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Ultrasonic Studies of Some Alkali Metal Chlorides in Aqueous Citric Acid at Different Temperatures

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Abstract: The density (ρ) and sound velocity (u) has been measured for LiCl, NaCl and KCl in 0.01 mol kg^{-1} aqueous citric acid solution at four different temperatures T =((303.15, 308.15, 313.15, and 318.15) K).These parameters were then used to obtain different acoustic functions such as adiabatic compressibility (β), intermolecular free length (L_f),specific acousticimpedance (Z), solvation number(S_N) and molar compressibility(W). The ion- solvent and ion-ion interactions in the system have been discussed using these parameters. The effect of LiCl, NaCl and KCl on these interactions as well as on the solvent structure has also been discussed.

Key words: Ultrasonic velocity, adiabatic compressibility, Alkali chlorides and Citric acid.

INTRODUCTION

Acoustic parameters can be used to study the physiochemical behavior and molecular interactions of various liquid mixtures. Ion-ion and ion-solvent interactions play an important role [1-2] in the solution chemistry. Number of proteins, carbohydrates and amino acids gives such type of interactions [4-8]. Citric acid is a weak organic acid. Citric acid is one of a series of compounds involved in the physiological oxidation of fats, proteins, and carbohydrates to carbon dioxide and water.Citric acid stimulates the liver to produce more bile, which is a primary aid in food digestion. Lithium, sodium and potassium are metalswhose ions are present in some amount in biological system. Ions of Li^+, Na^+, K^+ and Cl^- are also found in body in some extent. Lithium ion is used as a mood stabilizing drug in the form of lithium carbonate sold under name carbolith and attained 0.06 to 1.2mmol Li+/liter in plasma. Whereas, sodium is critical for generation of electrical signals in the body, especially in the brain, nervous system and muscles.

Potassium ions control nervous system and heartbeats. Irregular levels of chloride ions leads todiarrhea, certain kidney diseases, and sometimes in over activity of the parathyroid glands. The interactions of Li^+, Na^+, and K^+ ions in citric acid + water have been investigated in this work. In the presentstudy the solute-solute and solute-solvent interactions of chlorides of lithium, sodium and potassium in aqueous (0.01m) citric acid at 303.15, 308.15, 313.15 and 318.15K temperatures were carried out by measuring their densities and sound velocities. These parameters were used to calculate acoustic parameters such as adiabatic compressibility (β),intermolecular free length (L_f), specific acoustic impedance (Z), molar compressibility(W) and solvation number (S_N).

EXPERIMENTAL SECTION

Materials: Lithium chloride, sodium chloride and potassium chloride of AR grade with mass purity> 98% were driedunder vacuumbefore use. Citric acid with mass purity>99% was used and 0.01m citric acid used as a solvent. Specific conductance of distilled water used for preparationof the solutions were taken in the range of 0.1×10^{-6} to 1.0×10^{-6} Ω^{-1} cm^{-1}.Seven concentrations between the range (0.01m to 0.12m) were used for LiCl, NaCl and KCl.

Instruments used: Analytical balance (precision $1x10^{-5}$ g) was used for weighing. Seven concentrations (0.01, 0.02, 0.04, 0.06, 0.08, 0.10 and 0.12m) were prepared for LiCl, NaCl and KCl. Capillary type viscometer is used for determination of the viscosity [9]. Thermostat is used to maintain the temperature. The densities and sound velocitieswere measured with the helpof Density and Sound Analyzer (DSA 5000) Anton Paar, GmbH, Garz, Austria. Reproducibility of sound velocity and density is ± $0.2ms^{-1}$ and ± 2 x 10^{-6} g cm^{-3}.These studies were carried out at fourdifferent temperatures T = (303.15, 308.15, 313.15 and 318.15) K with an accuracy of ± 0.05.

RESULT AND DISCUSSION

Acoustic parameters like adiabatic compressibility (β), ultrasonic velocity (U),inter- molecular free length (L_f), Solvation Number (S_N), specific acoustic impedance (Z) and molar compressibility (W) for LiCl, NaCl and KCl in 0.01m citric at different temperatures are shown in Table 1.

Newton- Laplace equation (1) was used to obtain the adiabatic compressibility (β) [10],defined as$\beta = (-1/V)(\partial V/\partial P)_S$:$\beta = \left(-\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_S$

$\beta = 1/U^2\rho$ (1)

Where ρ is the density and U is the ultrasonic velocity of solutions. For every system there is decrease in the limiting adiabatic compressibility with the increase in the concentration of the solution showing presence of ion-solvent interactions. Almost linear decrease in adiabatic compressibility with the increase in concentration suggested that interaction strength increases with the concentration [11-12]. U increases steadily with increase in concentration and temperature, which suggests that ion-solvent interaction increases with increase in concentration and temperature. Ultrasonic velocity has increased with increase in citric acid content of the solvent indicating thereby stronger ion-solvent interactions. Also there is decrease in adiabatic compressibility with increase in temperature **(Fig.1, Fig.2 and Fig.3).**

Adiabatic compressibility (β) was further used to obtain intermolecular free length (L_f) eqn. 2 [13]:

$L_f = K\beta^{1/2}$ ... (2)

Where K is a constant depend upon temperature (= (93.875 + 0.375T) × 10-8)[14]. L_f decreases with increase in concentration of electrolyte and increases with increase in temperature [15-17] which suggested increase in the strength of ion-solvent interactions **(Fig.4, Fig.5 and Fig.6).**

Specific acoustic impedance (Z) and molar compressibility (W) were also obtained for the studied system using eqns. [18-19]3 and 4:

$Z = U\rho$ ... (3)

$W = (M/\rho)\ \beta^{-1/7}$ ... (4)

Where M represents the apparent molecular weight of the solution and was calculated as:

$M = M_1W_1 + M_2W_2$

where W_1 and $W_2$are weight fractions and M_1 and M_2 are molecular weights of solvent and solute respectively. The acoustic impedance (Z) is the product of ultrasonic velocity and density of the solution. The value of acoustic impedance increases with increase in the concentration of solute as well as with increase in temperature suggesting the presence of ion-solvent interaction [20] **(Fig.7, Fig.8 and Fig.9)**. Also the value of W increases with the increase in the concentration of the solute indicating the ion- solvent interactions in the system.

Another parameter studied was solvation number (S_N), obtained by eqn. 5 [21-22]:

$S_N = (n_1/n_2).(1-\beta/\beta_o)$ ... (5)

Where n_1 and n_2 are the numbers of moles of the solvent and the solute and β and β0are compressibility coefficients of the solution and the pure solvent. Considerably high solvation numbers **(Table 1)** obtained especially at low solute concentrations and at low temperatures indicate either strong electrostriction around the chloride ions and/or cationelectrostrictive interaction exceeding the first solvation shell [23].

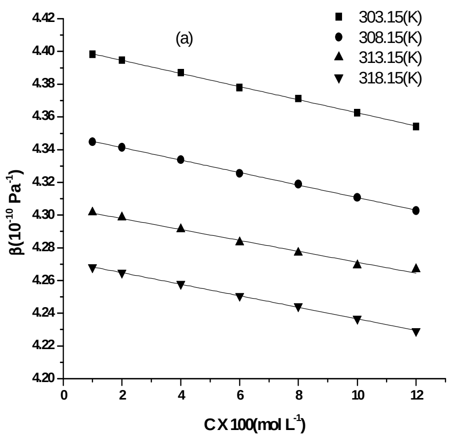
Table- 1: Adiabatic compressibility (β), intermolecular free length (L_f), specific acoustic impedance (Z), solvation number (S_N) and molar compressibility (W) for LiCl, NaCl and KCl in 0.01 m aqueous citric acid.

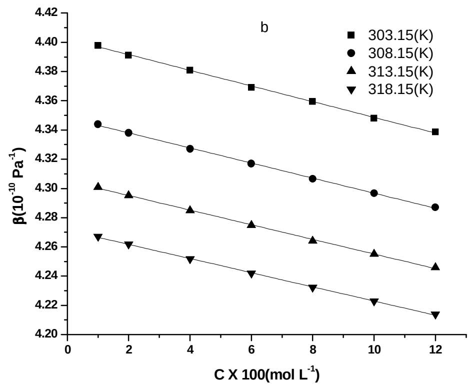
C X 10^2 (mol lit^{-1})	**ρ (g cm^{-3})**	**U (m s^{-1})**	**L_f (10^{-11}m)**	**β ($10^{-10}Pa^{-1}$)**	**Z X 10^6 (kg $m^{-2}s^{-1}$)**	**S_N**	**W X 10^4 ($m^3mol^{-1}Pa^{1/7}$)**
LiCl in 0.01m aqueous citric acid							
T= 303.15K		**β_o= 4.40291**		**ρ_o= 0.996425g cm^{-3}**		**U_o=1509.76m s^{-1}**	
0.996193	0.996615	1510.43	4.3528	4.3982	1.5053	5.9760	3.9290
1.991905	0.996797	1510.91	4.3510	4.3946	1.5061	5.2532	3.9297
3.981838	0.997147	1511.93	4.3473	4.3871	1.5076	4.9782	3.9312
5.969721	0.997484	1513.25	4.3428	4.3780	1.5094	5.2353	3.9329
7.955501	0.99781	1514.17	4.3395	4.3712	1.5109	4.9889	3.9344
9.939118	0.998125	1515.43	4.3352	4.3626	1.5126	5.0796	3.9362

11.92051	0.998429	1516.68	4.3310	4.3541	1.5143	5.1268	3.9380
T= 308.15K		**β_o= 4.34897**		**ρ_o= 0.994778g cm^{-3}**		**U_o=1520.35m s^{-1}**	
0.994539	0.994961	1520.94	4.3654	4.3448	1.5133	5.3187	3.9424
1.988586	0.995136	1521.41	4.3637	4.3414	1.5140	4.8596	3.9431
3.975167	0.995477	1522.46	4.3599	4.3339	1.5156	4.8110	3.9446
5.959678	0.995806	1523.69	4.3557	4.3255	1.5173	4.9979	3.9464
7.942076	0.996126	1524.59	4.3524	4.3190	1.5187	4.7837	3.9479
9.922329	0.996439	1525.79	4.3483	4.3108	1.5204	4.8655	3.9496
11.90035	0.99674	1526.99	4.3442	4.3027	1.5220	4.9124	3.9514
T= 313.15K		**β_o= 4.30569**		**ρ_o= 0.992895g cm^{-3}**		**U_o=1529.42m s^{-1}**	
0.992652	0.993073	1530.00	4.3826	4.3017	1.5194	5.1956	3.9555
1.984807	0.993245	1530.42	4.3810	4.2986	1.5201	4.5973	3.9562
3.967591	0.99358	1531.46	4.3773	4.2913	1.5216	4.6443	3.9578
5.948282	0.993902	1532.61	4.3733	4.2834	1.5233	4.7758	3.9594
7.92686	0.994218	1533.52	4.3700	4.2770	1.5247	4.6191	3.9610
9.90327	0.994525	1534.67	4.3661	4.2693	1.5263	4.6905	3.9627
11.8775	0.994827	1534.84	4.3649	4.2670	1.5269	4.1495	3.9637
T= 318.15K		**β_o= 4.2719**		**ρ_o= 0.990954g cm^{-3}**		**U_o=1536.96m s^{-1}**	
0.990709	0.991129	1537.53	4.4041	4.2680	1.5239	5.0881	3.9677
1.980917	0.991298	1537.97	4.4025	4.2648	1.5246	4.6019	3.9684
3.959801	0.991629	1538.96	4.3989	4.2579	1.5261	4.5424	3.9700
5.936589	0.991948	1540.03	4.3952	4.2506	1.5276	4.6041	3.9716
7.911251	0.99226	1540.96	4.3918	4.2442	1.5290	4.5019	3.9731
9.883763	0.992566	1542.07	4.3880	4.2367	1.5306	4.5640	3.9748
11.85412	0.992868	1543.22	4.3840	4.2291	1.5322	4.6256	3.9766
NaCl in 0.01m aqueous citric acid							
T= 303.15K		**β_o= 4.40291**		**ρ_o= 0.996425g cm^{-3}**		**U_o=1509.76m s^{-1}**	
0.9963	0.996890	1510.29	4.3526	4.3978	1.5056	6.4746	3.9286
1.9923	0.997337	1511.06	4.3494	4.3913	1.5070	7.3008	3.9292
3.9835	0.998201	1512.20	4.3443	4.3809	1.5095	6.9293	3.9303
5.9732	0.999032	1513.62	4.3384	4.3690	1.5122	7.1081	3.9318
7.9615	0.999839	1514.66	4.3337	4.3595	1.5144	6.8299	3.9330
9.9481	1.000624	1516.03	4.3281	4.3482	1.5170	6.8862	3.9345
11.9330	1.001393	1517.11	4.3233	4.3387	1.5192	6.7381	3.9359
T= 308.15K		**β_o= 4.34897**		**ρ_o= 0.994778g cm^{-3}**		**U_o=1520.35m s^{-1}**	
0.9947	0.995231	1520.89	4.3650	4.3439	1.5136	6.4623	3.9421

1.9890	0.995669	1521.57	4.3621	4.3381	1.5150	6.9221	3.9427
3.9768	0.996516	1522.85	4.3565	4.3271	1.5175	6.9587	3.9439
5.9631	0.997331	1524.01	4.3515	4.3170	1.5199	6.7890	3.9452
7.9478	0.998125	1525.25	4.3465	4.3066	1.5224	6.7567	3.9466
9.9309	0.998898	1526.42	4.3412	4.2967	1.5247	6.6713	3.9480
11.9123	0.999656	1527.54	4.3363	4.2871	1.5270	6.5744	3.9494
T= 313.15K		**β_o= 4.3057**		**ρ_o= 0.992895g cm^{-3}**		**U_o=1529.42m s^{-1}**	
0.9928	0.993339	1529.95	4.3821	4.3008	1.5198	6.3161	3.9552
1.9852	0.993768	1530.59	4.3794	4.2953	1.5211	6.6691	3.9558
3.9691	0.994601	1531.82	4.3740	4.2849	1.5235	6.7117	3.9571
5.9516	0.995408	1532.98	4.3689	4.2749	1.5259	6.6107	3.9584
7.9325	0.996195	1534.16	4.3638	4.2640	1.5283	6.5593	3.9597
9.9117	0.99696	1535.32	4.3589	4.2552	1.5307	6.4982	3.9612
11.8891	0.997709	1536.42	4.3541	4.2460	1.5329	6.4112	3.9626
T= 318.15K		**β_o= 4.2719**		**ρ_o= 0.990954g cm^{-3}**		**U_o=1536.96m s^{-1}**	
0.9908	0.991391	1537.50	4.4036	4.2670	1.5243	6.3364	3.9675
1.9813	0.991814	1538.12	4.4009	4.2618	1.5255	6.5818	3.9681
3.9613	0.992638	1539.29	4.3958	4.2518	1.5280	6.5392	3.9693
5.9398	0.993438	1540.46	4.3906	4.2419	1.5304	6.4961	3.9706
7.9167	0.994215	1541.60	4.3857	4.2323	1.5327	6.4269	3.9720
9.8920	0.994981	1542.74	4.3808	4.2228	1.5350	6.3757	3.9734
11.8656	0.995731	1543.81	4.3761	4.2138	1.5372	6.2895	3.9748
KCl in 0.01m aqueous citric acid							
T= 303.15K		[illegible]		**ρ_o= 0.996425g cm^{-3}**		**U_o=1509.76m s^{-1}**	
0.996181	0.996924	1510.27	4.3526	4.3977	1.5056	6.5190	3.9291
1.991859	0.997414	1510.78	4.3501	4.3926	1.5069	6.4901	3.9300
3.98163	0.998376	1512.03	4.3444	4.3811	1.5096	6.8612	3.9322
5.96922	0.99932	1513.06	4.3394	4.3710	1.5120	6.6942	3.9342
7.954567	1.000251	1514.10	4.3344	4.3610	1.5145	6.6052	3.9362
9.937605	1.001169	1515.15	4.3294	4.3509	1.5169	6.5486	3.9383
11.91822	1.00207	1516.19	4.3245	4.3410	1.5193	6.4940	3.9404
T= 308.15K		**β_o= 4.34897**		**ρ_o= 0.994778g cm^{-3}**		**U_o=1520.35m s^{-1}**	
0.994528	0.995269	1520.89	4.3649	4.3437	1.5137	6.6740	3.9426
1.988539	0.995752	1521.39	4.3624	4.3388	1.5149	6.4985	3.9435
3.974959	0.996703	1522.52	4.3571	4.3282	1.5175	6.6200	3.9456
5.959168	0.997637	1523.50	4.3522	4.3186	1.5199	6.4567	3.9476

7.941151	0.998564	1524.53	4.3473	4.3088	1.5223	6.4106	3.9496
9.920761	0.999472	1525.52	4.3425	4.2993	1.5247	6.3396	3.9517
11.898	1.00037	1526.52	4.3377	4.2898	1.5271	6.2917	3.9538
T= 313.15K		**β_o= 4.30569**		**ρ_o= 0.992895g cm^{-3}**		**U_o=1529.42m s^{-1}**	
0.992641	0.993381	1529.95	4.3820	4.3006	1.5198	6.5520	3.9557
1.984759	0.993859	1530.43	4.3796	4.2958	1.5210	6.3455	3.9567
3.967373	0.994801	1531.53	4.3744	4.2856	1.5236	6.4671	3.9587
5.94777	0.995729	1532.48	4.3697	4.2763	1.5259	6.3083	3.9607
7.92589	0.996645	1533.46	4.3649	4.2669	1.5283	6.2429	3.9628
9.901683	0.99755	1534.44	4.3601	4.2576	1.5307	6.1945	3.9649
11.87512	0.998446	1535.38	4.3555	4.2486	1.5330	6.1310	3.9669
T= 318.15K		**β_o= 4.2719**		**ρ_o= 0.990954g cm^{-3}**		**U_o=1536.96m s^{-1}**	
0.990697	0.991436	1537.51	4.4035	4.2668	1.5243	6.6605	3.9679
1.980868	0.991911	1537.97	4.4011	4.2622	1.5255	6.3119	3.9689
3.959586	0.992848	1539.06	4.3959	4.2521	1.5281	6.4193	3.9710
5.936076	0.993771	1539.99	4.3912	4.2430	1.5304	6.2440	3.9730
7.910295	0.994684	1540.92	4.3866	4.2340	1.5327	6.1449	3.9750
9.882215	0.995589	1541.86	4.3819	4.2250	1.5351	6.0851	3.9770
11.85178	0.996484	1542.78	4.3773	4.2162	1.5374	6.0260	3.9791





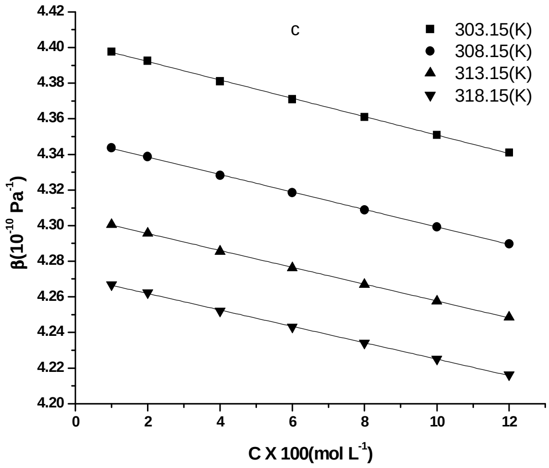


Fig. 1: Adiabatic Compressibility (β) as a function of molality (m) for (a)LiCl (b) NaCl and (c) KCl in 0.01m aqueous citric acid at different temperatures.

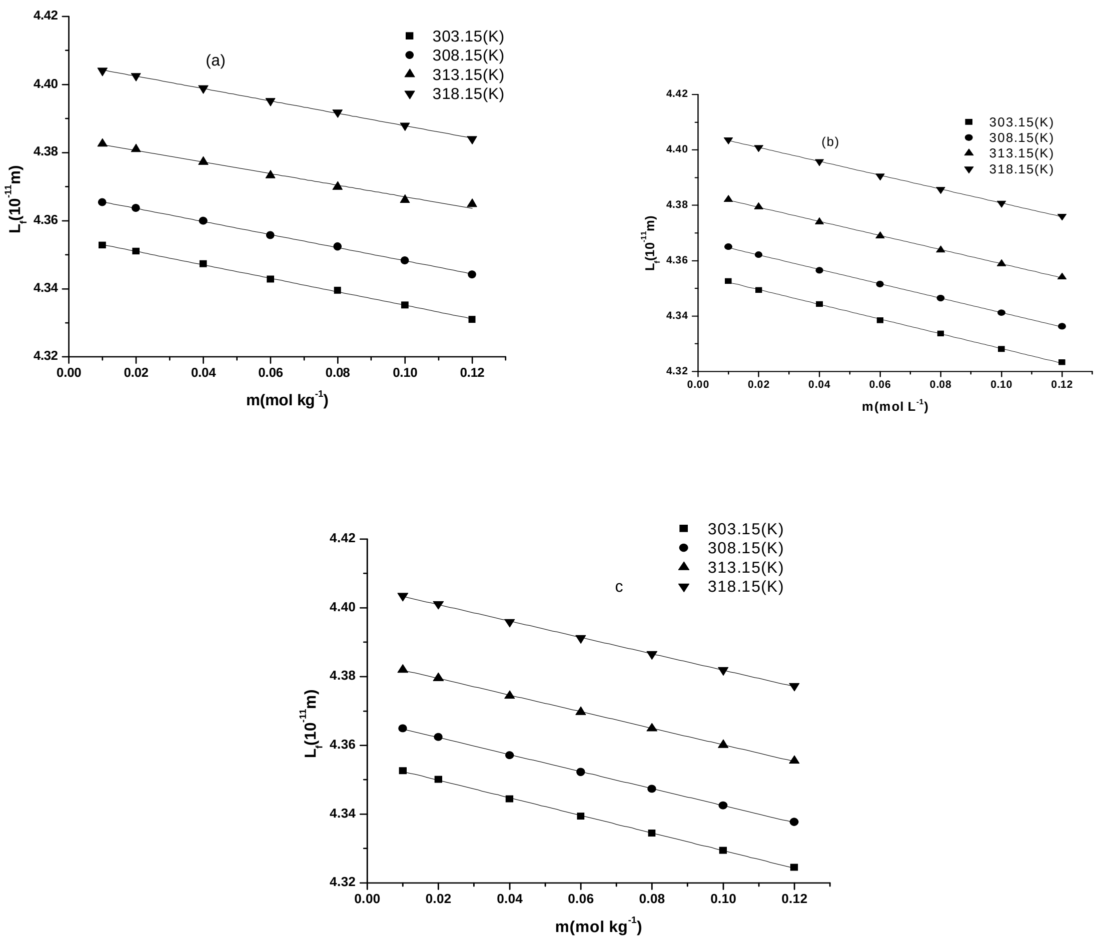


Fig. 2: Intermolecular free length (L_f) as a function of molality (m) for (a) LiCl (b) NaCl and (c) KCl in 0.01m aqueous citric acid at different temperatures.

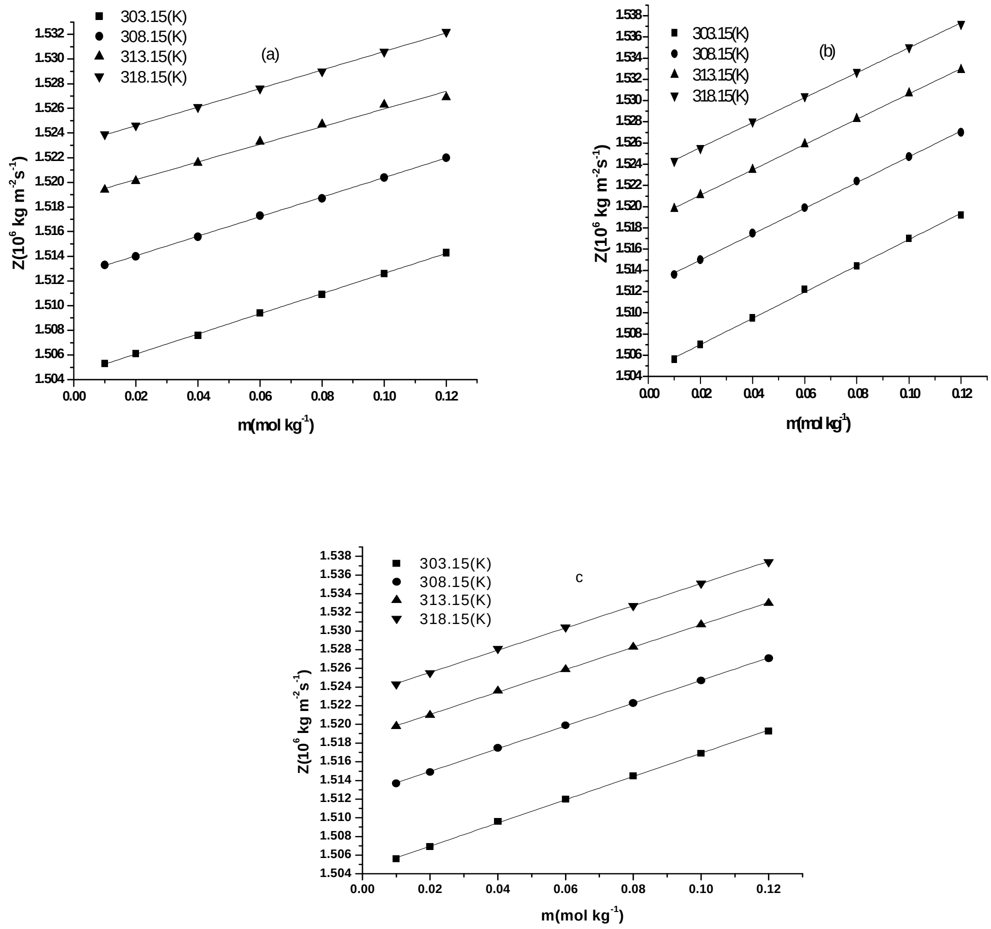


Fig. 3: Specific acoustic impedance(Z) as a function of molality (m) for (a) LiCl (b) NaCl and (c) KCl in 0.01m aqueous citric acid at different temperatures

CONCLUSION

The decrease in adiabatic compressibility (β), increase in intermolecular free length (L_f) and increase in molar compressibility (W) show presence of strong ion-solvent interactions of LiCl, NaCl and KCl with 0.01 mol kg^{-1} of citric acid in water as solvent. Acoustic parameters such as specific acoustic impedance, molar compressibility, solvation number were reported. All these parameters indicate that there is increase in ion-solvent interactions with increase in temperature, increase in concentration of the solution and citric acid content of the solvent.

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