

Ultrasonic and Thermodynamic Studies of 1-1 Electrolyte in Aqueous Solution

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Abstract

In the present investigation, density of and ultrasonic speed in aqueous solutions of alkali metal halides viz. LiCl, NaCl and KCl at 298.15, 303.15, 308.15, 313.15 and 318.15K have been measured. The results were used to test the applicability of simple equations for the ultrasonic velocity and density of electrolytic solutions, and their thermo acoustic properties e.g. apparent molar volume, Φ_V , adiabatic compressibility, K_S , apparent molar adiabatic compressibility, Φ_K , acoustic impedance, Z , relative association, R_A , hydration number, n_H have been used to study the interaction in the solutions.

Keywords: electrolyte, density, ultrasonic velocity, binary mixture, thermodynamic properties

Introduction

The aqueous electrolytic solutions show significant thermodynamic properties which makes it unique in its application in scientific fields. It is widely used as a natural, biomedical and industrial fluid. To name a few are Na, K, Ca, Mg, Cl, HPO_4^{2-} and HCO_3^{-1} . The electrolytic drink, Oral Rehydration solutions (ORS) prescribed by World Health Organization (WHO) and United Nations Children's Fund (UNICEF) has been used in diarrhea or dehydration, kidney complications is a mixture of salt, sugar and water it restores mineral losses after vomiting. Sportsmen drink electrolytic drinks (Gatorade, PowerAde) to replenish the loss of minerals from the body after high intensity exercise or lots of sweating. Electrolytes are isotonic that is has same mineral concentration as blood. Coconut water contains more of potassium ions rather than sodium is of key importance for sportsman. Herbal teas, sea salts used nowadays are a good source of electrolytes. In order to compensate the loss of water due to hot weather, illness or stress animals such as dogs, kittens are administered with electrolytic solutions which contain more sugar than salt in water ratio as dogs do not lose sodium quickly. Artificial sweetener such as xylitol is not used in case of canine electrolyte as it causes death of the animal. Milk contains four important electrolytes namely sodium, potassium, calcium, magnesium. 99% calcium is used to build bones and teeth and the remaining 1% acts as an electrolyte in blood helps in contraction and relaxation of muscles, triggers muscle contraction.

If there is deficiency of calcium ion in blood it takes from bones and teeth to maintain it. Magnesium relaxes heart muscles and lowers blood pressure. More the magnesium in blood less is the chance of cardiovascular disease. Sodium and potassium maintain our nervous system. After digestion, some minerals dissolve into small particles called ions, which carry an electrical charge. While these ions support our metabolism in a number of ways, their ability to conduct electricity makes them responsible for triggering and maintaining nerve impulses and muscle contractions. Our body strictly regulates the concentration of electrolytes in the system to ensure we have an amount necessary to maintain all vital

functions. When electrolyte levels get too low or too high, serious medical problems can develop. In biomedical engineering electrodes of Ag/AgCl are used in cardiogram, micropipette electrode, eye movement and ECG. In electronic devices such as batteries, fuel cells, capacitor, hygrometer, dry polymer electrolytes, organic ionic plastic crystals electrolytic solutions are used.

The thermodynamic properties aid in completion fluids optimization in petroleum and gas well drilling. In recent years [1,2] there has been considerable interest in describing the properties of aqueous electrolyte solutions. Pitzer and co-workers [3-5] have developed number of equations describing the thermodynamic properties of pure electrolytes and their solutions over a wide range of concentration and at different temperature. Many investigations have confirmed that the Pitzer equations yield accurate representations of the experimental data for several binary mixtures of electrolyte containing a common ion. Khoo et al [5-7], Boyd [8-10] White et al [11-15], Ananthaswamy and Atkinson [16], Kumar and Atkinson [17] have successfully used these equations to describe the thermodynamic properties of a variety of electrolyte solutions. The behavior of electrolytes in aqueous and non-aqueous medium has been subject of interest in recent years. There are some characteristic differences between aqueous and non-aqueous solvents. Non-aqueous solvents are media other than water which have tendency to dissolve reasonable number of compounds and many chemical reactions [18] occur in it.

Water is known to be an amphoteric solvent according to Bronsted [19]. This classification broadly agrees with Parker's differentiation [20] between the protic and dipolar aprotic solvents and strong hydrogen donor like methanol, ammonia, hydrogen fluoride and water as protic solvent. In aqueous solutions the water molecules can be considered to be in dynamic equilibrium [21] between the bulky tetrahedrally hydrogen bonded clusters and denser monomer molecules.

When a solute is added in water, the former shifts the equilibrium in either direction. A solute which causes a shift, so as to increase the number and average half life of the clustered, is called structure maker, and solute which has an effect in the opposite direction called the structure breaker [21]. The water is quantitatively most important in many biological systems as well as play significant role in cellular metabolism of plants and animals, and perform many biological functions in living organism. The thermodynamic properties of electrolytic solutions have been studied by numerous workers [22-24] in an attempt to assist the elucidation of the interaction (ion-ion, ion-solvent and solute-solvent) and present in aqueous and non-aqueous solvents. Mathieson and Conway [25] determined the values of Φ_K in various electrolytes in a very low concentration range. Apparent molar compressibility of aqueous solutions of chloride, sulphate, nitrate of zinc and cadmium has been reported by Jha and Jha [26].

Also partial molar compressibilities are negative and increase with increasing concentration of water in each set of solutions. Bachem [27], Scott and Wilson [28], Krishna Murthy [29], Rao and Rao [30] studied the apparent molar compressibilities in several solutions of electrolytes of different valence types and reported deviation from the limiting law. During recent years a number of workers [31,32] have utilized density and ultrasonic speed data to deduce a number of thermodynamic properties (adiabatic compressibility, apparent molar adiabatic compressibility, apparent molar volume, acoustic impedance and limiting values of these properties etc) of a number of pure electrolytes in aqueous solutions. The present work embodies the results of experimental studies of these properties of aqueous LiCl, NaCl and KCl at different temperatures (25^oC-45^oC) over a wide range of concentration (0.01-0.1).

Experimental

The salts Lithium, Sodium and Potassium chloride used were dried over night in an oven, and afterwards stored over silica gel in desiccators for use. The solutions of electrolyte were prepared by

weight dilution method then putting in stoppered bottles with a syringe to prevent preferential evaporation and to reduce possible errors in molarity calculation. Density and ultrasonic speed were measured at 298.15, 303.15, 308.15, 313.15 and 318.15K. The temperature was maintained constant by a thermostatically controlled water bath and was not allowed to exceed $\pm 0.10^\circ\text{C}$. Density measurements were made using bicapillary pycnometer with an accuracy of $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$. Ultrasonic velocity measurements were made using a crystal controlled variable path ultrasonic interferometer (Model, M-78) operating at a frequency of 2MHz an accuracy of $\pm 0.1 \text{ ms}^{-1}$. The method of calibration and experimental procedures has been described in literature [33, 34].

Formulation

The apparent molar volume, Φ_V , of the solute at different concentrations is calculated from density data as in equation 1

$$\phi_v = \frac{1000(\rho_0 - \rho)}{c\rho_0} + \frac{M_2}{\rho_0} \quad (1)$$

Isentropic compressibility, K_S is calculated by Laplace's equation as in equation 2

$$K_S = (u^2 \rho)^{-1} \quad (2)$$

Apparent molar adiabatic compressibility, Φ_K of aqueous electrolytic solution is represented as in equation 3

$$\phi_K = \frac{1000(K_S \rho_0 + K_S^0 \rho)}{c\rho\rho_0} + \frac{MK_S^0}{\rho_0} \quad (3)$$

Acoustic Impedance, Z is represented in equation 4

$$Z = u\rho \quad (4)$$

Relative Association, R_A of electrolyte solutions is calculated from equation 5

$$R_A = \frac{\rho}{\rho_0} \left(\frac{u_0}{u} \right)^{1/3} \quad (5)$$

Hydration number is represented by the relation A.6

$$n_H = \left(\frac{n_1}{n_2} \right) \left(1 - \frac{K}{K_0} \right) \quad (6)$$

Results and Discussion

Densities and ultrasonic velocities in aqueous solutions of LiCl, NaCl and KCl at different concentrations (0.01-0.1M) have been measured at temperatures 298.15, 303.15, 308.15 and 318.15K and the results are presented in Tables 1,2. These data have been used to deduce adiabatic compressibility, K_S , apparent molar adiabatic compressibility, Φ_K , apparent molar volume, Φ_V , acoustic impedance, Z , and also hydration number, n_H . Ultrasonic velocities in all the solutions are found to increase with increasing concentration and temperatures of the electrolytic solutions [35]. Ultrasonic velocity appears to increase (structure making) with increasing concentration of the solutions and this increase in the velocity is due to structure making. Cl^- ions are therefore structure maker. Further, since the ultrasonic velocity is slightly greater in NaCl than LiCl and KCl. This fact shows that structure making properties of ions decrease with increasing ionic size.

Table 1 Density (ρ , x 10^{-3} Kgm $^{-3}$) of aqueous solution of LiCl, NaCl, and KCl solution as a function of concentration and temperature.					
		LiCl			
c (mol lit $^{-1}$)	298.15	303.15	308.15	313.15	318.15
0.10	1.0008	1.0007	1.0004	1.0001	0.9954
0.09	1.0006	1.0005	1.0002	0.9998	0.9940
0.08	1.0005	1.0003	0.9999	0.9996	0.9947
0.07	1.0003	1.0001	0.9988	0.9982	0.9937
0.06	1.0002	0.9998	0.9980	0.9974	0.9922
0.05	0.9999	0.9989	0.9973	0.9965	0.9914
0.04	0.9990	0.9981	0.9966	0.9956	0.9906
0.03	0.9982	0.9969	0.9960	0.9945	0.9899
0.02	0.9975	0.9964	0.9953	0.9936	0.9890
0.01	0.9969	0.9956	0.9942	0.9923	0.9880
0.00	0.9968	0.9955	0.9940	0.9921	0.9879
		NaCl			
c (mol lit $^{-1}$)	298.15	303.15	308.15	313.15	318.15
0.10	1.0010	1.0009	1.0005	1.0003	0.9967
0.09	1.0008	1.0006	1.0003	1.0001	0.9948
0.08	1.0007	1.0005	1.0000	0.9999	0.9941
0.07	1.0006	1.0003	0.9990	0.9984	0.9940
0.06	1.0004	1.0002	0.9983	0.9977	0.9930
0.05	1.0001	0.9990	0.9974	0.9968	0.9925
0.04	0.9995	0.9982	0.9968	0.9960	0.9920
0.03	0.9987	0.9970	0.9961	0.9947	0.9913
0.02	0.9980	0.9965	0.9955	0.9940	0.9909
0.01	0.9972	0.9960	0.9947	0.9926	0.9899
0.00	0.9968	0.9955	0.9940	0.9921	0.9880
		KCl			
c (mol lit $^{-1}$)	298.15	303.15	308.15	313.15	318.15
0.10	1.0012	1.0010	1.0008	1.0006	0.9999
0.09	1.0011	1.0008	1.0007	1.0004	0.9962
0.08	1.0009	1.0006	1.0005	1.0003	0.9953
0.07	1.0007	1.0005	1.0003	1.0002	0.9949
0.06	1.0006	1.0004	1.0001	0.9998	0.9941
0.05	1.0005	1.0003	0.9999	0.9980	0.9938
0.04	1.0003	0.9995	0.9985	0.9970	0.9931
0.03	1.0001	0.9982	0.9978	0.9958	0.9926
0.02	0.9998	0.9975	0.9967	0.9951	0.9915
0.01	0.9978	0.9967	0.9956	0.9934	0.9905
0.00	0.9968	0.9955	0.9940	0.9921	0.9880

Table 2 Density (ρ , $\times 10^{-3}$ Kgm $^{-3}$) of aqueous solution of LiCl, NaCl, and KCl solution as a function of concentration and temperature..

	LiCl		
c (mol lit $^{-1}$)	298.15	303.15	318.15
0.10	1504.5	1516.0	1549.4
0.09	1504.0	1515.5	1549.0
0.08	1503.7	1515.0	1547.9
0.07	1503.2	1514.5	1547.0
0.06	1502.7	1514.0	1546.1
0.05	1502.0	1513.6	1545.0
0.04	1501.7	1513.0	1544.3
0.03	1501.2	1512.6	1543.5
0.02	1500.5	1512.0	1542.9
0.01	1499.7	1511.4	1541.6
0.00	1498.0	1508.0	1536.0
	NaCl		
c (mol lit $^{-1}$)	298.15	303.15	318.15
0.10	1505.9	1516.7	1549.9
0.09	1504.4	1516.1	1549.2
0.08	1504.1	1515.3	1548.5
0.07	1503.6	1515.0	1547.9
0.06	1502.9	1514.7	1547.1
0.05	1502.3	1514.2	1545.8
0.04	1501.9	1513.7	1545.0
0.03	1501.4	1513.1	1544.1
0.02	1500.8	1512.6	1543.2
0.01	1499.9	1512.0	1542.0
0.00	1498.0	1508.0	1536.0
	KCl		
c (mol lit $^{-1}$)	298.15	303.15	318.15
0.10	1501.9	1510.1	1540.2
0.09	1499.4	1509.9	1532.4
0.08	1499.1	1508.7	1533.3
0.07	1498.9	1508.1	1538.2
0.06	1498.3	1507.0	1538.0
0.05	1498.0	1503.0	1535.0
0.04	1497.9	1501.0	1536.7
0.03	1487.5	1499.9	1537.0
0.02	1487.2	1498.7	1538.2
0.01	1487.0	1498.2	1537.3
0.00	1498.0	1508.0	1536.0

Table 3 Density (ρ , x 10^{-3} Kgm $^{-3}$) of aqueous solution of LiCl, NaCl, and KCl solution as a function of concentration and temperature.				
	LiCl			
c(mol lit $^{-1}$)	298.15	303.15	308.15	313.15
0.1	2.43	-9.78	-21.42	-37.70
0.09	0.20	-13.37	-26.64	-43.27
0.08	-3.84	-17.23	-31.15	-51.51
0.07	-7.60	-23.62	-25.88	-44.81
0.06	-14.28	-29.63	-23.89	-45.96
0.05	-19.62	-26.00	-23.12	-45.56
0.04	-12.59	-23.05	-21.96	-44.95
0.03	-4.21	-4.75	-23.37	-37.23
0.02	7.52	-3.31	-21.18	-31.85
0.01	32.70	31.14	25.65	24.59
	NaCl			
c (mol lit $^{-1}$)	298.15	303.15	308.15	313.15
0.10	16.57	4.38	-6.23	-23.49
0.09	13.90	1.69	-11.22	-30.41
0.08	9.81	-4.19	-16.21	-39.06
0.07	4.26	-10.32	-12.56	-31.46
0.06	-1.47	-20.16	-12.73	-34.77
0.05	-7.48	-11.83	-8.93	-35.38
0.04	-8.98	-9.39	-10.79	-38.81
0.03	-4.78	8.07	-10.53	-27.72
0.02	-1.40	7.84	-15.54	-35.28
0.01	18.76	7.13	-8.45	10.58
	KCl			
c (mol lit $^{-1}$)	298.15	303.15	308.15	313.15
0.10	30.68	19.51	6.91	-10.32
0.09	26.89	15.59	0.46	-17.58
0.08	23.41	10.68	-6.34	-27.91
0.07	18.93	2.94	-15.09	-41.19
0.06	11.30	-7.37	-26.75	-53.86
0.05	0.60	-21.82	-43.08	-43.38
0.04	-12.93	-25.91	-37.39	-47.82
0.03	-35.49	-15.98	-51.38	-48.49
0.02	-75.58	-26.26	-59.24	-75.03
0.01	-25.32	-47.05	-82.83	-53.86

			LiCl	
c (mol lit ⁻¹)	298.15	303.15	308.15	313.15
0.10	4.4144	4.3481	4.2821	4.2277
0.09	4.4182	4.3518	4.2922	4.2328
0.08	4.4204	4.3558	4.3003	4.2361
0.07	4.4242	4.3593	4.3023	4.2468
0.06	4.4276	4.3635	4.3085	4.2556
0.05	4.4331	4.3697	4.3155	4.2657
0.04	4.4388	4.3767	4.3214	4.2740
0.03	4.4453	4.3843	4.3302	4.2826
0.02	4.4526	4.3900	4.3378	4.2898
0.01	4.4600	4.3970	4.3476	4.2994
0.00	4.4587	4.4097	4.3657	4.3312
			NaCl	
c (mol lit ⁻¹)	298.15	303.15	308.15	313.15
0.10	4.4056	4.3431	4.2798	4.2219
0.09	4.4147	4.3477	4.2829	4.2266
0.08	4.4169	4.3531	4.2881	4.2307
0.07	4.4207	4.3558	4.2952	4.2398
0.06	4.4255	4.3576	4.3010	4.2461
0.05	4.4304	4.3658	4.3072	4.2527
0.04	4.4354	4.3722	4.3126	4.2606
0.03	4.4419	4.3810	4.3196	4.2689
0.02	4.4486	4.3861	4.3250	4.2759
0.01	4.4575	4.3917	4.3342	4.2869
0.00	4.4587	4.4097	4.3657	4.3312
			KCl	
c (mol lit ⁻¹)	298.15	303.15	308.15	313.15
0.10	4.4279	4.3806	4.3223	4.2813
0.09	4.4434	4.3831	4.3293	4.2645
0.08	4.4457	4.3906	4.3400	4.2857
0.07	4.4479	4.3944	4.2882	4.2495
0.06	4.4517	4.4015	4.3515	4.2719
0.05	4.4541	4.4255	4.3570	4.2940
0.04	4.4558	4.4409	4.3684	4.3048
0.03	4.5193	4.4531	4.3722	4.2842
0.02	4.5222	4.4633	4.3812	4.2957
0.01	4.5324	4.4698	4.3893	4.3066
0.00	4.4587	4.4097	4.3657	4.3312

Table 5 Adiabatic compressibility ($K_{idl} \times 10^{10}, m^2 N^{-1}$) as a function of concentration of aqueous solution of LiCl, NaCl and KCl at different temperatures					
	LiCl				
c (mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.10	4.4699	4.4165	4.3676	4.3210	4.2889
0.09	4.4700	4.4166	4.3678	4.3212	4.2891
0.08	4.4701	4.4168	4.3679	4.3213	4.2892
0.07	4.4702	4.4169	4.3680	4.3215	4.2894
0.06	4.4703	4.4170	4.3682	4.3217	4.2896
0.05	4.4704	4.4171	4.3683	4.3218	4.2897
0.04	4.4705	4.4172	4.3684	4.3219	4.2898
0.03	4.4705	4.4172	4.3685	4.3220	4.2899
0.02	4.4706	4.4173	4.3685	4.3221	4.2900
0.10	4.4706	4.4173	4.3686	4.3221	4.2901
c	NaCl				
(mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.10	4.4584	4.4412	4.3220	4.2778	4.2431
0.09	4.4587	4.4587	4.4587	4.4587	4.4587
0.08	4.4587	4.4587	4.4587	4.4587	4.4587
0.07	4.4552	4.3745	4.2972	4.2425	4.2019
0.06	4.4537	4.3677	4.3020	4.2474	4.2089
0.05	4.4551	4.3751	4.3081	4.2540	4.2181
0.04	4.4563	4.3809	4.3135	4.2618	4.2245
0.03	4.4573	4.3887	4.3204	4.2701	4.2324
0.02	4.4581	4.3933	4.3258	4.2770	4.2390
0.10	4.4587	4.3984	4.3349	4.2879	4.2498
c	KCl				
(mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.10	4.4585	4.3905	4.3657	4.2911	4.2360
0.09	4.4586	4.3931	4.3657	4.2776	4.2830
0.08	4.4586	4.4006	4.3657	4.2947	4.2822
0.07	4.4586	4.4044	4.3657	4.2655	4.2619
0.06	4.4587	4.4050	4.3657	4.2835	4.2652
0.05	4.4587	4.4256	4.3657	4.3013	4.2797
0.04	4.4587	4.4409	4.3657	4.3099	4.2744
0.03	4.4588	4.4535	4.3657	4.2934	4.2749
0.02	4.4588	4.4638	4.3657	4.3026	4.2736
0.10	4.4588	4.4700	4.3657	4.3114	4.2809

Table 6 Apparent molar adiabatic compressibility (ϕ_{ks} , $\times 10^{-7}$, $\text{m}^2 \text{N}^{-1}$) as a function of concentration of aqueous solution of LiCl, NaCl, and KCl at different temperatures.

LiCl					
c (mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.32	8.9148	8.8012	8.6939	8.6022	8.5648
0.30	9.9085	9.7822	9.6698	9.5630	9.5301
0.28	11.1479	11.0089	10.8882	10.7613	10.7193
0.26	12.7445	12.5849	12.4504	12.3198	12.2669
0.24	14.8718	14.6884	14.5386	14.3904	14.3375
0.22	17.8559	17.6427	17.4627	17.2927	17.2277
0.20	22.3396	22.0749	21.8461	21.6418	21.5569
0.17	29.8134	29.4699	29.1602	28.8944	28.7713
0.14	44.7627	44.2349	43.7844	43.3883	43.2034
0.10	89.6078	88.5570	87.6967	86.9109	86.5480
NaCl					
c (mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.32	8.9003	8.7949	8.6953	8.6118	8.5864
0.30	9.8974	9.7757	9.6630	9.5720	9.5597
0.28	11.1347	11.0017	10.8757	10.7715	10.7636
0.26	12.7276	12.5748	12.4420	12.3288	12.3029
0.24	14.8540	14.6701	14.5262	14.3948	14.3709
0.22	17.8321	17.6258	17.4464	17.2895	17.2628
0.20	22.3028	22.0506	21.8216	21.6338	21.5938
0.17	29.7619	29.4389	29.1205	28.8832	28.8199
0.14	44.6788	44.1820	43.7079	43.3623	43.2592
0.10	89.4566	88.4172	87.5180	86.8703	86.6460
KCl					
c (mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.32	8.9289	8.8390	8.7436	8.6769	8.6193
0.30	9.9351	9.8212	9.7196	9.6197	9.6559
0.28	11.1767	11.0552	10.9449	10.8452	10.8625
0.26	12.7731	12.6358	12.4311	12.3386	12.3758
0.24	14.9034	14.7489	14.6044	14.4298	14.4458
0.22	17.8831	17.7408	17.5314	17.3690	17.3672
0.20	22.3519	22.2151	21.9499	21.7410	21.6919
0.17	30.0062	29.6693	29.2787	28.9256	28.9207
0.14	45.0141	44.5543	43.9709	43.4450	43.3805
0.10	90.1874	89.1761	88.0394	87.0410	86.8635

Table 7 Acoustic impedance (Z , $\times 10^3 \text{ Kg m}^{-2}\text{s}^{-1}$) as a function of concentration of aqueous solution of LiCl, NaCl, and KCl at different temperatures.

			LiCl		
c (mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.10	1505.7	1517.1	1528.5	1538.1	1542.3
0.09	1504.9	1516.3	1526.6	1536.9	1539.7
0.08	1504.5	1515.4	1524.8	1536.1	1539.7
0.07	1503.7	1514.7	1523.7	1533.1	1537.3
0.06	1503.0	1513.7	1522.0	1530.9	1534.1
0.05	1501.8	1511.9	1520.2	1528.4	1531.7
0.04	1500.2	1510.1	1518.6	1526.3	1529.8
0.03	1498.5	1507.9	1516.6	1523.9	1527.9
0.02	1496.7	1506.6	1514.7	1521.9	1525.9
0.10	1495.1	1504.7	1512.2	1519.2	1523.1
0.00	1495.2	1502.5	1508.9	1513.5	1512.7
c			NaCl		
(mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.10	1507.4	1518.1	1529.0	1539.3	1544.7
0.09	1505.7	1517.0	1528.3	1538.3	1541.1
0.08	1505.2	1516.0	1527.1	1537.3	1539.3
0.07	1504.5	1515.4	1525.1	1534.5	1538.6
0.06	1503.5	1515.0	1523.5	1532.9	1536.3
0.05	1502.5	1512.7	1521.7	1531.0	1534.2
0.04	1501.1	1511.0	1520.3	1529.0	1532.6
0.03	1499.4	1508.6	1518.6	1526.5	1530.7
0.02	1497.8	1507.3	1517.2	1524.7	1529.2
0.10	1495.7	1506.0	1514.9	1521.7	1526.4
0.00	1495.2	1502.5	1508.9	1513.5	1512.7
c			KCl		
(mol lit ⁻¹)	298.15	303.15	308.15	313.15	318.15
0.10	1503.7	1511.7	1521.6	1528.8	1540.0
0.09	1501.0	1511.1	1520.4	1531.6	1526.6
0.08	1500.5	1509.6	1518.3	1527.7	1526.1
0.07	1499.9	1508.9	1527.3	1534.2	1530.3
0.06	1499.2	1507.6	1516.0	1529.8	1528.9
0.05	1498.7	1503.4	1514.9	1524.5	1525.5
0.04	1498.3	1500.2	1511.9	1521.9	1526.1
0.03	1487.6	1497.2	1510.7	1524.6	1525.6
0.02	1486.9	1495.0	1508.3	1522.0	1525.1
0.10	1483.7	1493.3	1506.1	1518.8	1522.7
0.00	1495.2	1502.5	1508.9	1513.5	1512.7

Table 8

Table 8				
		LiCl		
298.15	303.15	308.15	313.15	318.15
1.0027	1.0035	1.0041	1.0057	1.0046
1.0025	1.0034	1.0043	1.0055	1.0033
1.0024	1.0032	1.0043	1.0054	1.0042
1.0024	1.0032	1.0030	1.0042	1.0034
1.0024	1.0030	1.0023	1.0036	1.0021
1.0022	1.0022	1.0018	1.0030	1.0015
1.0014	1.0015	1.0012	1.0022	1.0009
1.0007	1.0004	1.0008	1.0013	1.0003
1.0001	1.0000	1.0003	1.0005	0.9995
0.9997	0.9994	0.9994	0.9993	0.9988
		NaCl		
298.15	303.15	308.15	313.15	318.15
1.0029	1.0037	1.0043	1.0053	1.0047
1.0030	1.0036	1.0042	1.0053	1.0029
1.0030	1.0037	1.0040	1.0052	1.0024
1.0030	1.0036	1.0031	1.0038	1.0025
1.0030	1.0035	1.0025	1.0032	1.0016
1.0028	1.0024	1.0017	1.0024	1.0014
1.0023	1.0018	1.0012	1.0018	1.0010
1.0016	1.0007	1.0007	1.0006	1.0005
1.0010	1.0003	1.0002	1.0001	1.0003
1.0004	0.9999	0.9996	0.9988	0.9996
		KCl		
298.15	303.15	308.15	313.15	318.15
1.0040	1.0054	1.0063	1.0080	1.0101
1.0045	1.0052	1.0064	1.0071	1.0080
1.0043	1.0053	1.0066	1.0079	1.0069
1.0042	1.0053	1.0044	1.0063	1.0055
1.0042	1.0054	1.0066	1.0067	1.0047
1.0042	1.0062	1.0066	1.0055	1.0050
1.0040	1.0059	1.0053	1.0047	1.0040
1.0061	1.0048	1.0047	1.0025	1.0034
1.0059	1.0044	1.0037	1.0021	1.0020
1.0039	1.0037	1.0027	1.0006	1.0012

Table 9

		LiCl		
T (K)	298.15	303.15	308.15	313.15
c (mol lit ⁻¹)				
0.10	2.44	3.02	3.81	4.21
0.09	2.51	3.18	3.75	4.43
0.08	2.71	3.36	3.77	4.80
0.07	2.86	3.63	4.19	4.81
0.06	3.10	3.93	4.43	4.96
0.05	3.25	4.17	4.71	5.06
0.04	3.45	4.46	5.24	5.40
0.03	3.66	4.84	5.68	5.92
0.02	3.91	6.02	6.84	7.27
0.10	4.60	8.97	9.35	10.25
c			NaCl	
(mol lit ⁻¹)	298.15	303.15	308.15	313.15
0.10	6.58	8.29	10.87	13.94
0.09	6.05	8.64	11.65	14.84
0.08	6.47	8.88	12.29	16.04
0.07	6.75	9.67	12.77	16.68
0.06	6.88	10.91	13.67	18.13
0.05	7.03	11.03	14.86	20.08
0.04	7.23	11.79	16.86	22.61
0.03	6.95	12.07	19.54	26.60
0.02	6.28	14.90	25.89	35.47
0.10	1.48	22.67	40.11	56.85
c			KCl	
(mol lit ⁻¹)	298.15	303.15	308.15	313.15
0.10	3.81	3.65	5.48	6.36
0.09	2.10	3.70	5.12	9.44
0.08	2.02	2.99	4.07	7.25
0.07	1.91	2.75	14.03	14.90
0.06	1.45	1.71	3.01	12.63
0.05	1.14	-3.94	2.22	9.52
0.04	0.92	-9.77	-0.84	8.46
0.03	-25.11	-18.17	-2.74	20.05
0.02	-39.53	-33.69	-9.82	22.75
0.10	-91.76	-75.55	-30.01	31.57

(T K)	298.15	303.15	308.15	313.15	318.15
φ_{ks}^0	9.42E-06	9.31E-06	9.22E-06	9.13E-06	9.10E-06
S_k	21.98	20.47	13.77	10.51	36.85
φ_v^0	-3.05E-05	-3.01E-05	-2.98E-05	-2.96E-05	-2.95E-05
S_v	-153.38	-101.68	-149.4	-209.37	-260.12
φ_{ks}^0	9.40E-06	9.30E-06	9.20E-06	9.13E-06	9.11E-06
S_k	-4.58	7.65	-11.75	-6.54	-150.73
φ_v^0	-3.04E-05	-3.01E-05	-2.98E-05	-2.96E-05	-2.95E-05
S_v	38.55	-46.31	1.95	-98.81	465.77
φ_{ks}^0	9.48E-06	9.38E-06	9.25E-06	9.14E-06	9.13E-06
S_k	-94.65	-73.07	-119.05	-91.49	-196.94
φ_v^0	-3.07E-05	-3.04E-05	-3.00E-05	-2.96E-05	-2.95E-05
S_v	410.73	286.97	395.74	223.87	618.19

The change in ultrasonic velocities in the case of solutions of LiCl, NaCl and KCl are found to be in the order [35,36] NaCl>LiCl>KCl. The densities are found to increase with increasing concentration of solutions. The value of K_S show that it is inversely proportional to ultrasonic velocity and density of electrolytic solutions, these variations have been found to be linearly convergent in the case of electrolytic solutions showing the weak interactions. This decrease in adiabatic compressibility is expected due to structure making effect of LiCl, NaCl and KCl. Table 4, 5 shows that the values of adiabatic compressibility appear to decrease with increasing solute content i.e. metal halides and rise in temperatures. Such a decrease in adiabatic compressibility and ideal adiabatic compressibility observed in this aqueous metal halide with water in the present system, confirms the conclusion drawn from the velocity data.

The increasing electrostatic compression of water around the molecules may result in a large decrease in the compressibility of the solutions. The decrease in adiabatic compressibility is attributed to the influence of the electrostatic field [37] of ions (Li^+ , Na^+ , Cl^- , K^+) on the surrounding solvent molecules. The compressibility appears to be decreasing with decrease in hydrogen bond strength formed by solute and solvent molecules. The behavior of compressibility depicts the existence of interaction between solute and solvent molecules in which the structural arrangement in the neighborhood of consistent solutes is considerably affected.

Lowering in the compressibilities, ΔK_S , of the electrolytic solution has been studied and it is found to increase with increasing concentration of electrolytic solutions. The values of ΔK_S indicate weak solute-solvent interactions.

Calculated values of Φ_K for LiCl, NaCl and KCl solutions at different concentrations are presented in Table 6. The positive values of Φ_K confirm the presence of strong solute-solvent interactions.

Plots of Φ_K vs \sqrt{c} are found to be linear for these electrolytic solutions. The limiting apparent molar compressibilities, Φ_K^0 are obtained from the plots of Φ_K vs \sqrt{c} by the method of extrapolation. The value of Φ_K provides information regarding solute-solute interaction and related constant S_{KS} , also used to investigate the solute-solvent interactions. The positive values of Φ_K indicate the presence of strong solute-solute interactions and negative values of S_{KS} as depicted in Table 10 indicating the presence of weak solute-solvent interactions. Table 3 show the apparent molar volume values of LiCl, NaCl and KCl in aqueous solutions at different concentrations and temperature. The data in Table 3 depicts negative and positive values of Φ_V which is found to vary linearly with the square root of the concentration of the electrolytes [38-40]. The partial molar volume at infinite dilution, Φ_V^0 and the experimental slope, S_V for all the electrolytic solutions at different temperatures are reported in Table 10. Slopes are negative in case of LiCl and NaCl which indicates weak solute-solute or ion-ion interactions.

S_V are positive and large which indicates that ion-ion interactions are quite strong for KCl. Φ_V^0 values are positive for LiCl indicating the presence of solute-solvent interactions and negative for KCl and NaCl indicating weak solute-solute interactions. Table 7 compiles the data of acoustic impedance values of LiCl, NaCl and KCl at different concentrations. The values of Z are found to increase with increase in concentrations of LiCl, NaCl and KCl at different temperatures. The values of Z also increase with increase in temperatures and ionic size indicating structure making properties of ions. Table 8 is a tabular summation of values of R_A which is found to increase with increasing concentrations of electrolytic solutions and temperature respectively. It is influenced by two factors firstly breaking up of the associated solvent molecules on addition of solute in it and secondly on the solvation of solute molecules.

The hydration number, n_H values of all the electrolytes in aqueous solutions at different concentrations and temperatures are found to be positive. The values of n_H are found to decrease with increasing concentrations of LiCl, NaCl and KCl at different temperatures. The values of n_H increase with increasing temperatures. Further, the interaction between the solute and the water molecules present in the solvent is called as hydration. From the data in Table 9 it is observed that the values of n_H are positive in all the systems studied and such positive values of n_H indicate an appreciable solvation of solutes. This is an added support, not only for the structure promoting tendency of the solutes, but also the presence of appreciable dipole-dipole interactions between solute and water molecules. This also leads further suggestions that the compressibility of the solutions will be less than that of the solvent. As a result, solute will gain mobility and hence there will be more probability of conducting solvent molecules. This may further enhance the interaction between solute and solvent molecules. The values of n_H seem to be decreasing with increase in solute content in an aqueous medium as well as aqueous halide content and the rise of temperature too. Such a decrease in value of n_H show the strength of interaction which gets weakened in the solute-solvent molecules.

Conclusions

The results show that equation can yield good prediction for the densities and ultrasonic velocity of electrolytic solutions. From the behavior of acoustical parameters, it can be concluded that solute-solvent interaction gets weakened with addition of alkali metal halides as well as rising of temperature. It is further concluded that solute-solute interactions are dominating over the solute-solvent interactions.

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