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Study of acoustic nature of tetrapentylammonium bromide in N,N-dimethyl-ethylmethyl ketone systems at different temperatures

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ABSTRACT

Ultrasonic velocity, viscosity and density studies on solution of tetrapentylammonium bromide (Pen_4NBr) in N,N-dimethylformamide, ethylmethylketone (EMK) and DMF-EMK solvent mixtures containing 0, 20, 40, 60, 80 and 100 mol % of DMF at 298, 308 and 318K have been reported. 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

1. INTRODUCTION

The principle related to acoustic behavior, viscosity etc. can be used to study the physicochemical behavior and molecular interaction such as ion-solvent interactions and solvent-solvent interactions involved in any electrolyte system[1-2]. The knowledge of solvation behavior of a species is very essential to understand the solution chemistry[1]. The study of thermodynamic properties of binary liquid mixtures has proved to be a useful tool in elucidating structural interactions of components[3-5]. Ultrasonic velocity and other acoustic parameters such as adiabatic compressibility (β), Intermolecular free length (L_f), specific acoustic impedance (Z), free volume (V_f), internal pressure (π_i) and relaxation time (τ) are very useful to detect the solute-solvent interactions[7]. The present investigation reports the ultrasonic velocity, density and viscosity studies of tetrapentylammonium bromide (Pen_4NBr) in ethylmethylketone (EMK) and N,N-dimethylformamide (DMF) at 298, 308 and 318. K. Both EMK and DMF belong to similar class of dipolar solvents. In pure state both have no tendencies to associate through dipole-dipole interactions which have been observed in dimethylsulphoxide (DMSO)[9-10].

In order to understand the molecular interactions between the participating of components of these mixtures ultrasonic velocities, densities and viscosities are measured over the entire composition range at 298, 308 and 318 K 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.

2. EXPERIMENTAL

Water required for the calibration of the viscometer, pycnometer and ultrasonic velocity liquid cell was twice distilled over acidified $KMnO_4$ 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 x 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[3,11-12].

Ultrasonic velocity were measured using interferometer (Model-81, supplied by Mittal Enterprises, New-Delhi) operating at a frequency 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 ±0.01% using sealable pycnometer of capacity 20 cm^3, of pure solvents as well as solvent mixtures in a water thermostat, whose temperature was kept constant within the range of ±0.5%.

Viscosity measurement were carried out with a precision of ±0.2% by using an calibrated Ubbelehode bulb level viscometer, whose flow time for doubly distilled water was found to be 584.2 ± 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[3,11-12].

Dimethylformamide (DMF) and ethylmethylketone (EMK) (both from Research Laboratories Pvt Ltd Bombay) have been purified by the methods reported earlier[3,12].

Tetrapentyl ammonium bromide (Pen_4NBr) of analytical grade, Fluka, was dried and used as described earlier[13-15].

Different acoustical parameters such as adiabatic compressibility(β), specific acoustic impedance (Z), intermolecular free length (L_f) viscous relaxation time(τ), free volume (V_f) and internal pressure(π_i) have been calculated at different temperatures, with the help of ultrasonic velocity (u), density(ρ) and viscosity(η) values using the following relations[3,16-19]:

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)

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

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 199.53×10^{-8} in MKS system.

Acoustic Impedance (Z)

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

$$Z = u\rho$$

Relaxation Time (τ)

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

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

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 MKS system and M_{eff} effective molecular weight of the liquid is given by

$$M_{eff} = X_1M_1 + X_2M_2$$

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

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

Where, b is the cubic packing factor which is assumed to be 2 in liquid systems.
K = 4.28×10^9 and is independent to the nature of liquid.
R is gas constant.

3. RESULTS AND DISCUSSION

The ultrasonic velocity, density and viscosity were measured for Pen_4NBr 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 increase of EMK content. This trend suggests that the dipole – dipole 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.

3.1. 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), viscous relaxation time (τ), free volume (V_f) and internal pressure (π_i) at different temperatures are reported in the table 1.

Table 1. Summary of experimental data: Concentration (c), Density (ρ), ultrasonic velocity (u), viscosity (η) and the derived acoustical parameters of Pen_4NBr DMF-EMK mixtures at different temperatures.

Temperature	c	u (ms^{-1})	ρ ($Kg\ m^{-3}$)	$\eta x10^{-3}$ ($Nm^{-2}s$)	$\beta x10^{11}$ ($Kg^{-1}m\ s^{-1}$)	$Zx10^{-3}$ ($Kg^{-1}m^{-2}s^{-1}$)	$L_f x10^{12}$ (m)	$\tau x10^{11}$ (s)	$V_f x10^{8}$ (m^3mol^{-1})	πi (atm)
100% DMF										
298K	0.00	1456.70	944.40	0.8025	49.92	1375.13	44.58	53.42	17.29	48.35
	0.02	1458.20	945.08	0.8232	49.76	1378.12	44.51	54.62	16.57	49.14
	0.04	1459.60	945.76	0.8440	49.63	1380.43	44.45	55.85	15.92	49.91
	0.06	1460.80	946.44	0.8635	49.51	1382.56	44.40	57.01	15.34	50.65
	0.08	1461.80	947.11	0.883	49.41	1384.49	44.35	58.17	14.79	51.38
	0.10	1462.80	947.77	0.9034	49.31	1386.40	44.43	59.39	14.25	52.15
308K	0.00	1424.20	934.60	0.7103	52.75	1331.06	45.83	49.96	20.04	47.23
	0.02	1425.70	935.28	0.7279	52.60	1333.43	45.76	51.05	19.27	47.97
	0.04	1427.00	935.95	0.7447	52.47	1335.60	45.70	52.10	18.57	48.66
	0.06	1428.30	936.62	0.7612	52.34	1337.77	45.65	53.11	17.92	49.36
	0.08	1429.40	937.28	0.7776	52.22	1339.75	45.60	51.14	17.31	50.04
	0.10	1430.40	937.94	0.7944	52.11	1341.63	45.55	55.19	16.71	50.75
318K	0.00	1396.70	925.80	0.6348	55.37	1293.07	46.87	46.87	23.03	46.26
	0.02	1388.20	926.49	0.6509	56.01	1286.15	48.61	48.61	21.89	47.16
	0.04	1389.50	927.17	0.6652	55.86	1288.30	49.55	49.55	21.14	47.82

	0.06	1390.70	927.85	0.6793	55.73	1290.36	50.47	50.47	20.42	48.49
	0.08	1391.80	928.53	0.6934	55.60	1292.33	51.40	51.40	19.75	49.14
	0.10	1392.80	929.20	0.7070	55.48	1294.19	52.30	52.30	19.12	49.79
80%DMF										
298K	0.00	1402.80	913.80	0.6987	55.61	1281.88	47.05	51.81	20.08	44.99
	0.02	1404.50	914.74	0.7167	55.42	1284.75	46.97	52.96	19.28	45.71
	0.04	1406.00	915.68	0.7338	55.24	1287.45	46.90	54.05	18.57	46.40
	0.06	1407.40	916.61	0.7505	55.08	1290.04	46.83	55.12	17.90	47.09
	0.08	1408.90	917.54	0.7675	54.91	1292.72	46.75	56.19	17.27	47.77
	0.10	1410.00	918.47	0.7851	54.76	1295.04	46.69	57.33	16.64	48.49
308K	0.00	1368.40	904.10	0.6118	59.07	1237.17	48.49	48.18	23.61	43.74
	0.02	1369.9	905.07	0.6271	58.88	1239.86	48.41	49.23	22.69	44.44
	0.04	1371.4	906.03	0.6414	58.69	1242.53	48.34	50.19	21.89	45.08
	0.06	1372.7	906.99	0.6554	58.51	1245.03	48.26	51.13	21.13	45.73
	0.08	1374.1	907.94	0.6693	58.33	1247.60	48.19	52.06	20.43	46.36
	0.10	1375.1	908.88	0.6833	58.19	1249.80	48.13	53.01	19.74	47.01
318K	0.00	1334.8	894.80	0.5408	62.73	1194.38	49.97	45.23	27.36	42.70
	0.02	1336.4	895.75	0.5590	62.51	1197.80	49.89	46.59	25.98	43.55
	0.04	1337.9	896.70	0.5731	62.30	1199.70	49.80	47.61	24.97	44.24
	0.06	1339.5	897.64	0.5863	62.09	1203.39	49.72	48.54	24.08	44.90
	0.08	1340.8	898.58	0.5992	61.90	1204.82	49.64	49.46	23.24	45.53
	0.10	1342.00	899.52	0.6118	61.73	1207.16	49.57	50.35	22.47	46.17
60%DMF										
298K	0.00	1351.10	884.80	0.6058	61.91	1195.45	49.65	50.01	23.50	41.78
	0.02	1352.80	885.99	0.6213	61.67	1198.57	49.55	51.09	22.58	42.46
	0.04	1354.30	887.17	0.6362	61.46	1201.49	49.46	52.13	21.74	43.11
	0.06	1355.90	888.34	0.6501	61.23	1204.50	49.37	53.07	21.00	43.73
	0.08	1357.30	889.51	0.6646	61.02	1207.32	49.29	54.08	21.27	44.36
	0.10	1358.7	890.69	0.6800	60.82	1210.18	49.21	55.14	19.53	45.04
308K	0.00	1316.00	874.60	0.5295	66.02	1150.97	51.27	46.61	27.65	40.59
	0.02	1317.60	875.82	0.5433	65.77	1153.98	51.17	47.64	26.54	41.26
	0.04	1319.20	877.04	0.5557	65.52	1156.99	51.07	48.54	25.61	41.87
	0.06	1320.70	878.25	0.5678	65.28	1159.91	50.98	49.42	24.73	42.47
	0.08	1322.20	879.46	0.5797	65.04	1162.82	50.89	50.27	23.92	43.06
	0.10	1323.60	880.66	0.5919	64.82	1165.64	50.80	51.15	23.13	43.67
318K	0.00	1275.80	864.70	0.4633	71.05	1103.18	53.19	43.89	32.25	39.51
	0.02	1277.50	865.91	0.4789	70.76	1106.20	53.08	45.18	30.62	40.31
	0.04	1279.10	867.11	0.4906	70.49	1109.12	52.97	46.11	29.47	40.94
	0.06	1280.80	868.31	0.5018	70.20	1112.13	52.87	46.97	28.43	41.55
	0.08	1282.20	869.51	0.5125	69.95	1114.89	52.77	47.80	27.48	42.13
	0.10	1283.80	870.69	0.5232	69.69	1117.79	52.67	48.61	26.58	42.72
40%DMF										
298K	0.00	1300.10	856.30	0.5210	69.09	1113.28	52.45	48.00	27.82	38.64
	0.02	1301.70	857.75	0.5349	68.80	1116.53	52.33	49.07	26.68	39.30
	0.04	1303.20	859.30	0.5476	68.52	1119.84	52.30	50.03	25.70	39.91
	0.06	1304.70	860.64	0.5603	68.26	1122.88	52.13	50.99	24.77	40.52
	0.08	1306.00	862.08	0.5728	68.01	1125.88	52.04	51.94	23.90	41.12
	0.10	1307.40	863.51	0.5855	67.75	1128.95	51.93	52.89	23.08	41.73
308K	0.00	1263.80	846.00	0.4554	74.01	1069.18	54.28	44.94	32.62	37.57
	0.02	1265.40	847.50	0.4694	73.69	1072.43	54.16	46.12	31.11	38.29
	0.04	166.90	849.00	0.4808	73.39	1075.60	54.05	47.04	29.94	38.89

	0.06	1268.40	850.49	0.4918	73.08	1078.76	53.94	47.92	28.87	39.48
	0.08	1269.80	851.97	0.5025	72.80	1081.83	53.83	48.77	27.89	40.05
	0.10	1271.20	853.45	0.5132	72.51	1084.91	53.73	49.62	26.96	40.63
318K	0.00	1222.50	835.30	0.3940	80.11	1021.15	56.47	42.08	38.57	36.37
	0.02	1224.00	836.80	0.4092	79.77	1024.24	56.35	43.52	36.55	37.21
	0.04	1225.30	838.30	0.4200	79.45	1027.17	56.24	44.49	34.88	37.84
	0.06	1227.10	839.79	0.4299	79.08	1030.51	56.11	45.33	33.62	38.42
	0.08	1228.60	841.28	0.4395	78.75	1033.60	55.99	46.15	32.45	38.99
	0.10	1230.00	842.77	0.4488	78.43	1036.61	55.88	46.93	31.38	39.55
20%DMF										
298K	0.00	1245.70	827.50	0.4467	77.88	1030.82	55.68	46.38	32.86	35.73
	0.02	1247.30	829.20	0.4590	77.52	1034.26	55.55	47.44	32.48	36.36
	0.04	1248.80	830.90	0.4707	77.17	1037.63	55.43	48.43	30.25	36.96
	0.06	1250.20	832.60	0.4810	76.84	1040.92	55.31	49.28	29.21	37.52
	0.08	1251.60	834.29	0.4918	76.52	1044.20	55.19	50.17	28.19	38.08
	0.10	1253.00	835.98	0.5025	76.19	1047.48	55.08	51.05	27.23	39.65
308K	0.00	1206.40	817.50	0.3914	84.05	986.23	57.85	43.86	38.19	34.84
	0.02	1207.90	819.26	0.4505	83.66	989.58	57.71	45.18	30.86	37.53
	0.04	1209.30	521.02	0.4155	83.29	992.86	57.58	46.14	34.76	36.18
	0.06	1210.70	822.78	0.4252	82.92	996.14	57.46	47.01	33.49	36.75
	0.08	1212.10	824.52	0.4348	82.55	999.40	57.33	47.86	32.32	37.31
	0.10	1213.40	826.26	0.4441	82.20	1002.58	57.21	48.67	31.23	37.86
318K	0.00	1165.00	806.50	0.3365	91.35	939.57	60.31	40.99	45.46	33.64
	0.02	1166.50	808.24	0.3496	90.93	942.81	60.17	42.38	42.84	34.42
	0.04	1168.50	809.97	0.6589	90.42	946.45	60.00	43.27	41.26	35.01
	0.06	1169.50	811.70	0.3674	90.07	949.28	59.88	44.12	39.59	35.57
	0.08	1170.90	813.43	0.3755	89.67	952.45	59.75	44.89	38.24	36.10
	0.10	1172.30	815.15	0.3835	89.27	955.60	59.61	45.64	36.96	36.63
0%DMF(Pure EMK)										
298K	0.00	1195.60	799.90	0.3855	87.46	956.36	59.01	44.95	38.54	33.12
	0.02	1197.10	801.84	0.3962	87.03	959.88	58.86	45.97	36.91	33.72
	0.04	1198.50	803.77	0.4060	86.61	963.32	58.72	46.89	35.51	34.27
	0.06	1199.90	805.70	0.4153	86.21	966.76	58.84	47.74	34.24	34.81
	0.08	1201.20	807.63	0.4246	85.81	970.13	58.45	48.58	33.04	35.34
	0.10	1202.50	809.56	0.4339	85.42	973.50	58.32	49.42	31.90	35.88
308K	0.00	1153.30	788.80	0.3441	95.31	909.72	62.60	43.73	43.30	32.63
	0.02	1154.70	790.79	0.3551	94.84	913.13	61.45	44.90	41.21	33.29
	0.04	1156.10	792.78	0.3637	94.37	916.53	61.30	45.77	39.67	33.83
	0.06	1157.50	794.77	0.3720	93.91	919.95	61.15	46.58	38.27	34.36
	0.08	1158.90	796.76	0.3802	93.45	923.37	61.00	47.37	36.96	34.88
	0.10	1160.20	798.74	0.3880	93.01	926.70	60.85	48.12	35.76	35.39
318K	0.00	1110.30	776.60	0.2975	104.45	862.26	64.49	41.43	50.88	34.59
	0.02	1111.70	778.60	0.3092	103.92	865.57	64.32	42.84	47.91	32.35
	0.04	1113.10	780.60	0.3173	103.40	868.89	64.16	43.74	45.99	32.90
	0.06	1114.50	782.59	0.3247	102.87	872.20	64.00	44.54	44.33	33.43
	0.08	1115.90	784.58	0.3320	102.36	875.51	63.84	45.31	42.79	33.94
	0.10	1117.30	786.57	0.3391	104.84	878.83	63.68	46.05	41.36	34.45

3.2. 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 Pen_4NBr 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 works[20-21].

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 Syal et al[19] and Kumar et al[22]. With the increase of temperatures, β- values of mixture increase, indicating temperature dependence of β and increase of interactions between molecules of solvents mixture.

3.3. Intermolecular Free 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 Kincaid[23] 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 Pen_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 in DMF-EMK mixtures. The decrease of L_f with increase of concentration suggests the presence of strong solute - solvent interaction[24].

L_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[25].

With increase in temperature, the magnitude of L_f increases showing the presence of solute-solvent interactions. Similar observations were made by Syal et al[19] and Ali[25].

3.4. Acoustic Impedance (Z)

The acoustic impedance (Z) values of Pen4NBr 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[25].

3.5. 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 Pen_4NBr 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 τ 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 et[26] and for tetraalkylammonoum salts by Patial et al[15].

The increase of relaxation time of pyrogallol[27] solution with concentration as reported in literature is also in agreement with our results.

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.

3.6. 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 Pen_4NBr. 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 + H_2O system[26].

3.7. 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 Pen_4NBr 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 with increase of solute concentration and decrease with increase of temperature in all composition.

Increase of π_i with concentration of Pen_4NBr 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 (πi) 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 Chauhan et al[28].

4. CONCLUSION

Ultrasonic velocity, viscosity and density studies on solution of tetrapentylammonium bromide (Pen_4NBr) in N,N-dimethylformamide, ethylmethylketone (EMK) and DMF-EMK solvent mixtures containing 0, 20, 40, 60, 80 and 100 mol % of DMF at 298, 308 and 318K have been reported. 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.

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