Acoustical and Transport Behavior of Tetrapropylammonium Bromide in 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 tetrapropylammoniumBromide(Pr_4NBr) have been carried outin 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.

1. Introduction

In recent year, there has been considerable progress in the determination of thermodynamic, acoustic and transport properties of working fluids from sound speed, density and viscosity measurements[1-5]. Transport properties of electrolytes in aqueous, non-aqueous and mixed solvents are of interest in various technologies and industrial units like high energy density batteries, photo electrochemical cells, electro position and wet electrolytic capacitors and in electro-organic synthesis. The physico-chemical behavior of liquid mixtures has been assessed by such studies in our earlier works[6-15].

Viscosity, density and ultrasonic velocity measurements and the properties derived from these are excellent tools to detect solute-solute and solute interactions. Such interactions have been studied in DMF and EMK mixture by usingPr_4NBr 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.

2. Experimental

Density measurement were carried out within a precision of ±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 ±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[6-7,15-16].

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[6-7,15-16].

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.

Dimethyl formamide(DMF) and ethylmethylketone (EMK) (both from Research Laboratories Pvt Ltd Bombay) have been purified by the methods reported earlier[6-7,13-16].

Tetrapropyl ammonium Bromide (Pr_4NBr) of analytical grade, Fluka, was dried and used as described earlier[6-7,13-14]. 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[14-15,17-19]:

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)

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

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:

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

whereK_T is time dependent constant whose value is 199.53x10^{-8} in MKS system.

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 x 10^9 in MKSsystem 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 x 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 forPr_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 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), ultrasonic velocity (u), viscosity (η)and the derived acoustical parameters of Pr_4NBr DMF-EMK mixtures at different temperatures.

Temperature	c	u (ms^{-1})	ρ ($Kg\,m^{-3}$)	ηx10^{-3} ($Nm^{-2}s$)	βx10^{11} ($Kg^{-1}m\,s^{-1}$)	Zx10^{-3} ($Kg^{-1}m^{-2}s^{-1}$)	L_fx10^{12} (m)	τx10^{11} (s)	V_f x10^8 (m^3mol^{-1})	πi (atm)
100% DMF										
298K	0.00	1456.7	944.40	0.8025	49.90	1375.70	44.57	53.39	17.26	48.37
	0.02	1458.7	945.72	0.8204	49.69	1379.52	44.48	54.36	16.66	49.07
	0.04	1460.3	946.68	0.8343	49.54	1382.44	44.41	55.10	16.21	49.64
	0.06	1461.8	947.68	0.8538	49.38	1385.32	44.34	56.22	15.62	50.39
	0.08	1463.4	948.92	0.8716	49.21	1388.65	44.26	57.19	15.11	51.09
	0.10	1464.9	950.32	0.8932	49.04	1392.12	44.18	58.40	14.53	51.91
308K	0.00	1424.2	934.6	0.7103	52.75	1331.06	45.83	49.96	20.04	47.23
	0.02	1426.1	935.78	0.7246	52.54	1334.52	45.74	50.76	19.41	47.87
	0.04	1427.8	937.1	0.7102	52.35	1337.99	45.65	49.57	19.96	47.55
	0.06	1429.3	937.86	0.7542	52.19	1340.48	45.58	52.49	18.19	49.16
	0.08	1430.7	939.14	0.7712	52.02	1343.63	45.51	53.49	17.55	49.88
	0.10	1431.9	939.98	0.7856	51.89	1345.96	45.45	54.35	17.02	50.52
318K	0.00	1386.7	925.8	0.6348	56.17	1283.81	47.29	47.54	22.78	46.43
	0.02	1388.7	927.26	0.6462	55.92	1287.69	47.18	48.18	22.14	47.01
	0.04	1390.4	928.38	0.6582	55.72	1290.82	47.10	48.90	21.49	47.60
	0.06	1392.1	929.36	0.6712	55.52	1293.76	47.02	49.69	20.82	48.22

	0.08	1393.7	930.32	0.6842	55.34	1296.59	46.94	50.48	20.19	48.84
	0.10	1395.2	931.45	0.6958	55.15	1299.56	46.86	51.17	19.34	49.43
80%DMF										
298K	0.00	1402.8	913.8	0.6987	55.61	1281.88	47.05	51.81	20.08	44.99
	0.02	1404.9	915.18	0.7142	55.36	1285.74	46.95	52.72	19.39	45.64
	0.04	1406.5	916.48	0.7315	55.16	1289.03	46.86	53.80	18.66	46.35
	0.06	1408.4	917.58	0.7468	54.94	1292.32	46.77	54.71	18.06	46.99
	0.08	1409.9	918.88	0.7648	54.75	1295.53	46.69	55.83	17.38	47.72
	0.10	1411.5	920.24	0.7816	54.54	1298.92	46.60	56.84	16.78	48.42
308K	0.00	1368.4	904.1	0.6118	59.07	1237.17	48.49	48.18	23.61	43.74
	0.02	1370.5	905.86	0.6258	58.77	1241.48	48.37	49.04	22.78	44.41
	0.04	1372.2	907.18	0.6405	58.54	1244.83	48.28	50.00	21.95	45.08
	0.06	1373.6	907.98	0.6532	58.37	1247.20	48.21	50.84	21.26	45.67
	0.08	1375.4	909.16	0.6664	58.14	1250.46	48.11	51.66	20.59	46.28
	0.10	1377	910.16	0.6792	57.94	1253.29	48.03	52.47	19.96	46.88
318K	0.00	1334.8	894.8	0.5408	62.73	1194.38	49.97	45.23	27.36	42.70
	0.02	1336.9	896.64	0.5524	62.40	1198.72	49.84	45.96	26.46	43.32
	0.04	1338.5	897.86	0.5582	62.17	1201.79	49.75	46.27	25.99	43.69
	0.06	1340.1	898.92	0.5762	61.95	1204.64	49.66	47.59	24.73	44.54
	0.08	1341.7	900.16	0.5862	61.71	1207.75	49.57	48.23	24.05	45.08
	0.10	1343.6	901.3	0.5945	61.46	1210.99	49.47	48.72	23.50	45.55
60%DMF										
298K	0.00	1351.1	884.8	0.6058	61.91	1195.45	49.65	50.01	23.50	41.78
	0.02	1353.1	886.78	0.6208	61.59	1199.90	49.52	50.98	22.61	42.46
	0.04	1354.7	887.82	0.6342	61.37	1202.73	49.43	51.90	21.86	43.05
	0.06	1356.3	888.34	0.6482	61.19	1204.86	49.36	52.89	21.10	43.66
	0.08	1357.9	890.48	0.6624	60.90	1209.18	49.24	53.79	20.38	44.31
	0.10	1359.5	891.94	0.6764	60.66	1213.59	49.14	54.71	19.71	44.95
308K	0.00	1316	874.6	0.5295	66.02	1150.97	51.27	46.61	27.65	40.59
	0.02	1317.9	876.22	0.5418	65.71	1154.77	51.15	47.47	26.66	41.21
	0.04	1319.6	877.8	0.5534	65.42	1158.35	51.04	48.27	25.78	41.80
	0.06	1321.3	879.05	0.5652	65.16	1167.49	50.93	49.10	24.92	42.39
	0.08	1322.8	880.46	0.5767	64.90	1164.67	50.83	49.91	24.12	42.97
	0.10	1324.3	881.98	0.5858	64.65	1168.01	50.73	50.50	23.51	43.48
318K	0.00	1275.8	864.7	0.4633	71.05	1103.18	53.19	43.89	32.25	39.51
	0.02	1277.7	866.68	0.4738	70.68	1107.36	53.05	44.65	31.12	40.12
	0.04	1279.8	868.15	0.4832	70.33	1111.06	52.91	45.31	30.18	40.65
	0.06	1280.9	869.25	0.4924	70.12	1113.42	52.83	46.03	29.25	41.18
	0.08	1282.4	870.86	0.5012	69.82	1116.79	52.72	46.66	28.42	41.70
	0.10	1284	872.26	0.5116	69.54	1119.98	52.62	47.34	27.50	42.29
40%DMF										
298K	0.00	1300.1	856.3	0.521	69.09	1113.98	52.45	48.00	27.82	38.64
	0.02	1301.1	858.24	0.5328	68.83	1116.66	52.35	48.90	26.82	39.24
	0.04	1303.6	859.78	0.5462	68.44	1120.81	52.20	49.84	25.81	39.87
	0.06	1305.3	861.26	0.5564	68.15	1124.20	52.09	50.56	25.05	40.39
	0.08	1306.9	862.78	0.5674	67.86	1127.57	51.98	51.34	24.28	40.93
	0.10	1308.5	864.16	0.5812	67.59	1130.75	51.87	52.37	23.36	41.58
308K	0.00	1263.8	846.00	0.4554	74.01	1069.18	54.28	44.94	32.62	37.57
	0.02	1265.6	848.08	0.4646	73.62	1073.33	54.14	45.61	31.60	38.10
	0.04	1267.3	849.56	0.476	73.29	1076.65	54.02	46.52	30.41	38.70
	0.06	1268.9	851.22	0.4872	72.96	1080.11	53.90	47.40	29.30	39.31
	0.08	1270.6	852.36	0.496	72.67	1083.01	53.79	48.06	28.47	39.79
	0.10	1272.2	853.86	0.5062	72.36	1086.28	53.67	48.84	27.55	40.35
318K	0.00	1222.5	835.3	0.394	80.11	1021.15	56.47	42.09	38.57	36.37
	0.02	1224.3	837.2	0.4024	79.69	1024.98	56.33	42.76	37.30	36.91
	0.04	1226.1	838.98	0.4116	79.29	1028.67	56.18	43.51	35.99	37.46
	0.06	1227.8	840.68	0.4202	78.91	1032.19	56.05	44.21	34.82	38.00
	0.08	1229.4	842.25	0.4282	78.55	1035.46	55.92	44.85	33.78	38.50
	0.10	1230.8	843.82	0.4352	78.23	1038.57	55.81	45.40	32.89	38.97
20%DMF										
298K	0.00	1245.7	827.5	0.4467	77.88	1030.82	55.68	46.38	32.86	35.73
	0.02	1247.5	829.68	0.4564	77.45	1035.03	55.53	47.13	31.76	36.27
	0.04	1249.1	831.18	0.4666	77.11	1038.23	55.41	47.97	30.66	36.81
	0.06	1250.7	832.98	0.4762	76.75	1041.81	55.28	48.93	29.67	37.33
	0.08	1252.3	834.68	0.4856	76.39	1045.27	55.15	49.46	28.76	37.84
	0.10	1253.9	836.2	0.4972	76.01	1048.51	55.03	50.42	27.70	38.44
	0.00	1206.4	817.5	0.3914	84.05	986.23	57.85	43.86	38.19	34.84

308K	0.02	1208.2	819.7	0.4012	83.57	990.36	57.68	44.71	36.73	35.43
	0.04	1209.7	821.26	0.4092	83.21	934.78	57.56	45.40	35.84	35.91
	0.06	1211.2	823.1	0.4182	82.82	996.94	57.42	46.18	34.36	36.45
	0.08	1212.6	824.78	0.4262	82.46	1000.13	57.30	46.86	33.34	36.94
	0.10	1214.2	826.32	0.4366	82.09	1003.32	57.17	47.78	32.07	37.53
318K	0.00	1165	806.5	0.3365	91.36	939.57	60.31	40.99	45.46	33.64
	0.02	1166.5	808.86	0.3463	90.86	943.54	60.14	41.95	43.45	34.28
	0.04	1168.1	810.56	0.3542	90.42	946.82	60.00	42.70	41.93	34.80
	0.06	1169.5	812.26	0.3622	90.01	949.94	59.86	43.47	40.45	35.33
	0.08	1170.9	813.98	0.3702	89.61	953.09	59.73	44.23	39.01	35.86
	0.10	1172.4	815.86	0.3758	89.17	956.51	59.58	44.68	38.11	36.28
0%DMF(Pure EMK)										
298K	0.00	1195.6	799.9	0.3855	87.46	956.36	59.01	44.95	38.54	33.12
	0.02	1197.3	802.16	0.3942	86.96	960.43	58.84	45.70	37.20	33.64
	0.04	1198.8	803.98	0.4022	86.45	963.81	58.70	46.41	36.02	34.12
	0.06	1200.3	805.92	0.4117	86.12	967.35	58.56	47.27	34.71	34.66
	0.08	1201.8	807.68	0.421	85.72	970.67	58.42	48.12	33.49	35.19
	0.10	1203.2	809.16	0.4303	85.37	973.58	58.30	48.98	32.34	35.71
308K	0.00	1153.3	788.8	0.3441	95.31	909.72	61.60	43.73	43.30	32.63
	0.02	1154.9	791.24	0.3432	94.76	913.80	61.42	43.36	43.38	32.73
	0.04	1156.3	792.92	0.3616	94.33	916.85	61.28	45.48	40.03	33.73
	0.06	1157.7	794.86	0.3679	93.87	920.21	61.13	46.05	38.92	34.17
	0.08	1159.1	796.78	0.3762	93.42	923.55	60.98	46.86	37.56	34.69
	0.10	1160.5	798.6	0.3822	92.88	926.76	60.84	47.38	36.59	35.11
318K	0.00	1110.3	776.6	0.2975	104.45	962.26	64.49	41.43	50.88	31.59
	0.02	1111.7	778.89	0.3024	103.88	965.89	34.31	41.89	49.54	32.00
	0.04	1113.2	781.04	0.3098	103.32	969.45	64.14	42.68	47.68	32.52
	0.06	1114.5	782.79	0.3134	102.85	872.42	63.99	42.98	46.75	32.85
	0.08	1115.7	784.88	0.3208	102.35	875.69	63.84	43.78	45.04	33.37
	0.10	1117	786.77	0.3272	101.87	878.82	63.68	44.44	43.62	33.85

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 Pr_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 Patial[14], Syalet 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.

Acoustic Impedance (Z)

The acoustic impedance (Z) values of Pr_4NBr 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 molecules EMK and DMF with the addition of EMK to DMF in mixture[14,23].

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 Kincaid[24] have proposed that L_f is a predominating factor in determining the variation of ultrasonic velocityin 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 Pr_4NBrat 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 interaction[25-26].

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[14,23]. With increase in temperature, the magnitude of L_f increases showing the presence of solute-solvent interactions. Similar observations were made by Syalet al[19], Patial[14] and Ali[23]. 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.

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 Pr_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[27] and for tetraalkylammonoum salts by Patialet al[7].The increase of relaxation time of pyrogallol solution with concentration as reported in literature[28] is also in agreement with our results.

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 Pr_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[27].

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 Pr_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 thatπ_i values increase with increase with increase of solute concentration and decrease with increase of temperature in all composition.

Increase of $\pi_i$with concentration of Pr_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 Chauhanet al[29] and Patial[14].

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