

Ultrasonic velocity and allied parameters of tetrahexylammonium iodidein binary mixtures of N, N-dimethylformamide and ethylmethylketone at different temperatures

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ABSTRACT:

Ultrasonic velocity, viscosity and density studies on solution of tetrahexylammonium Iodide (Hex₄NI) have been carried out in N,N-dimethylformamide (DMF), ethylmethylketone (EMK) and DMF-EMK solvent mixtures containing 0, 20, 40, 60, 80 and 100 mol % of DMF at 298, 308 and 318K. From the velocity, viscosity and density data values, various parameters namely, the adiabatic compressibility (β), Intermolecular free length (L_f), specific acoustic impedance (Z), free volume (V_f), internal pressure (π_i) and relaxation time (τ) have been calculated. All these parameters have been discussed separately to throw light on the solute-solvent and solvent-solvent interactions.

KEYWORDS: Adiabatic compressibility, intermolecular free length, specific acoustic impedance, free volume, internal pressure, relaxation time.

I. INTRODUCTION:

Ultrasonic study of liquids is a useful technique for understanding its physico-chemical properties. In recent years, ultrasonic velocity studies in many of the aqueous¹⁻², pure non-aqueous³⁻⁵ and mixed⁶⁻⁸ electrolytic solutions have led to new insights into the process of ion-ion and ion-solvent interactions. Only very little experimental data on the solvation behavior of ions are available in mixed non-aqueous solvents⁹. Whenever studies in mixed non-aqueous solvents are reported, attention has never given to the mutual interactions of the solvent molecules. Recently, ionic interactions and ion-solvent interactions for the tetraalkylammonium salts have been reported¹¹⁻¹⁴ from density and viscosity measurements.

Viscosity, density and ultrasonic velocity measurements and allied parameters derived from these are excellent tools to detect solute-solute and solute interactions. Such interactions have been studied in DMF and EMK mixture by usingHex₄NI as solute.

Ultrasonic velocities, densities and viscosities are measured over the entire composition range at 298, 308and 318K in order to understand the molecular interactions between the participating of components of these mixtures. Using the experimental data, various acoustical parameters like adiabatic compressibility (β), specific acoustic impedance (Z), intermolecular free length (L_f), viscous relaxation time (τ), free volume and internal pressure (π_i) are estimated. These parameters are used to interpret the intermolecular interactions such as solute–solvent and solute-solute interactions existing between these two components of binary mixtures.

II. EXPERIMENTAL:

Ultrasonic velocity were measured using interferometer (Model-81, supplied by Mittal Enterprises, New-Delhi) operating at afrequency of 1 MHz, which is a direct and simple device for measuring ultrasonic velocity in liquids.

Density measurement were carried out within a precision of $\pm 0.01\%$ using sealable pycnometer of capacity 20cm^3 , of pure solvents as well as solvent mixtures in a water thermostat, whose temperature was kept constant within the range of $\pm 0.5\%$.

Viscosity measurement were carried out with a precision of $\pm 0.2\%$ by using an calibrated Ubbelehode bulb level viscometer, whose flow time for doubly distilled water was found to be 584.2 \pm 0.1 s at 298.15 K. No kinetic energy correction was applied as the flow time was greater than 400 s. The values of viscosity and density of pure EMK and DMF were found to be in good agreement as reported in literature^{6,14-16}.

Water required for the calibration of the viscometer, pycnometer and ultrasonic velocity liquid cell was twice distilled over acidified KMnO₄ through a 750 mm long vertical fractionating column. Middle fraction of about 800-1000 ml was collected and stored in coloured bottle for use. The conductivity of distilled water was found to be $1-2 \times 10^{-6}$ s. The value of ultrasonic velocity for the conductivity water was found to be 1490 m/s at 298.15 K at 1 MHz, which is agreed well with literature value^{6,14-16}.

Dimethylformamide(DMF) and ethylmethylketone (EMK) (both from Research Laboratories Pvt Ltd Bombay) have been purified by the methods reported earlier¹⁴⁻¹⁶.

Tetrahexyl ammonium iodide (Hex₄NI) of analytical grade, Fluka, was dried and used as described earlier^{6,14}.

Different acoustical parameters such as adiabatic compressibility(β), specific acoustic impedance (Z), intermolecular free length (L_f), free volume (V_f), internal pressure(π_i) and viscous relaxation time (τ) have been calculated at different temperatures, with the help of ultrasonic velocity (u), density(ρ) and viscosity(η) values using the following relations^{14,17-20}:

Adiabatic compressibility (β):

The adiabatic compressibility values for various compositions of the binary solvent mixtures have been calculated from the measured ultrasonic velocities (u) and densities (ρ)

$$\beta = \frac{1}{u^2 \rho}$$

Acoustic Impedance (Z):

The specific acoustic impedance is related to density and ultrasonic velocity by the relation:

$$Z = u\rho$$

Free length (L_f) :

The free length in a solvent mixture is related to ultrasonic velocity and density as:

$$L_f = K_T \sqrt{\beta}$$

where K_T is time dependent constant whose value is 199.53x10⁻⁸ in MKS system.

Free Volume (V_f):

The free volume of binary mixture is given by

$$V_f = \left[\frac{M_{eff} u}{K\eta}\right]^{3/2}$$

where K is time independent constant whose value is 4.28×10^9 in MKSsystem and M_{eff}effective molecular weight of the liquid is given by

$$M_{eff} = X_1 M_1 + X_2 M_2$$

where $X_1 \& X_2$ are the mole fraction of first and second components and $M_1 \& M_2$ are the molecular weights of first and second components respectively.

Internal Pressure (π_i) :

Internal pressure is given by

$$\pi_i = \frac{bRT[K'\eta]^{\frac{1}{2}}}{M_{eff}c_{f}^{\frac{7}{6}}}\rho^{\frac{2}{3}}$$

where, b is the cubic packing factor which is assumed to be 2 in liquid systems.

 $K = 4.28 \times 10^9$ and is independent to the nature of liquid.

R is gas constant.

Relaxation Time (τ):

Relaxation can be calculated from viscosity coefficient (η), density and ultrasonic velocity of binary mixtures and given by

$$\tau = \frac{4\eta}{3\rho u^2}$$

III. RESULTS AND DISCUSSION:

The ultrasonic velocity, density and viscosity were measured forHex₄NI in DMF, EMK and EMK+DMF mixtures containing 0, 10, 20, 30, 40, 50, 60,70, 80, 90, 100 mol% of DMF in concentration range (0.02 - 0.1) mol dm⁻³ at 298, 308 and 318K.

The density, viscosity and ultrasonic velocity were found to vary linearly with solvent composition. Their values are, however, maximum in pure DMF and decrease with increaseof EMK content. This trend suggests that the molecular interactions are more at higher concentration of DMF in the binary mixture. With the increase in temperature, decrease in velocity, density and viscosity observed. This trend reveals that at higher temperature the molecular interactions between the components are low.

With increase in solute concentration, an increase in density, viscosity and ultrasonic velocity is observed. This may be interpreted to the structure former of the solvent due to the added solute and strong solvent-solvent and solute-solvent interactions.

Acoustical Parameters:

The experimentally determined values of ultrasonic velocity (u), density (ρ) and viscosity (η) along with calculated values of different acoustical parameters such as adiabatic compressibility (β), specific acoustic impedance (Z), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and viscous relaxation time (τ), at different temperatures are reported in the table 1.

Table -1:Summary of experimental data:concentration (c),density (ρ), ultrasonicvelocity (u),
viscosity (η)and the derived acoustical parameters of Hex ₄ NIin DMF-EMK
mixtures at different temperatures.

Temperature	c	<u> </u>	ρ	ηx10 ⁻³	βx10 ¹¹	Zx10 ⁻³	L _f x10 ¹²	τx10 ¹¹	$V_{f} x 10^{8}$	πi
		(ms ⁻¹)	(Kg m^{-3})	$(Nm^{-2}s)$	$(Kg^{-1}m s^{-1})$	$(Kg^{-1}m^{-2}s^{-1})$	(m)	(s)	$(m^3 mol^{-1})$	(atm)
100% DMF										
	0.00	1456.70	944.40	0.8025	49.90	1375.71	44.57	53.39	17.26	48.37
	0.02	1458.10	945.73	0.8259	49.73	1378.97	44.50	54.77	16.49	49.25
298K	0.04	1459.30	947.05	0.8480	49.84	1382.03	44.43	56.06	15.80	50.08
	0.06	1460.30	948.37	0.8696	49.45	1384.91	44.37	57.33	15.17	50.90
	0.08	1460.90	949.68	0.8916	49.34	1387.39	44.32	58.65	14.56	51.74
	0.10	1461.50	950.99	0.9120	49.23	1389.87	44.27	59.86	14.03	52.54
	0.00	1424.20	934.60	0.7103	52.75	1331.06	45.82	49.96	20.04	47.23
	0.02	1425.70	935.91	0.7314	52.57	1334.33	45.75	51.26	190.13	48.10
308K	0.04	1427.00	937.22	0.7502	52.40	1337.41	45.67	52.41	18.37	48.89
	0.06	1428.20	938.52	0.7687	52.24	1340.39	45.60	53.54	17.66	49.67
	0.08	1429.10	939.82	0.7866	52.10	1357.39	45.54	54.64	17.01	50.43
	0.10	1429.8	941.12	0.8046	51.98	1345.61	45.89	55.78	16.37	51.22
	0.00	1386.70	925.80	0.6348	56.17	1283.81	47.29	47.54	22.78	46.43
	0.02	1388.40	927.09	0.6535	55.96	1287.17	47.20	48.76	21.76	47.28
318K	0.04	1389.90	928.38	0.6647	55.76	1290.36	47.12	49.76	20.95	48.00
	0.06	1391.30	929.66	0.6847	55.57	1293.44	47.04	50.73	20.19	48.73
	0.08	1392.50	930.94	0.7002	55.40	1296.33	46.96	51.72	19.48	49.45
	0.10	1393.60	932.22	0.7151	55.23	1299.14	46.89	52.66	18.81	50.17
				8	0%DMF					
	0.00	1402.80	913.80	0.6987	55.61	1281.88	47.05	51.81	20.07	44.99
	0.02	1404.30	915.45	0.7199	55.39	1285.57	46.96	53.17	19.14	45.84
	0.04	1405.60	917.09	0.7387	55.19	1289.06	46.87	54.36	18.38	46.61
298K	0.06	1406.60	918.72	0.7566	55.01	1292.27	46.80	55.50	1767	47.37
	0.08	1407.50	920.35	0.7762	54.85	1295.39	46.73	56.76	16.96	48.16
	0.10	1408.30	921.97	0.7956	54.69	1298.41	46.66	58.01	16.29	48.96
	0.00	1368.40	904.10	0.6118	59.07	1237.17	48.49	48.18	23.61	43.74
	0.02	1370.00	905.69	0.6321	58.83	1240.80	48.39	49.58	22.42	44.63
308K	0.04	1371.60	907.28	0.6487	58.59	1244.43	48.30	50.67	21.52	45.38
	0.06	1372.80	908.87	0.6650	58.38	1247.70	48.21	51.77	20.68	46.13
	0.08	1374.10	910.46	0.6808	58.17	1251.06	48.12	52.80	19.91	46.84
	0.10	1375.10	912.04	0.6966	57.99	1254.15	48.05	53.86	19.18	47.58
	0.00	1334.80	894.80	0.5408	62.73	1194.38	49.97	45.23	27.36	42.70
	0.02	1336.60	896.42	0.5579	62.44	1198.16	49.86	46.45	26.06	43.53
318K	0.04	1338.20	898.03	0.5720	62.18	1201.74	49.76	47.42	25.05	44.24
	0.06	1339.70	899.64	0.5851	61.93	1205.25	49.66	48.32	24.16	44.91
	0.08	1341.00	901.24	0.5981	61.70	1208.56	49.56	49.21	23.31	45.57

	0.10	1342.10	902.84	0.6109	61.49	1211.70	49.48	50.09	22.52	46.25
				6	0%DMF	1				
	0.00	1351.10	884.80	0.6058	61.91	1195.45	49.65	50.01	23.50	41.78
	0.02	1352.80	886.71	0.6249	61.62	1199.54	49.53	51.35	22.39	42.60
298K	0.04	1354.20	888.61	0.6412	61.36	1203.36	49.43	52.46	21.49	43.32
	0.06	1355.50	890.51	0.6574	61.12	1207.09	49.33	53.57	20.64	44.05
	0.08	1356.80	892.41	0.6539	60.87	1210.82	49.23	54.69	19.84	44.78
	0.10	1357.90	894.30	0.6912	60.64	1214.37	49.14	55.89	19.04	45.54
	0.00	1316.00	874.60	0.5295	66.02	1150.97	51.27	46.61	27.65	40.59
	0.02	1317.70	876.52	0.5455	65.71	1154.99	51.15	47.79	26.39	41.36
308K	0.04	1319.20	888.43	0.5590	64.68	1172.02	50.74	48.21	25.38	42.36
	0.06	1320.70	880.34	0.5721	35.12	1162.67	50.92	49.68	24.45	42.70
	0.08	1322.00	882.24	0.5857	64.86	1166.32	50.81	50.65	23.55	43.38
	0.10	1323.20	884.14	0.5985	64.60	1169.89	50.71	51.55	22.73	44.04
	0.00	1275.80	864.70	0.4633	71.05	1103.18	53.19	43.89	32.25	39.51
	0.02	1277.60	866.64	0.4792	70.69	1107.22	53.05	45.17	30.59	40.34
318K	0.04	1279.30	868 58	0 4913	70.35	1111117	52.92	46.08	29.42	41.01
	0.04	1280.90	870.51	0.5031	70.02	1115.04	52.92	46.00	29.42	41.66
	0.08	1282.30	872 11	0.5051	69.71	1118 73	52.68	40.27	20.32	42.67
	0.00	1282.50	874 35	0.5252	60.41	1110.75	52.00	47.77	27.55	42.07
	0.10	1203.00	074.33	0.5252	09.41 0%DMF	1122.32	54.51	+0.01	20.42	72.72
40%DMF										
	0.00	1300.10	859 51	0.5210	68 72	1113.20	52.45	40.00	21.02	30.04
	0.02	1202.20	860.70	0.5349	68.40	1117.01	52.51	49.02	20.08	39.32
208K	0.04	1303.30	860.70	0.5470	68.40	1121.73	52.18	49.94 50.96	23.70	39.93
290K	0.06	1304.70	862.90	0.5603	68.08	1125.83	52.06	50.86	24.77	40.59
	0.08	1306.10	865.10	0.5728	67.76	1129.91	51.94	51.75	23.91	41.21
	0.10	1307.10	867.29	0.5855	67.49	1133.64	51.83	52.68	23.07	41.86
2001	0.00	1263.80	846.00	0.4554	74.01	1069.18	54.28	44.94	32.62	37.57
	0.02	1265.50	848.20	0.4719	73.62	1073.40	54.14	46.32	30.86	38.41
308K	0.04	1267.20	850.38	0.4851	73.23	1077.60	54.00	47.37	29.56	39.10
	0.06	1268.80	852.56	0.4969	72.86	1081.73	53.86	48.27	28.44	39.74
	0.08	1270.20	854.74	0.5089	72.51	1085.69	53.73	49.20	27.83	40.39
	0.10	1271.50	856.91	0.5205	72.18	1089.56	53.61	50.09	26.40	41.03
	0.00	1222.50	835.30	0.3940	80.11	1021.15	56.47	42.08	38.57	36.37
	0.02	1224.30	837.52	0.4101	79.66	1025.38	56.31	43.56	36.25	37.27
	0.04	1226.10	839.73	0.4212	79.22	1029.59	56.19	44.49	34.77	37.92
318K	0.06	1227.80	841.93	0.4318	78.79	1033.72	56.01	45.36	33.43	38.56
	0.08	1229.40	844.13	0.4420	78.38	1037.77	55.86	46.19	32.21	39.18
	0.10	1230.80	846.33	0.4518	78.00	1041.66	55.73	46.99	31.09	39.78
				2	0%DMF					
	0.00	1245.70	827.50	0.4467	77.88	1030.82	55.68	46.38	32.86	35.73
	0.02	1247.30	830.01	0.4602	77.44	1035.27	55.53	47.52	31.36	36.43
298K	0.04	1248.80	832.51	0.4721	77.02	1039.64	55.38	48.48	30.12	37.06
	0.06	1250.20	835.00	0.4834	76.62	1043.92	55.23	49.39	29.00	37.68
	0.08	1251.50	837.49	0.4954	76.24	1048.12	55.09	50.36	27.88	38.32
	0.10	1252.70	839.98	0.5080	75.86	1052.24	54.96	51.85	26.78	38.99
	0.00	1206.40	817.50	0.3914	84.05	986.23	57.85	46.86	38.19	34.84
	0.02	1208.10	819.99	0.4080	83.56	990.63	57.68	45.46	35.81	35.74
308K	0.04	1209.80	822.47	0.4201	83.07	995.03	57.51	46.53	34.21	36.42
	0.06	1211.30	824.95	0.4310	82.62	999.26	57.35	47.48	32.85	37.06
	0.08	1212.80	827.42	0.4417	82.17	1003.50	57.19	48.39	31.60	37.68
	0.10	1214.30	829.89	0.4523	81.72	1007.74	57.04	49.28	30.42	38.31
318K	0.00	1165.00	806.50	0.3365	91.36	939.57	60.31	40.99	45.46	33.64
	0.02	1166.70	809.00	0.3504	90.81	943.86	60.13	42.43	42.70	34 48
	0.02	1168.40	811 50	0.3602	90.27	948.16	59.95	43 35	40.90	35.11
	0.04	1170.00	813.90	0.3690	89.74	952 37	59.77	44 15	39.36	35 70
	0.00	1171.60	816.48	0 3776	89.74	956.59	59.60	44.92	37.95	36.78
	0.00	1173.00	818 07	0.3850	88 7/	960.65	59.00	45.66	36.65	36.20
	0.10	1175.00	010.77	0.5057	00.74	700.05	57.77	-J.00	50.05	50.04

Ultrasonic velocity and allied parameters of tetrahexylammonium...

0%DMF(Pure EMK)										
-	0.00	1195.60	799.90	0.3855	87.46	956.36	59.01	44.95	38.54	33.12
298K	0.02	1197.10	802.69	0.3972	86.93	960.90	58.83	46.04	36.77	33.78
	0.04	1198.50	805.48	0.4075	86.43	965.37	58.66	46.96	35.31	34.39
	0.06	1199.90	808.26	0.4173	85.93	969.83	58.49	47.81	33.99	34.97
	0.08	1201.20	811.04	0.4274	85.45	974.22	58.33	48.70	31.72	35.56
	0.10	1202.40	813.81	0.4385	84.99	978.53	58.17	49.69	31.40	36.20
	0.00	1153.30	788.80	0.3441	95.31	909.72	61.60	43.73	43.30	32.63
308K	0.02	1154.90	791.58	0.3577	94.71	914.20	61.41	45.17	40.77	33.43
	0.04	1156.40	794.36	0.3678	94.14	918.60	61.22	46.17	39.03	34.06
	0.06	1157.90	797.12	0.3771	93.57	922.99	61.03	47.05	37.51	34.65
	0.08	1159.30	799.89	0.3862	93.02	927.31	60.86	47.90	36.12	35.24
	0.10	1160.00	802.65	0.3952	92.59	931.07	60.71	48.79	34.78	35.83
318K	0.00	1110.30	776.60	0.2975	104.45	862.26	64.49	41.43	50.09	31.59
	0.02	1111.90	779.40	0.3100	103.78	866.61	64.28	42.89	47.74	32.41
	0.04	1113.40	782.19	0.3186	103.13	870.89	64.08	43.81	45.73	33.01
	0.06	1114.90	784.99	0.3265	102.49	875.19	63.88	44.62	43.99	33.58
	0.08	1116.30	787.78	0.3342	101.87	879.40	63.68	45.39	42.39	34.14
	0.10	1117.80	790.56	0.3414	101.24	883.69	63.49	46.08	40.97	34.68

Ultrasonic velocity and allied parameters of tetrahexylammonium...

Adiabatic Compressibility

The adiabatic compressibilities (β) have been evaluated at 298, 308 and 318K of the electrolyte solutions reported in Table-1. It may be noted that a slight decrease in the adiabatic compressibility (β) is observed with increase in concentration of Hex₄NI at all the temperatures. This decrease can be interpreted in terms of electrostatic effect of the solute on the surrounding solvent molecules, which results to relatively incompressible. This also gives an indication of the fact that decrease in compressibility is due to electrostriction effect i.e. caused by solute at a particular ionic strength and dielectric constant of the medium. This observation is consistent with some previous works²¹⁻²².

The adiabatic compressibility (β) increases with the increase in content of EMK in the mixture at all the temperatures. This trend shows that the molecular attraction are more at lower concentration of EMK and higher concentrations the attractions are less due to steric hindrance and for EMK+DMF system the dipole- dipole interactions/associations between EMK and DMF molecules are more at higher temperature than at lower temperature.Similar observations were made by Patial¹⁴, Syalet al²⁰ and Kumar et al²³. With the increase of temperatures, β - values of mixture increase, indicating temperature dependence of β and increase of interactions between molecules of solvents mixture.

Acoustic Impedance (Z)

The acoustic impedance (Z) values of Hex₄NI in DMF, EMK and DMF-EMK mixtures have been evaluated for different concentrations at different temperatures from the velocity and density data using equation given earlier. The calculated Z values given in the Table-1 for various compositions show a gradual increase with increase in concentration of solute in DMF, EMK and DMF-EMK mixtures. This is in agreement with theoretical requirement as both ultrasonic velocity (u) and density (ρ) increase with the increase of concentration salt. Linear increase of Z with concentration can be attributed to the presence of strong solute-solvent interaction. With increase of temperature, Z values decrease for all the studied mixtures, this is in accordance with u and ρ , as both u and ρ decrease with increase with temperature.

The acoustic impedance (Z) values decrease with the decrease of DMF content to EMK+DMF mixture. This may be due to change of intermolecular and solute – solvent interaction between EMK and DMF molecules with the addition of EMK to DMF in mixture^{14,24}.

IntermolecularFree Length (L_f)

The free length of system is a measure of intermolecular interaction between the components in the binary mixtures. The increase in free length indicates weakening of intermolecular attraction. The velocity of ultrasonic waves should increase if the intermolecular free length decreases as a result of mixing of two components. Erying and Kincaid²⁵ have proposed that L_f is a predominating factor in determining the variation of ultrasonic velocity in solutions. The change in free length also indicates that there is significant interaction between the solute and solvent molecules due which structural arrangement is also affected.

The calculated values of intermolecular free length (L_f) of the studied solution solutions for Bu_4NBr at different temperatures are presented in Table-1. The intermolecular free length (L_f) values decreases with increase of salt concentration and increase with the decrease of DMF content inDMF-EMK mixtures. The decrease of L_f with increase of concentration suggests the presence of strong solute - solvent interaction²⁶⁻²⁷.

 $L_{\rm f}$ values decrease with the increase of DMF content in the DMF-EMK mixtures at all temperatures which show dipole-dipole interactions are more at higher content of DMF in the given system^{14,24}.

With increase in temperature, the magnitude of L_f increases showing the presence of solute-solvent interactions. Similar observations were made by Syalet al²⁰, Patial¹⁴ and Ali²⁴.

Thus relaxation time data which include the values of velocity (u), density (ρ) and viscosity (η) of solution systems are quite valuable in understanding the structure of solution systems, solute-solvent interactions inter-molecular and intra-molecular interactions.

Free Volume (V_f):

It can be defined as the average volume in which the central molecule can move inside the hypothetical cell due to repulsion of surrounding molecules. Free volume can also be referred as the void space between the molecules i.e. volume present as holes of monomeric size, due to irregular packing of molecules.

It is evident from the Table-1 that V_f values in general decrease in magnitude with the increase of concentration of Hex₄NI. However, with the increase of EMK content in EMK-DMF mixture, V_f values increase. Increase of temperature also increases the magnitudes of V_f .

This behavior of V_f is opposite to that observed for internal pressure (π_i) with regard to composition of solvent system and increase of temperature. Similar behavior has been reported in DMSO + H₂O system²⁸.

Internal Pressure (π_i) :

Internal pressure (π_i) is the resultant of forces of attraction and repulsion between solute and solvent molecules of solution.

Internal pressure (π_i) values for Hex₄NI at different temperatures in EMK-DMF mixtures have been calculated by the equation given and have been presented in Table-1.

It is evident from the Table-1 that π_i values increase with increase of solute concentration and decrease with increase of temperature in all composition.

Increase of π_i with concentration of Hex₄NI indicates increase in intermolecular interactions due to the forming of aggregates of solvent molecules around the solute, which affect the structural arrangement of solution system. This may also be attributed to the presence of solute-solvent interactions.

Internal pressure (π_i) values show decreasing trend with the increase of EMK content in the EMK + DMF system and also decrease with rise in temperature. This predicts the presence of solute- solvent interactions.

Internal pressure (π i) decreases with rise in temperature because of thermal agitation of ion from each other due to increasing thermal energy, which reduces the possibility for interactions and reduces the cohesive forces and ultimately leads to a decrease in the internal pressure. Similar observations were made by Chauhanet al²⁹ and Patial¹⁴.

Relaxation Time (τ):

As per equation given, viscous relaxation time (τ) is directly proportional to viscosity and adiabatic compressibility of solution or solvent system. Hence, viscosity, density and ultrasonic velocity of solution systems play important plays important in evaluation of acoustical relaxation time (τ) . The values of viscous relaxation time (τ) for Hex₄NI have been evaluated in DMF-EMK mixtures and have been given in the Table-1 at 298, 308 and 318K.

From the Table-1, it has been found that viscous relaxation time (τ) values increases with increase in concentration of solute in all the studied solvent systems at all the temperatures. Acoustic relaxation time decreases with rise in temperature, in accordance with the increase of temperature.

The relaxation time (τ) values decrease with increase of EMK content in DMF-EMK mixtures. Tis may be account for the decrease of dielectric constant of the medium and change of intermolecular and intra-molecular interactions between the DMF and EMK molecules.

Increase of $\boldsymbol{\tau}$ with increase of solute concentration may be attributed to the presence of solute-solvent interaction.

Similar results for PVP polymer as solute in DMSO+ H_2O has been reported by Syal et²⁸ and for tetraalkylammonoum salts by Patialet al⁶.

The increase of relaxation time of pyrogallol solution with concentration as reported in literature³⁰ is also in agreement with our results.

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