreases.

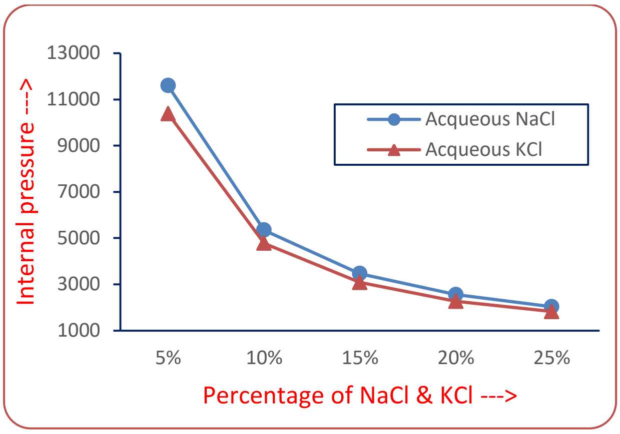

Fig 3: Variation of internal pressure with % of NaCl or KCl

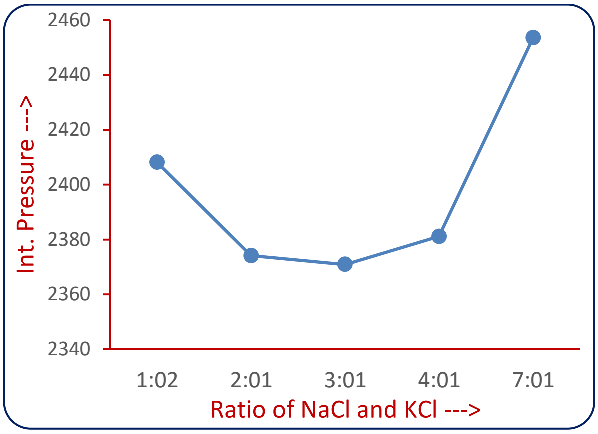

Fig 4: Variation of internal pressure with ratio of NaCl & KCl

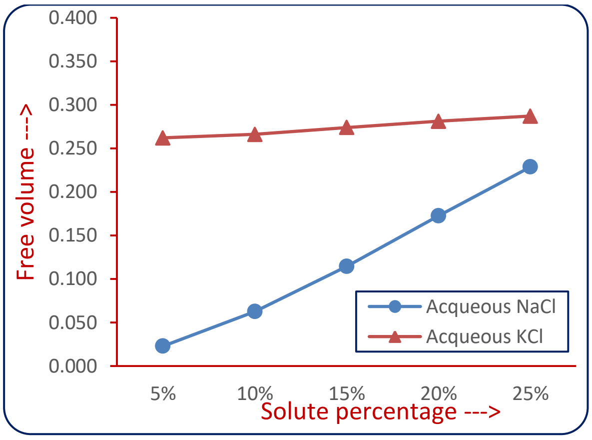

Fig 5: Variation of free volume with % of NaCl or KCl

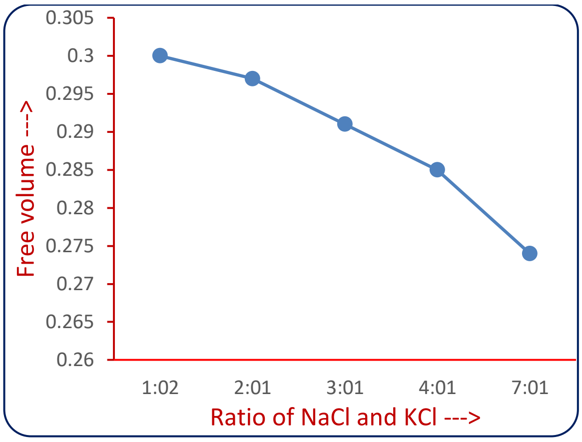

Fig 6: Variation of free volume with ratio of NaCl & KCl

Table III(A), III(B), III(C) represent the calculated values of surface tension for three solutions. Surface tension increases as concentration of KCl solution or NaCl solution increases, indicating increase in molecular association which causes strong surface films. As temperature increases, this attraction should decrease and hence surface tension should decrease. However, the liquid being ionic, the change is slow because of electrostatic interaction between the sodium, potassium ions and the water molecules which are attached to the ions. Surface tension increases as the NaCl:KCl ratio increases indicating increase in molecular association. This is because sodium ions are more hydrated and are less mobile. Surface tension should decrease as temperature increases for a particular ratio. However, it increases slowly. This may be due to the same reason as above. Sodium ions being more hydrated move slowly and further are bound by electrostatic forces.

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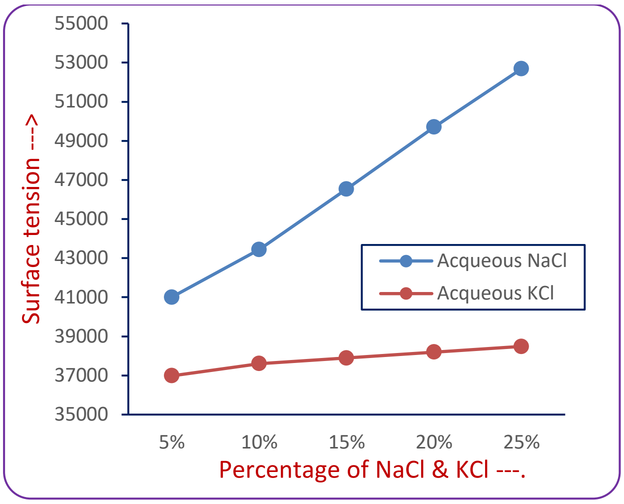

Fig 7: Variation of surface tension with % of NaCl or KCl

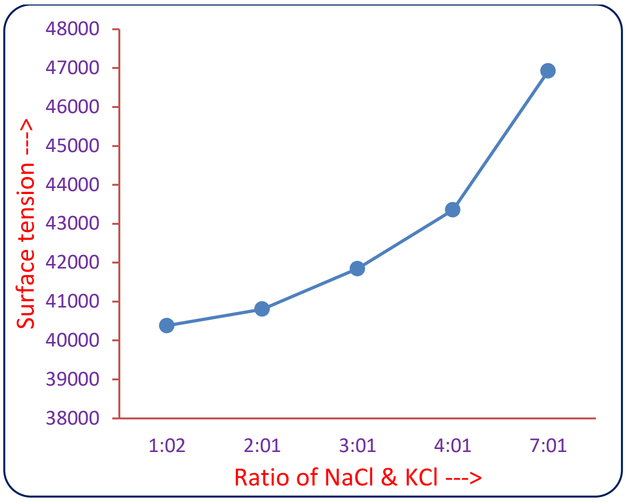

Fig 8: Variation of surface tension with ratio of NaCl & KCl

V. CONCLUSION

The computed acoustical parameters and their values point to the presence of specific molecular interaction in the aqueous solutions of NaCl, KCl and NaCl + KCl mixture. The increase in the ultrasonic velocity in any solution generally indicates a greater association of molecules in them. The greater association may be due to phenomena like hydrogen bonding or ionic hydration of the solutes. In the present case the increased cohesion between the molecules is due to the ionic hydration. The hydrated water molecule in all the solutions are held strongly by electrostatic forces.

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