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Molecular interaction of various transition metals with aqueous solutions at different temperature

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Abstract— The viscosities and densities of various transition metals $CuSO_4.5H_2O$, $MnSO_4.H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$ and $ZnSo4.7H_2O$ in aqueous medium have been calculated at different temperature like 303K, 306K, 309K, 312K and 315K. The experimental values of densities and viscosities have been used to compute Acoustic Impedance (Z), Adiabatic Compressibility (β), Intermolecular free length (L_f), Solvation number (S_n), Apparent volume (φ_v), Partial molar volume (φ^0_v), Solute-solvent interaction parameter (S_v) and Hepler's constant. These values indicate that all the transition metals are structure forming in aqueous medium.

Keywords— Apparent volume (φ_v), Partial molar volume (φ^0_v), Solute-solvent interaction parameter (S_v) and Hepler's constant.

1. Introduction

Ultrasonic velocity measurements are extremely helpful in understanding the ion solvent interactions in aqueous and non- aqueous solvents. The technique has been explored to determine the ion solvent interactions in aqueous solution containing electrolyte. In solvent, the attraction between the solute and solvent has essentially been of ion dipole interactions which depend mainly on ion size and polarity of the solvent. The strength of interactions is proportional to the size of the ion, charge and the magnitude of distance between the ion and dipolar molecule. Many researchers have used ultrasound to investigate the ion solvent interactions in aqueous solutions containing electrolytes [1,6]. A survey of literature [1-18], reveals that ultrasonic waves with low amplitude have been used by many scientists to investigate the nature of molecular interactions and physiochemical behavior or pure binary, ternary and quaternary liquid mixtures. Recently V.Kannappan and S.Chidambara Vinayagam [6] have studied ion-solvent interactions in aqueous and non-aqueous solutions of transition and inner transition metal ions by ultrasonic technique at 303.15K. The present work deals with the calculations and analysis of acoustical parameters which affect the ion-solvent interactions such as adiabatic Compressibility (β), acoustic impedances (Z), intermolecular free length (L_f) and solvations numbers (Sn) from the experimentally measured ultrasonic velocity (U) and density (ρ) values for the wide range of moderate concentrations of $CuSO_4.5H_2O$, $MnSO_4.H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $ZnSO_4.7H_2O$ in water for temperature 303, 306, 309, 312 and 315K.

2. Materials and Methods

Ultrasonic velocity (U) for the aqueous solutions was measured using a single crystal ultrasonic interferometer at 2MHZ frequency (Model F-81) supplied by Mittal Enterprises, New Delhi, that has an accuracy of 0.4 m/sec at 25°C. The temperature was kept constant by constant temperature water bath with an accuracy of ±0.1K. The temperature of the circulating water near the cell was measured by using PT-100 Sensor and found to be accurate at 23°C. The densities (ρ) of various concentrations have been measured using 25ml capacity specific gravity bottle and digital balance (Shink model HTR-220, made in Japan) with an accuracy of 0.0001gm. The qualigen made hydrated salt $CuSO_4.5H_2O$, $MnSO_4.H_2O$, $NiCl_2.6H_2O$,$CoCl_2.6H_2O$, $ZnSO_4.7H_2O$ of AR grade which has 99.5% assay was used without further purification for the present investigation. The aqueous solutions of given all were prepared in double distilled water in the presence of perchloric acid to avoid hydrolysis.

3. Theory and Calculation

From the measured values of ultrasonic velocity (U) and density (ρ) various acoustical parameters was calculated by using the following standard expressions.

Adiabatic compressibility $\beta = 1/U^2\rho$ $(kg^{-1}ms^{-2})$

Intermolecular free length $L_f = k\sqrt{\beta}$ (m)

Where k is temperature dependent constant called as Jacobson constant it is 2.075×10^{-6}, 2.082×10^{-6}, 2.093×10^{-6}, 2.104×10^{-6} and 2.116×10^{-6} for 303K, 306K, 309K, 312K and 315K respectively.

Acoustic impedance $Z = \rho U$ $(kgm^{-2}s^{-1})$

Solvation number $S_n = n_s/n_i\,(1-\beta/\beta_o)$

n_s = number of moles of solvent (mol/kg)

n_i = number of moles of solute (mol/kg)

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β = Adiabatic compressibility of solution at a particular temperature ($N^{-1}m^2$), β_o= Adiabatic compressibility of solvent at a particular temperature ($N^{-1}m^2$)

4. Results and Discussion

Experimentally measured values of ultrasonic velocity (U), density (ρ) and calculated values of acoustical parameters such as adiabatic compressibility (β), specific acoustic impedance (Z), intermolecular free length (L_f) and solvation number (Sn) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of moderate concentrations at 303, 306, 309, 312 and 315K are presented in Table 1, 2 and 3.

Table 1: Experimental results for aqueous $Cu^{2+}$and Mn^{2+}

Temp	Conc/M	U		P		Z		β		L_f		Sn	
		Cu	Mn	Cu	Mn	Cu	Mn	Cu	Mn	Cu	Mn	Cu	Mn
	0.1	1560.8	1504	1015	1009	1.58	1.51	4.04	4.32	0.41	0.43	4.3776	7.0384
	0.2	1562.6	1566.7	1024.3	1021	1.6	1.59	3.99	4.03	0.41	0.41	4.3056	6.4236
	0.3	1572	1578	1046.9	1041	1.64	1.64	3.86	3.85	0.4	0.4	4.1184	6.042
303K	0.4	1582.6	1585.3	1065.3	1057	1.68	1.67	3.74	3.82	0.4	0.4	3.9456	5.9784
	0.5	1585.3	1601.9	1080.7	1072	1.71	1.71	3.68	3.63	0.39	0.39	3.8592	5.5756
	0.6	1604	1634.2	1094.5	1088	1.75	1.77	3.55	3.44	0.39	0.38	3.672	5.1728
	0.7	1634	1650.1	1117.9	1113.8	1.79	1.83	3.47	3.29	0.38	0.37	3.5568	4.8548
	0.8	1653	1665.2	1125.7	1120	1.86	1.86	3.25	3.21	0.37	0.37	3.24	4.6852
	0.1	1462	1470.6	1013	1004	1.48	1.47	4.61	4.6	0.44	0.44	5.1984	7.632
	0.2	1534.6	1481.1	1019.2	1017	1.56	1.5	4.16	4.48	0.42	0.44	4.5504	7.3776
	0.3	1572	1533.3	1039.9	1037	1.63	1.59	3.89	4.1	0.41	0.42	4.1616	6.572
306K	0.4	1577	1565.3	1059.8	1053	1.67	1.65	3.79	3.87	0.4	0.4	4.0176	6.0844
	0.5	1584	1568	1077.2	1068	1.71	1.67	3.69	3.8	0.39	0.4	3.8736	5.936
	0.6	1585.3	1573	1090.4	1084	1.72	1.7	3.65	3.72	0.39	0.4	3.816	5.7664
	0.7	1610.6	1584	1113.2	1108.9	1.79	1.75	3.46	3.59	0.39	0.39	3.5424	5.4908
	0.8	1628	1599.5	1121.8	1117	1.91	1.78	3.05	3.5	0.37	0.38	2.952	5.3
	0.1	1520.4	1506	1009	1001	1.53	1.5	4.28	4.4	0.43	0.43	4.7232	7.208
	0.2	1539.4	1514.6	1016.7	1014.2	1.56	1.53	4.15	4.29	0.42	0.43	4.536	6.9748
	0.3	1550	1522	1035.9	1033.9	1.6	1.57	4.01	4.17	0.41	0.42	4.3344	6.7204
309K	0.4	1573	1530.6	1056.4	1049.2	1.66	1.6	3.82	4.06	0.4	0.41	4.0608	6.4872
	0.5	1581.3	1550.6	1074	1064.1	1.69	1.64	3.72	3.9	0.4	0.41	3.9168	6.148
	0.6	1592	1559.3	1085.4	1079.6	1.72	1.68	3.63	3.8	0.39	0.4	3.7872	5.936
	0.7	1597.3	1566	1109.4	1103.2	1.77	1.72	3.53	3.72	0.39	0.4	3.6432	5.7664
	0.8	1630.6	1604	1119.4	1113.4	1.82	1.78	3.35	3.49	0.38	0.4	3.384	5.2788
	0.1	1482.6	1530.6	1006	997.4	1.49	1.52	4.52	4.27	0.44	0.43	5.0688	6.9324
	0.2	1532	1533	1015.4	1011.5	1.55	1.55	4.19	4.2	0.43	0.43	4.5936	6.784
	0.3	1562.6	1554.6	1031.2	1029.4	1.61	1.6	3.97	4.01	0.41	0.42	4.2768	6.3812
312K	0.4	1565.3	1564	1052.7	1037.1	1.64	1.62	3.87	3.94	0.41	0.41	4.1328	6.2328
	0.5	1573.3	1568	1069.4	1061.4	1.68	1.66	3.77	3.83	0.4	0.41	3.9888	5.9996
	0.6	1589	1631	1081.2	1075.2	1.71	1.75	3.66	3.49	0.4	0.39	3.8304	5.2788
	0.7	1589.3	1640	1105.4	1099.4	1.75	1.8	3.58	3.38	0.39	0.39	3.7152	5.0456
	0.8	1598.6	1644	1115.5	1111.9	1.78	1.82	3.5	3.32	0.39	0.38	3.6	4.9184
	0.1	1421.3	1499	1002.8	995.4	1.43	1.49	4.93	4.47	0.46	0.44	5.6592	7.3564
	0.2	1472	1513.3	1011.9	1008.2	1.48	1.52	4.56	4.33	0.45	0.44	5.1264	7.0596
	0.3	1560	1518	1027.2	1025.3	1.6	1.55	4	4.23	0.42	0.43	4.32	6.8476
315K	0.4	1565.3	1520	1048.9	1033.5	1.64	1.57	3.89	4.18	0.41	0.43	4.1616	6.7416
	0.5	1566	1521	1064.4	1057.8	1.66	1.6	3.83	4.08	0.41	0.42	4.0752	6.5296
	0.6	1572.6	1525	1077.4	1071.9	1.69	1.63	3.75	4.01	0.4	0.42	3.96	6.321
	0.7	1577.3	1549	1101.4	1095.4	1.73	1.69	3.64	3.8	0.4	0.41	3.8016	5.936
	0.8	1605	1562.6	1111.4	1107.4	1.83	1.73	3.49	3.69	0.39	0.4	3.5856	5.702

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Table 2: Experimental results for aqueous Ni^{2+} and Co^{2+}

Temp	Conc/M	U		ρ		Z		β		Lf		Sn	
		Ni	Co	Ni	Co	Ni	Co	Ni	Co	Ni	Co	Ni	Co
	0.1	1506	1482	998.1	991.4	1.5	1.46	4.41	4.58	0.43	0.44	5.1491	5.4058
	0.2	1536	1510.4	1008.4	1004.4	1.54	1.51	4.2	4.36	0.42	0.43	4.832	5.0736
	0.3	1572	1550	1024.5	1021.3	1.61	1.58	3.94	4.07	0.4	0.41	4.4394	4.6357
303K	0.4	1583	1584	1044.5	1029.4	1.65	1.63	3.82	3.87	0.4	0.4	4.2582	4.3337
	0.5	1590.6	1594	1060.2	1054.5	1.68	1.67	3.72	3.77	0.39	0.4	4.1072	4.1827
	0.6	1616	1605.3	1072.8	1068.4	1.73	1.71	3.56	3.63	0.39	0.39	3.8656	3.9713
	0.7	1618	1633	1097.5	1091.4	1.77	1.78	3.48	3.43	0.38	0.38	3.7448	3.6693
	0.8	1677.3	1658.6	1108.2	1103.6	1.85	1.83	3.2	3.29	0.37	0.37	3.322	3.4579
	0.1	1487.2	1519.3	994.2	987.4	1.47	1.5	4.54	4.38	0.44	0.43	5.3454	5.1038
	0.2	1499	1560	1004.2	1000.4	1.5	1.56	4.43	4.1	0.43	0.42	5.1793	4.681
	0.3	1512.4	1570.6	1020.6	1018.3	1.54	1.59	4.28	3.98	0.42	0.41	4.9528	4.4998
306K	0.4	1524.6	1573.3	1040.5	1025.4	1.58	1.61	4.13	3.93	0.42	0.41	4.7263	4.4243
	0.5	1544.8	1590.6	1050.2	1051.3	1.62	1.67	3.99	3.75	0.41	0.4	4.5149	4.1525
	0.6	1555.6	1609.3	1068.2	1064.4	1.66	1.71	3.86	3.62	0.4	0.39	4.3186	3.9562
	0.7	1578.1	1616	1094.3	1087.5	1.72	1.75	3.66	3.52	0.39	0.39	4.0166	3.8052
	0.8	1596	1644	1104.4	1099.9	1.76	1.8	3.55	3.36	0.39	0.38	3.8052	3.5636
	0.1	1481.3	1466.6	990.4	983.4	1.44	1.38	4.6	4.72	0.44	0.45	5.436	5.6172
	0.2	1491.3	1482.6	1000.4	996.4	1.48	1.47	4.55	4.56	0.44	0.44	5.3605	5.3756
	0.3	1497.3	1518.6	1016.3	1014.3	1.52	1.54	4.38	4.27	0.43	0.43	5.1038	4.9377
309K	0.4	1517	1528	1036.4	1020.6	1.55	1.55	4.3	4.19	0.43	0.42	4.983	4.8169
	0.5	1530.6	1554.6	1045.1	1048.4	1.59	1.62	4.08	3.94	0.42	0.41	4.6508	4.4394
	0.6	1548	1577.3	1064.4	1060.4	1.64	1.67	3.92	3.79	0.41	0.4	4.4092	4.2129
	0.7	1590	1601.3	1090.5	1083.9	1.73	1.73	3.62	3.58	0.39	39	3.9562	3.8958
	0.8	1634.6	1604	1100.4	1095.3	1.79	1.75	3.4	3.56	0.38	0.39	3.624	3.8656
	0.1	1480.5	1510.6	986.3	979.2	1.46	1.47	4.62	4.47	0.45	0.44	5.4662	5.2397
	0.2	1479.9	1569.3	996.2	992.5	1.49	1.55	4.47	4.09	0.44	0.42	5.2397	4.6659
	0.3	1506.6	1576	1012.4	1009.6	1.52	1.59	4.35	3.98	0.43	0.41	5.0585	4.4998
312K	0.4	1581.3	1602.6	1032.5	1016.7	1.63	1.62	3.87	3.82	41	0.41	4.3337	4.2582
	0.5	1594.6	1629.3	1041	1044.4	1.65	1.7	3.77	3.6	0.4	0.39	4.1827	3.926
	0.6	1612	1630.6	1060.7	1055.2	1.7	1.72	3.62	3.56	0.4	0.39	3.9562	3.8656
	0.7	1638.6	1644	1085	1079.9	1.77	1.77	3.43	3.42	0.38	0.38	3.6693	3.6542
	0.8	1665.3	1669	1095.4	1094.4	1.82	1.82	3.29	3.28	0.38	0.38	3.4579	3.4428
	0.1	1441	1470	983.4	976.5	1.41	1.43	4.89	4.73	0.46	0.46	5.8739	5.6323
	0.2	1456	1486.6	993.4	989.6	1.44	1.47	4.74	4.57	0.46	0.45	5.6474	5.3907
	0.3	1545.3	1552	1009.5	1006.6	1.55	1.56	4.4	4.12	0.44	0.42	5.134	4.7112
315K	0.4	1558.6	1564	1029.6	1013.5	1.6	1.58	4.06	4.03	0.42	0.42	4.6206	4.5753
	0.5	1576	1573	1038.6	1041.8	1.63	1.63	3.87	3.87	0.41	0.41	4.3337	4.3337
	0.6	1588	1588	1057.5	1052.6	1.67	1.67	3.74	3.76	0.4	0.41	4.1374	4.1676
	0.7	1612	1592	1082.4	1076.8	1.74	1.71	3.55	3.66	0.39	0.4	3.8505	4.0166
	0.8	1667	1600	1093.4	1091.6	1.82	1.74	3.29	3.57	0.38	0.39	3.4579	3.8807

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Table 3: Experimental results for aqueous Zn^{2+}

Temp	Conc/M	U Zn	P Zn	Z Zn	β Zn	Lf Zn	Sn Zn
	0.1	1521.5	1015	1.54	4.25	0.42	4.0625
	0.2	1529.5	1024.3	1.56	4.17	0.42	3.9625
	0.3	1537.5	1046.9	1.6	4.04	0.41	3.8
303K	0.4	1546.1	1065.3	1.64	3.92	0.41	3.65
	0.5	1555	1080.7	1.68	3.82	0.4	3.525
	0.6	1562.8	1094.5	1.71	3.74	0.4	3.425
	0.7	1574.2	1107.4	1.74	3.64	0.39	3.3
	0.8	1582.5	1125.7	1.78	3.54	0.38	3.17
	0.1	1530	1013	1.54	4.21	0.42	4.0125
	0.2	1554	1020.9	1.58	4.05	0.41	3.8125
	0.3	1564	1043.4	1.63	3.91	0.4	3.6375
306K	0.4	1582	1062.4	1.68	3.76	0.4	3.45
	0.5	1588	1077.4	1.71	3.68	0.4	3.35
	0.6	1597	1093.4	1.74	3.58	0.4	3.8958
	0.7	1612	1104.3	1.78	3.48	0.39	3.7448
	0.8	1630	1123.6	1.83	3.34	0.38	3.5334
	0.1	1456.3	1010	1.47	4.66	0.45	4.575
	0.2	1467.2	1017.2	1.49	4.56	0.44	4.45
	0.3	1472.9	1040.4	1.53	4.43	0.44	4.2875
309K	0.4	1488.9	1057.2	1.57	4.26	0.43	4.075
	0.5	1492.4	1074.4	1.6	4.17	0.42	3.9625
	0.6	15021.1	1090.6	1.63	4.06	0.42	3.825
	0.7	1512.2	1101.5	1.66	3.97	0.41	3.7125
	0.8	1523.6	1120.6	1.7	3.84	0.41	3.55
	0.1	1553.3	1007.5	1.54	4.22	0.43	4.025
	0.2	1545.3	1014.1	1.56	4.12	0.42	3.9
	0.3	1554.6	1037.5	1.61	3.98	0.41	3.725
312K	0.4	1565.3	1054.6	1.65	3.87	0.41	3.5875
	0.5	1584	1073.7	1.7	3.71	0.4	3.3875
	0.6	1598	1087.8	1.73	3.59	0.39	3.2375
	0.7	1608.6	1097.4	1.76	3.52	0.39	3.15
	0.8	1634.6	1117.4	1.82	3.34	0.38	2.925
	0.1	1460	1003.2	1.46	4.67	0.45	4.5875
	0.2	1496	1011.4	1.51	4.41	0.44	4.2625
	0.3	1564	1034.2	1.61	3.95	0.42	3.6875
315K	0.4	1585	1051.4	1.66	3.78	0.41	3.475
	0.5	1592	1070.2	1.7	3.68	0.4	3.35
	0.6	1602.6	1084.2	1.73	3.59	0.4	3.2375
	0.7	1618.6	1098.5	1.77	3.47	0.39	3.0875
	0.8	1640.6	1117.2	1.83	3.32	0.38	2.9

5. Figures

At all temperatures the values of U, ρ increases gradually with increasing concentration of all salts in water and as expected there is decrease in density and rise in temperature. The increase in ultrasonic velocity and density along with increase in concentration suggests a moderate strong electrolytic nature in which all metals ions tend to attract water molecules. The gradual increase in U and ρ along with an increase in metallic salt concentration at all temperatures may be due to the increase in electrostrictive forces between M^{2+} ions and dipolar water molecules.

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A rise in temperature leads to less ordered structure and more spacing between M^{2+} ions and water molecules. As the temperature rises ultrasonic velocity increases density decrease with rise in temperature. It indicates decrease in intermolecular forces due to increase in thermal energy of the system which causes increases in volume expansion and hence increase in free path length. These are similar to that of pure water, where ultrasonic velocity increases and density decreases in view of in temperature. While the temperature increases the hydrogen bonds among water molecules break down and water molecules are formed. As a result, the temperature increases which leads to an increase in number of compacted water structure [13]. Ultrasonic velocity increases when there is an increase in the temperature for both pure water and aqueous metallic salt solutions in various concentrations. As a result that metallic ions behave as structure maker for the cluster of water molecules suggesting strong metallic ion solvent interactions [8,9,13].

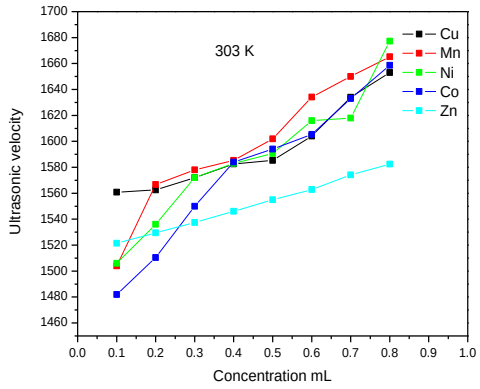

Figure 1: Ultrasonic velocity (U) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 303K

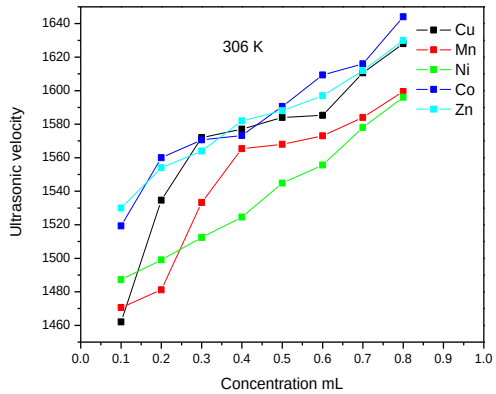

Figure 2: Ultrasonic velocity (U) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 306K

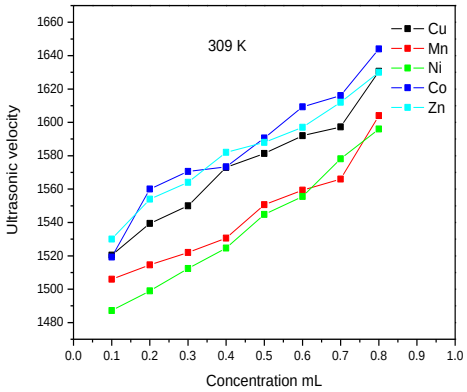

Figure 3: Ultrasonic velocity (U) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 309K

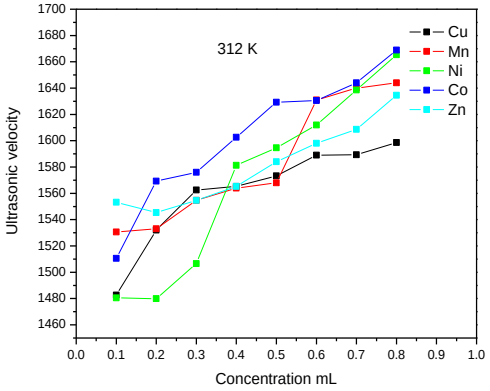

Figure 4: Ultrasonic velocity (U) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 312K

From table 1, 2 and 3 it is revealed that like ultrasonic velocity, Z shows a gradual increase with concentration and temperature. This conforms the increase in M^{2+} ions interactions with dipolar water molecules. When concentration of metallic salt increases, the thickness of charged ionic atmosphere may decrease due to the increase in ionic strength.

The compressibility of a solution is lower than that of solvent and it decreases with the increase in concentration of the solution. Moreover due to the increase in ionic concentration the electrostrictive forces make it the solute surrounded water molecules are more compactly packed and therefore compressibility decreases with increase in concentration. This suggests that there is a strong interactions between metallic ions and water molecules [12,13].

From table1,2 and 3 it is observed that intermolecular free length decreases with increase in metal ion

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concentration which confirms that there is a significant interaction between metal ions and water molecules. From this a structure promoting behaviour of metal ions and water molecules is observed. Therefore the increase in temperature and the intermolecular free length causes the increase in the thermal expansion of the solution.

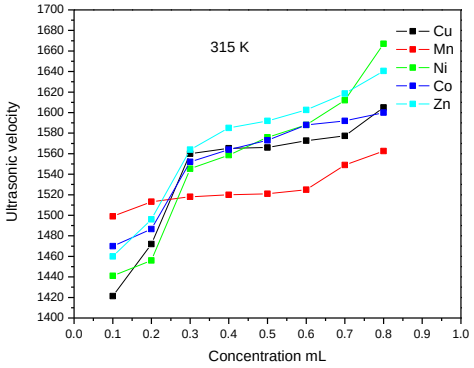

Figure 5: Ultrasonic velocity (U) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 315K

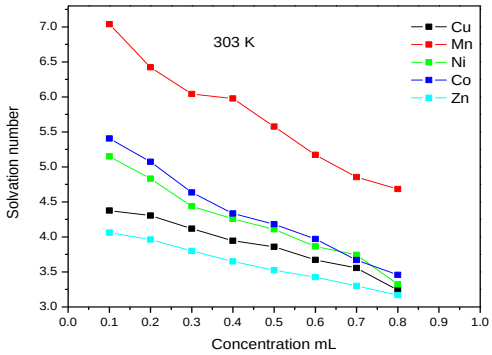

Figure 6: Solvation number (Sn) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 303K

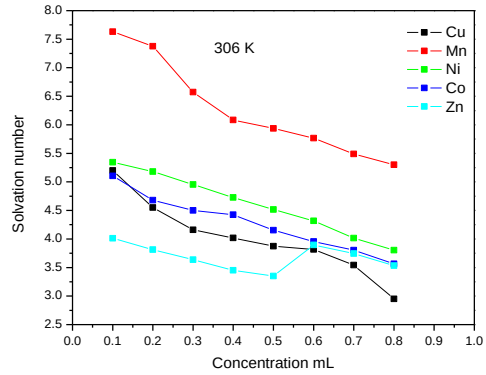

Figure 7: Solvation number (Sn) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 306K

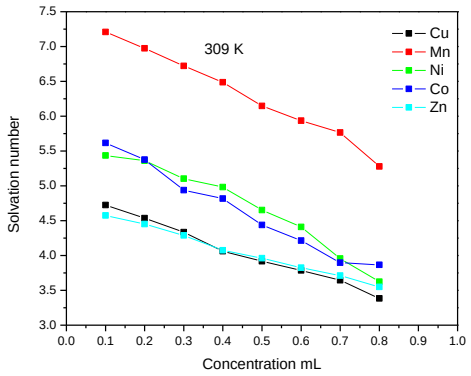

Figure 8 : Solvation number (Sn) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 309K

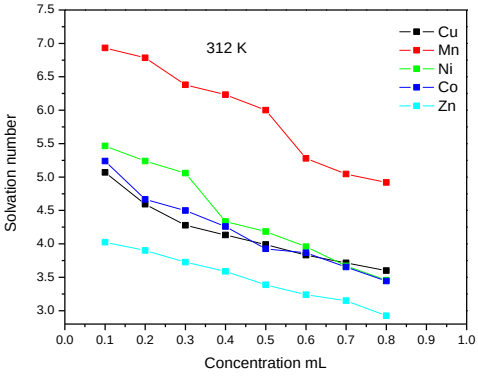

Figure 9: Solvation number (Sn) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 312K

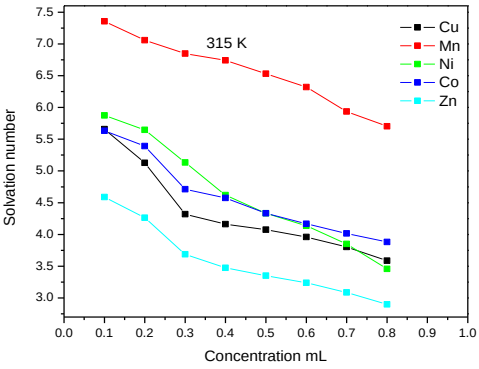

Figure 10 : Solvation number (Sn) for aqueous Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} solutions for wide range of various concentrations at 315K

The solvation number (Sn) of solute molecules shown on the basis of Frank & Wen model of solute solvent interactions [2,14], picture three different solvent structure regions in the neighborhood of solute. There is a layer of immobilized and compressed solvent molecules as a result

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of electrostrictive forces and other attractive forces exhibited by the metallic salt. This is called primary sheath of solvation. This layer is surrounded by slightly less compact or "structure – broken" affected by electrostrictive forces. This layer is called secondary sheath. The various forces should not affect outermost layer of the solvent. The solvation number in the primary sheath corresponds to coordination number. While the salvation number is concentration dependent, the coordination number is concentration independent.

From all the tables and Figure 2 it is suggested that Sn values decrease with an increase in the concentration and it may attain the primary solvation in pure crystalline state. The change in Sn with temperature is nonlinear for various concentration of metallic salt in aqueous medium. It shows that there is a strong interaction between metallic ions and water molecules.

Table 4: Experimental densities (ρ) and apparent molar volume (φ_v) for metallic salts in aqueous solutions.

T(K)	Molarity M ol dm^3	$\rho \times 10^{-3}$ kg m^{-3}					$\varphi_v \times 10^6$ m^3 mol^{-1}				
		Cu	Mn	Ni	Co	Zn	Cu	Mn	Ni	Co	Zn
303K	0.1	1015	1009	998.1	991.4	1015	125.2	78	256.8	326.3	162
	0.2	1024.3	1021	1008.4	1004.4	1024.3	97.9	62.6	193.9	214.8	135.2
	0.3	1046.9	1041	1024.5	1021.3	1046.9	89.1	31	152.2	163.7	125.2
	0.4	1065.3	1057	1044.5	1029.4	1065.3	84.1	25	121	159.7	121
	0.5	1080.7	1072	1060.2	1054.5	1080.7	82.1	23.3	110.5	122.2	118.7
	0.6	1094.5	1088	1072.8	1068.4	1094.5	81.6	20.4	108.4	115.9	116.5
	0.7	1117.9	1113.8	1097.5	1091.4	1107.4	81.1	17	92.4	98.4	117.1
	0.8	1125.7	1120	1108.2	1103.6	1125.7	72.6	5.8	89.6	98.2	115
306K	0.1	1013	1004	994.2	987.4	1013	152.2	128.2	297	368.2	179
	0.2	1019.2	1017	1004.2	1000.4	1020.9	117.9	82.5	215.6	235.7	155.1
	0.3	1039.9	1037	1020.6	1018.3	1043.4	112.1	43.9	165.5	173.6	137
	0.4	1059.8	1053	1040.5	1025.4	1062.4	94.5	38.9	131.7	170	125
	0.5	1077.2	1068	1050.2	1051.3	1077.4	90.8	34.6	130.7	128.7	124
	0.6	1090.4	1084	1068.2	1064.4	1093.4	88.4	26.7	116.1	122.7	123
	0.7	1113.2	1108.9	1094.3	1087.5	1104.3	86.8	20.33	97	103.8	120
	0.8	1121.8	1117	1104.4	1099.9	1123.6	79	12.06	94.1	102.8	118
309K	0.1	1009	1001	990.4	983.4	1010	163.3	158.6	336.5	410.4	197
	0.2	1016.7	1014.2	1000.4	996.4	1017.2	158	96.5	235.4	256.6	185
	0.3	1035.9	1033.9	1016.3	1014.3	1040.4	125.4	54.1	180.3	187.5	146
	0.4	1056.4	1049.2	1036.4	1020.6	1057.2	102.8	43.8	141.5	182.6	136
	0.5	1074	1064.1	1045.1	1048.4	1074.4	98.8	38.3	141.1	134.6	129
	0.6	1085.4	1079.6	1064.4	1060.4	1090.6	94.6	33.6	122.5	129.4	125
	0.7	1109.4	1103.2	1090.5	1083.9	1101.5	89.6	24.4	102	108.9	124
	0.8	1119.4	1113.4	1100.4	1095.3	1120.6	84.2	19.5	99.4	108.5	121
312K	0.1	1006	997.4	986.3	979.2	1007.5	188.3	195.3	379.5	455	213
	0.2	1015.4	1011.5	996.2	992.5	1014.1	169.9	110.1	257.4	274.2	210.5
	0.3	1031.2	1029.4	1012.4	1009.6	1037.5	141.2	73.3	193.8	245	156
	0.4	1052.7	1037.1	1032.5	1016.7	1054.6	112	68.9	151.5	203.9	143
	0.5	1069.4	1061.4	1041	1044.4	1073.7	105.7	43.4	149.5	142.2	134
	0.6	1081.2	1075.2	1060.7	1055.2	1087.8	103.6	40.58	128.6	138.2	130
	0.7	1105.4	1099.4	1085	1079.9	1097.4	94.3	24.5	121.1	109.6	129
	0.8	1115.5	1111.9	1095.4	1094.4	1117.4	89.6	21.6	108	69.6	125
315K	0.1	1002.8	995.4	983.4	976.5	1003.2	220.7	195.6	410.2	483.4	254
	0.2	1011.9	1008.2	993.4	989.6	1011.4	187.7	116.9	206.2	292.7	227
	0.3	1027.2	1025.3	1009.5	1006.6	1034.2	154.7	82.4	204	214.4	167
	0.4	1048.9	1033.5	1029.6	1013.5	1051.4	121.4	62.5	158.9	201.4	151
	0.5	1064.4	1057.8	1038.6	1041.8	1070.2	113.5	50.5	153.7	145.9	137
	0.6	1077.4	1071.9	1057.5	1052.6	1084.2	111.9	45.9	134.1	142.7	135
	0.7	1101.4	1095.4	1082.4	1076.8	1098.5	99.4	31.3	110.8	119	133
	0.8	1111.4	1107.4	1093.4	1091.6	1117.2	95.1	29.8	110.5	113	126

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From the experimental values of densities, apparent molar volume has been determined by respective relation [19,20].

$$\varphi_v = (M/\rho) - [1000 (\rho - \rho_0) /m\rho \rho_0] \text{ -------- } 1$$

M is the molar mass of metallic salt, ρ is the density of solute and ρ_0 is density of the solvent.

Table 5: Partial molar volume ($\varphi_v°$) and Solute-Solvent interaction parameter (S_v) of metallic salt in aqueous medium at various temperatures

	$\varphi_v°$X 10^6 m^3 mol^{-1}					S_v X 10^6 m^3 $mol^{-3/2}$ $kg^{1/2}$				
T(K)	Cu	Mn	Ni	Co	Zn	Cu	Mn	Ni	Co	Zn
303K	110.00	72.93	237.78	288.805	145.86	-46.2	-88.98	-215.97	-280.9	-43.55
306K	137.73	110.25	271.5	320.934	166.12	-77.82	-137.45	-256.75	-322.77	-69.13
309K	197.64	153.05	340.5	354.49	192.67	-184.56	-224.89	-296.55	-365.96	-105.11
312K	188.48	166.43	341.05	405.1	213.31	-139.809	-209.38	-251.28	-445.32	-129.46
315K	215.63	118.20	335.49	452.55	245.31	-172.42	-86.35	-332.11	-529.98	-175.71

The partial molar volume ($\varphi_v°$) of metallic salt has been calculated by using the Masson's equation [21]

$\varphi_v°$ and S_v have been calculated by the least square fitting of the apparent molar volume in the equation 2. The $\varphi_v°$ and S_v values are provided in table 5. The φv° are positive and S_v values are negative. The $\varphi_v°$ value gives the ion – solvent interactions and Sv value gives ion – ion interaction. The positive values of $\varphi_v°$ at all temperature provide the strong ion – solvent interactions [22]. The S_v values are negative but smaller than $\varphi_v°$ values, suggesting that there are weak ion-ion interactions [23]. The $\varphi_v°$ values decreases and S_v value also decreases with rise of temperature. The temperature dependence of $\varphi_v°$ can be expressed by the equation [24].

$$\varphi_v° = a_0 + a_1T + a_2T^2 \text{ ------- } 3$$

The Co – efficient a_i has been calculated by the least square fitting of $\varphi_v°$ in equation 3.

Table 6 : Hepler's Constant of metallic salt in aqueous medium ($\partial^2 \varphi_v°/\partial T^2$)

Hepler's Constant of metallic salt in aqueous medium (×10^6)				
Cu	Mn	Ni	Co	Zn
1.4495	2.52	8.3	5.328	1.405

For structure breaking solutes, the ($\partial^2 \varphi_v°/\partial T^2$) value is negative, and for structure forming solutes the ($\partial^2 \varphi_v°/\partial T^2$) value is positive [25]. From this the positive value of ($\partial^2 \varphi_v°/\partial T^{2)}$ suggests that all the metallic salt is water maker.

Table 7: Experimental viscosities (η) and constant A and B Calculated from Jone's Dole Equation for aqueous metallic salts solutions.

T(K)	Molarity	Cu			Mn			Ni		
		Viscosity	A	B	Viscosity	A	B	Viscosity	A	B
303K	0.1	0.9974			0.9899			1.1412		
	0.2	1.1402			0.9994			1.2268		
	0.3	1.2287			1.0442			1.3173		
	0.4	1.3463			1.1211			1.4242		
	0.5	1.4033	387.76	219.4	1.2366	185.49	88.21	1.5367	210.17	229.6

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	0.6	1.5116			1.3108			1.6268		
	0.7	1.6208			1.4805			1.7171		
	0.8	1.7109			1.5433			1.8601		
306K	0.1	0.8813			0.8742			1.0131		
	0.2	0.9964			0.9654			1.1261		
	0.3	1.1433			1.0642			1.2426		
	0.4	1.2326			1.1346			1.3171		
	0.5	1.3222	326.67	153.44	1.2776	179.53	62.69	1.4913	194.6	60.46
	0.6	1.4107			1.3314			1.5268		
	0.7	1.5633			1.4589			1.6364		
	0.8	1.6112			1.5677			1.7318		
309K	0.1	0.7914			0.7432			0.9918		
	0.2	0.8544			0.8914			1.0621		
	0.3	0.9602			0.9678			1.1264		
	0.4	1.0788			1.0541			1.2667		
	0.5	1.1227	286.27	136.88	1.1422	164.06	47.56	1.3168	180.3	59.98
	0.6	1.2465			1.2499			1.4117		
	0.7	1.3943			1.3488			1.5256		
	0.8	1.4772			1.4339			1.6727		
312K	0.1	0.6734			0.6399			0.8819		
	0.2	0.7533			0.7422			0.9221		
	0.3	0.8813			0.8361			1.0456		
	0.4	0.9427			0.9422			1.1231		
	0.5	1.0244	236.06	89.59	1.0456	149.42	18.86	1.2416	172.6	48.8
	0.6	1.1552			1.1229			1.3117		
	0.7	1.2602			1.3201			1.4146		
	0.8	1.3778			1.4226			1.5256		
315K	0.1	0.5989			0.5241			0.7164		
	0.2	0.6404			0.6672			0.8431		
	0.3	0.7207			0.7229			0.9425		
	0.4	0.8428			0.8422			1.0241		
	0.5	0.9842	199.5	63.62	0.9229	126.44	9.5	1.1245	119.94	30
	0.6	1.0932			1.0446			1.2813		
	0.7	1.1324			1.232			1.3461		
	0.8	1.2567			1.2498			1.4412		

Table 8: Experimental viscosities (η) and constant A and B Calculated from Jone's Dole Equation for aqueous metallic salts solutions

T (K)	Molarity	Co			Zn		
		Viscosity	A	B	Viscosity	A	B
303	0.1	1.008			0.9989		
	0.2	1.1145			1.1502		
	0.3	1.2261			1.2324		
	0.4	1.3451			1.3567		
	0.5	1.4561	207.91	60.2	1.4159	393.8	234.7
	0.6	1.5091			1.5226		
	0.7	1.6177			1.6379		

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	0.8	1.7022			1.7249		
306	0.1	0.9967			0.8974		
	0.2	1.004			0.9973		
	0.3	1.1717			1.1582		
	0.4	1.2791			1.2476		
	0.5	1.3451	199.67	55.8	1.3392	341.9	167.9
	0.6	1.4582			1.4258		
	0.7	1.5688			1.5788		
	0.8	1.6799			1.6244		
309	0.1	0.8881			0.7996		
	0.2	0.9998			0.8654		
	0.3	1.0122			0.9708		
	0.4	1.1889			1.0933		
	0.5	1.2762	185.34	50.4	1.1349	299.6	143.2
	0.6	1.3889			1.2568		
	0.7	1.4223			1.4095		
	0.8	1.5409			1.4864		
312	0.1	0.7699			0.6889		
	0.2	0.8921			0.7655		
	0.3	0.9468			0.8934		
	0.4	1.0954			0.9567		
	0.5	1.1224	169.64	41.3	1.0345	245	96.5
	0.6	1.2551			1.1677		
	0.7	1.3942			1.2779		
	0.8	1.4581			1.3854		
315	0.1	0.6734			0.6068		
	0.2	0.7881			0.6587		
	0.3	0.8219			0.7388		
	0.4	0.9841			0.8544		
	0.5	1.0459	158.08	29.26	0.9908	217.4	77.9
	0.6	1.1278			1.0998		
	0.7	1.2456			1.1487		
	0.8	1.3347			1.2699		

The viscosities values are listed in the table 7 & 8. From this it can be concluded as the temperature rises, η and concentration also increases. The viscosity data have been analyzed by using the Jones – Dole equation [26].

$$\eta/\eta_0 = 1 + A\, m^{1/2} + Bm \text{ ---------- } 4$$

Here, η and η_0 are the viscosities of solute and solvent respectively. A is constant independent of concentration and B is a Jones – Dole Co-efficient and is related to the effect of the ions on the structure of water [27,28]. Least square method is used to calculate the constant A and Jones – Dole Co- efficient B. The positive values of B at all temperatures indicate water structuring [28].

6. Conclusion

From ultrasonic velocity, density and viscosity values of $CuSO_4.5H_2O$, $MnSO_4.H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$ and ZnSo4.7H2O in aqueous solution at various temperatures are observed

i) Z, ρ and U increase, as the concentration and the temperature increase. Therefore there is strong interaction

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between transition metal ions and water molecules.

ii) β, L_f and S_n decrease, as the temperature and concentration increase. It is proved that there is a significant interaction between transition metal and water molecules.

iii) The $\varphi_v°$ values are positive at all temperatures and this indicates that there is a strong ion-solvent interaction in aqueous medium of all transition metals.

iv) The S_v values are negative suggesting the presence of weak ion-ion interactions.

v) The value of Jone-Dole coefficient B is positive. It denotes structure makering.

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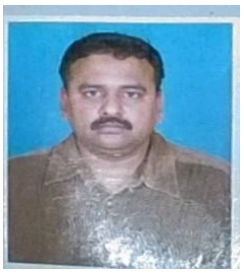

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