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Influence of Tetra Alkyl Ammonium Cation and Temperature on Molecular Interactions Involves in Binary Liquid Mixtures of Dioxane and DMF at Various Temperatures

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Abstract: *Ultrasonic velocity (u), density (ρ), viscosity (η) and related acoustical parameters such as adiabatic compressibility (β), free energy (ΔG), internal pressure (π_i), relaxation time (τ) and acoustic impedance (z) have been computed using standard relation for tetra alkyl ammonium cation (Et_4N^+, Pr_4N^+, Bu_4N^+, and Pen_4N^+) in binary liquid mixtures of 1, 4 - Dioxane and N, N – Dimethyl Formamide was prepared of 0.14M on different percentage compositions over the temperature range from 303.15K to 323.15K with the interval of 10K under room pressure to investigate inter - ionic interactions. The densities were measured by Magnetic Float Densitometer. Transport properties provide a deep and meaningful insight of various interactions taking place. It has been observed that the influence of small as well as large alkyl chain length of tetra alkyl ammonium cations (R_4N^+), in terms of shape and ionic size with the DMF solvent in the presence of Dioxane, is helpful in investigating the molecular interactions, molecular rearrangement, molecular association etc.*

Keywords: *Ultrasonic velocity, Density, Viscosity, Acoustical parameters, 1, 4-Dioxane, N, N-Dimethyl Formamide, R_4NI salts and molecular interactions.*

I. Introduction

The analysis of the reliable thermo-dynamical parameter and its deviation from the ideality of the properties of liquid mixtures provide some important information about the molecular organization and their interactions that is essential for the industrial design and attaining acceptable chemical theories. In many chemical engineering areas such as process design, oil fraction characterization, and others, accurate estimation of thermodynamic, optical, and ultrasonic properties as a function of composition and temperature is particularly important [1]. In recent years, ultrasonic techniques has become a powerful tool in providing information regarding the molecular interactions of liquid mixtures owing to its ability of characterizing physiochemical behavior of the medium [2-10]. The experimental values of acoustical parameters allow us to establish a new predictive structural interaction that tells about the structural information of the liquid mixtures at various temperatures that are desirable for many chemical industries in a fast reliable and economical way [11-15]. Therefore, a deep knowledge of thermo-physical properties of binary ILs mixtures containing cation (Et_4N^+, Pr_4N^+, Bu_4N^+, and Pen_4N^+) of mixed organic solvent are required for many practical applications have essentially required for scientific community [16].

The physiochemical properties such as density (ρ), viscosity (η) and ultrasonic velocity (u) of binary liquid mixtures of 1, 4 – Dioxane and N, N – Dimethyl Formamide containing R_4N^+ cation, are used to identify the behavior and its nature of structure, making or breaking effect through molecular interactions. Thermodynamic functions have also been used as a qualitative and quantitative inspect to predict the extent of complex formation, molecular interactions and molecular association in these types of liquid mixtures [17]. Many researchers have studied molecular interactions and structural properties of solution containing tetra alkyl ammonium salts in aqueous as well as non-aqueous binary solvent mixtures. Frank explained the high activity coefficient on the basis of his hypothesis according to which the structure of water is enforced around the R_4N^+ ions on account of water-hating influence of large alkyl chain [18]. This result confirms that formation of cavities inside the enhanced water structure and R_4N^+ ions are accommodated in the cavities so formed [19]. RN Pathak et al. reported various observations by taking aqueous and non-aqueous binary solvent mixture, adding R_4NI salts and showing the validity of Frank's hypothesis for salts solutions [20]. Their observations were confirmed that such solute – solvent hating effect is still there and structure of any of the binary solvents is affected by the ion – solvent interactions.

An adequate knowledge of the thermo-physical properties of ammonium-based molecular solvents are essentially required to clarify the nature of molecular interactions between these solvents, as well as to design new chemical and technological processes [21]. 1, 4 - Dioxane is found in two forms; one is the boat form (polar) and second is the chair form (non-polar). These confirmations depend on the energy of the molecular system. Dioxane is known as an inert solvent having low dielectric constant (ϵ) 2.2 as compared to DMF (36.71). DMF is a stable compound with a strong e^- pair donating and accepting ability and is widely used in setting such as solvent reactivity relationship.

II. Experimental And Theoretical Methods

Ultrasonic velocity (u) are measured for the binary liquid mixtures of DMF and Dioxane, in the presence of ammonium salt using a single crystal ultrasonic interferometer at 2 MHz frequency (Model-83S) supplied by Mittal enterprises, New Delhi, that has an accuracy of 0.4 m/Sec at 25^0C. The temperature was kept constant, by constant temperature water bath with an accuracy of ± 0.1K. The densities and viscosities of selected binary system were determined at different temperatures by magnetic float densitometer [22] and Ostwald's viscometer respectively and calculated by using eq. 1 & 2.

$$\text{Density } (\rho) = (W+w+f\times I)/(V+w/\rho_{pt}) \quad (1)$$

The terms involved in this equation have their usual meanings. The data of solution mixtures, *i.e*., weight, w used, current, I, passing in the circuit, $\rho_{pt,}$ density of pt and V, volume of float.

$$\eta_s / \eta_w = \rho_s/ \rho_w \times t_s/ t_w \quad (2)$$

Where, $\eta_{w,}$ ρ_w and t_w are the viscosity, density and time flow of water respectively and η_s, ρ_s and t_s are the viscosity, density and time flow of unknown liquid mixture respectively.

The tetra alkyl ammonium iodide salts, Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI which were used in present investigation were purified by the method of Conway et al [26]. 1, 4 - Dioxane and N, N - Dimethyl Formamide (DMF) of Qualigen's Glaxo grade, after drying on freshly ignited quicklime, was purified by distilling under reduced pressure. The middle fractions of the successive distillate were redistilled under reduced pressure till the electrical conductance of the final product was of the order of 10^{-7} ohm^{-1} cm^{-1}. The purified samples were stored in dark coloured bottles. 1, 4 - Dioxane was used to prepare 0, 20, 40, 60, 80 and 100% (v/v) solvent mixtures with N, N- Dimethyl Formamide of Fluka purum grade. We have been measured the values of dialectic constant (ϵ) for different % compositions of Dioxane and DMF with the help of BI-870 dielectric constant meter (absolute accuracy to ± 2%).

III. Result And Discussion

Virtually**,** the thermo-physical properties of liquid mixtures with R_4N^+ ions mainly depend on the nature, structure of ions and the alkyl chain length of the cation. It was observed that, for a given concentration and temperature, ultrasonic velocity (u), decreases with increasing the % composition of Dioxane in DMF as shown in Table 2, 3, 4 & 5. Such decrease in velocity gives an indication of existence of molecular association between the components of the mixture [23-25]. Again increasing trend of adiabatic compressibility (β_{ad}) is observed with increasing % composition of Dioxane in DMF. This increasing trend of β_{ad} values can be explained on the basis of the effect of dielectric constant (Є) of the solvent media. It is known that electrostatic forces of attraction, F, between the ions, is inversely proportional to dielectric constant of solvent medium (*i.e*. F α 1/Є), The decrease in the value of dielectric constant of the solvent medium results in strong electrostatic forces of attraction between the ions and hence ion - ion interactions become stronger and stronger as there is a gradual decrease of dielectric constant of the medium.

In the present study, the gradual decrease of dielectric constant of medium was done by increasing the Dioxane content in the DMF as given in Table 1. Hence the increase values of β_{ad} are obtained as shown in Fig. 1 & 2. This happens because there is a significant interaction between ions and solvent molecules suggesting a structure promoting behaviour of the added both compositions. This may also indicate that decrease in the number of free ions showing the occurrence of increase of ionic association due to strong electro-static force of attraction [27]. Here adiabatic compressibility (β_{ad}) and sound velocity (u) shows positive and negative deviation respectively. According to Eyring and Kincaid, the sound velocity decreases if the molecular association increases which are reflected in the present investigation [21].

Table 1: Measured values of dielectric constant (ϵ) by BI–870 Dielectric Constant Meter (absolute accuracy to ± 2%) for various compositions of 1, 4 – Dioxane and N, N – Dimethyl Formamide.

S.N.	% Compositions of Solvents		Dielectric Constants (ϵ)
	Dioxane	DMF	
1.	0	100	36.71
2.	20	80	29.50
3.	40	60	23.00
4.	60	40	15.00
5.	80	20	09.00
6.	100	0	02.10

Table 2: Summary of experimental data: Density (ρ), Ultrasonic velocity (u), Viscosity (η) and the derived acoustical parameters of 1, 4-Dioxane + N, N-Dimethyl Formamide + Et_4NI salt mixtures at different temperatures.

% Compositions of solvents		ρ (g/cm^3)	η × 10^3 (Nsm^{-2})	u (ms^{-1})	β×10^{-10} (Kg^{-1} ms^2)	ΔG×10^{-21} ($gjmol^{-1}$)	π_i (atm)	τ × 10^{-10} (s)	z×10^3 ($Kgm^{-2}s^{-1}$)
Dioxane	DMF								
At 303.15K									
0	100	0.9420	1.3310	1399	5.354	0.9285	14103.62	9.501	133.49
20	80	0.9584	1.3425	1375	5.543	0.8498	14188.67	9.921	132.34
40	60	0.9750	1.3625	1352	5.593	0.8067	16645.59	10.16	132.23
60	40	0.9937	1.4125	1327	5.681	0.7206	15148.03	10.699	133.39
80	20	1.0125	1.4575	1305	5.728	0.6408	15245.33	11.13	133.06
100	0	1.0266	1.5752	1290	5.804	0.4759	15853.11	12.19	132.55
At 313.15K									
0	100	0.9379	0.6520	1391	5.510	2.1835	10109.36	4.790	130.46
20	80	0.9532	0.6625	1365	5.630	2.1132	10267.23	4.973	130.11
40	60	0.9725	0.6751	1337	5.752	2.0378	12124.86	5.177	130.02
60	40	0.9860	0.6923	1315	5.865	1.9538	11718.90	5.414	130.65
80	20	1.0015	0.7115	1298	5.926	1.8834	10842.63	5.621	129.99
100	0	1.0164	0.7250	1267	6.128	1.7848	11069.26	5.924	128.77
At 323.15K									
0	100	0.9354	0.6102	1340	5.953	2.1711	10264.38	4.843	125.34
20	80	0.9475	0.6375	1315	6.103	2.0382	10546.91	5.187	124.59
40	60	0.9650	0.6715	1282	6.305	1.8743	12678.10	5.645	123.71
60	40	0.9875	0.6954	1255	6.429	1.7688	12419.28	5.961	123.93
80	20	1.0025	0.7376	1227	6.625	1.5967	11747.88	6.515	123.00
100	0	1.0295	0.7624	1205	6.689	1.5141	12119.17	6.799	122.88

Table 3: Summary of experimental data: Density (ρ), Ultrasonic velocity (u), Viscosity (η) and the derived acoustical parameters of 1, 4-Dioxane + N, N-Dimethyl Formamide + Pr_4NI salt mixtures at different temperatures.

% Compositions of solvents		ρ (g/cm^3)	η × 10^3 (Nsm^{-2})	u (ms^{-1})	β×10^{-10} (Kg^{-1} ms^2)	ΔG×10^{-21} ($gjmol^{-1}$)	π_i (atm)	τ × 10^{-10} (s)	z×10^3 ($Kgm^{-2}s^{-1}$)
Dioxane	DMF								
At 303.15K									
0	100	0.9498	1.5328	1366	5.632	0.5801	10232.61	11.510	129.74
20	80	0.9650	1.5875	1356	5.685	0.4993	10468.11	12.033	131.41
40	60	0.9807	1.6075	1346	5.701	0.4714	10591.87	12.219	132.40
60	40	1.0100	1.6325	1343	5.752	0.4272	10810.65	12.520	134.00
80	20	1.0125	1.6687	1322	5.811	0.3688	10923.67	12.929	135.21
100	0	1.0324	1.6993	1311	5.906	0.3064	11103.51	13.381	135.34
At 313.15K									
0	100	0.9387	0.6643	1360	5.489	2.0654	6919.58	5.101	127.66
20	80	0.9554	0.6801	1345	5.520	2.0128	7059.57	5.246	128.40
40	60	0.9750	0.6862	1337	5.737	1.9949	7144.85	5.296	129.23
60	40	0.9875	0.6950	1305	5.924	2.8066	7281.64	5.489	129.84
80	20	1.005	0.7052	1296	5.997	1.8774	7375.00	5.639	130.15
100	0	1.0169	0.7128	1282	6.205	1.7941	7376.60	5.895	130.26
At 323.15K									
0	100	0.9228	0.5627	1333	5.349	2.2813	6563.00	4.575	123.00
20	80	0.9375	0.5825	1307	5.542	2.1687	6753.76	4.849	123.67
40	60	0.9525	0.6153	1299	5.633	2.0385	6973.82	5.186	124.33
60	40	0.9795	0.6357	1281	5.759	1.9509	7214.34	5.426	124.82
80	20	1.0015	0.6625	1267	5.798	1.8420	7443.22	5.740	125.75
100	0	1.0162	0.6934	1224	5.807	1.7331	7754.79	6.072	125.38

Table 4: Summary of experimental data: Density (ρ), Ultrasonic velocity (u), Viscosity (η) and the derived acoustical parameters of 1, 4-Dioxane + N, N-Dimethyl Formamide + Bu_4NI salt mixtures at different temperatures.

% Compositions of solvents		ρ (g/cm^3)	η × 10^3 (Nsm^{-2})	u (ms^{-1})	β×10^{-10} (Kg^{-1} ms^2)	ΔG×10^{-21} ($gjmol^{-1}$)	π_i (atm)	τ × 10^{-10} (s)	z×10^3 ($Kgm^{-2}s^{-1}$)
Dioxane	DMF								
At 303.15K									

0	**100**	**0.9536**	**1.4483**	**1405**	**5.312**	**0.7892**	**8394.74**	**10.258**	**133.98**
20	**80**	**0.9657**	**1.4825**	**1393**	**5.336**	**0.7388**	**8534.15**	**10.547**	**134.52**
40	**60**	**0.9824**	**1.5250**	**1365**	**5.463**	**0.6446**	**8775.38**	**11.108**	**134.97**
60	**40**	**0.9990**	**1.5625**	**1344**	**5.541**	**0.5747**	**8982.08**	**11.544**	**134.26**
80	**20**	**1.0323**	**1.6025**	**1323**	**5.587**	**0.5138**	**9298.63**	**11.937**	**136.57**
100	**0**	**1.0396**	**1.6369**	**1315**	**6.106**	**0.3184**	**9398.32**	**13.326**	**136.70**
At 313.15K									
0	**100**	**0.9395**	**0.5989**	**1388**	**5.520**	**2.3396**	**5555.04**	**4.408**	**130.40**
20	**80**	**0.9553**	**0.6275**	**1370**	**5.577**	**2.2328**	**5741.85**	**4.666**	**130.87**
40	**60**	**0.9750**	**0.6575**	**1330**	**5.798**	**2.0722**	**5999.73**	**5.083**	**130.95**
60	**40**	**0.9875**	**0.6925**	**1304**	**5.955**	**1.9249**	**6223.54**	**5.498**	**134.20**
80	**20**	**1.0025**	**0.7250**	**1287**	**6.022**	**1.8178**	**6423.92**	**5.821**	**134.72**
100	**0**	**1.0177**	**0.7512**	**1276**	**6.135**	**1.7161**	**6582.52**	**6.145**	**135.15**
At 323.15K									
0	**100**	**0.9302**	**0.5672**	**1328**	**6.095**	**2.2670**	**5665.68**	**4.609**	**123.53**
20	**80**	**0.9502**	**0.5868**	**1313**	**6.104**	**2.1985**	**5832.12**	**4.775**	**124.76**
40	**60**	**0.9625**	**0.6025**	**1283**	**6.311**	**2.0828**	**5982.70**	**5.069**	**124.95**
60	**40**	**0.9725**	**0.6371**	**1264**	**6.436**	**1.9364**	**6192.68**	**5.467**	**125.24**
80	**20**	**1.0015**	**0.6532**	**1240**	**6.493**	**1.8709**	**6406.22**	**5.655**	**125.89**
100	**0**	**1.0173**	**0.6921**	**1218**	**6.626**	**1.7214**	**6671.82**	**6.109**	**126.35**

Table 5: Summary of experimental data: Density (ρ), Ultrasonic velocity (u), Viscosity (η) and the derived acoustical parameters of 1, 4-Dioxane + N, N-Dimethyl Formamide + Pen_4NI salt mixtures at different temperatures.

% Compositions of solvents		**ρ (g/cm^3)**	**$\eta \times 10^3$ (Nsm^{-2})**	**u (ms^{-1})**	**$\beta \times 10^{-10}$ ($Kg^{-1}\ ms^2$)**	**$\Delta G \times 10^{-21}$ ($gjmol^{-1}$)**	**π_i (atm)**	**$\tau \times 10^{-10}$ (s)**	**$z \times 10^3$ ($Kgm^{-2}s^{-1}$)**
Dioxane	**DMF**								
At 303.15K									
0	**100**	**0.9484**	**1.4284**	**1396**	**5.370**	**0.7947**	**7249.55**	**10.227**	**132.39**
20	**80**	**0.9665**	**1.4750**	**1388**	**5.410**	**0.7230**	**7430.13**	**10.639**	**133.15**
40	**60**	**0.9825**	**1.5020**	**1368**	**5.538**	**0.6476**	**8786.40**	**11.090**	**133.78**
60	**40**	**1.0025**	**1.5625**	**1354**	**5.640**	**0.5425**	**7824.25**	**11.750**	**134.06**
80	**20**	**1.0250**	**1.6013**	**1341**	**5.693**	**0.4810**	**8022.26**	**12.155**	**134.68**
100	**0**	**1.0348**	**1.6471**	**1311**	**5.712**	**0.4237**	**8224.55**	**12.544**	**135.66**
At 313.15K									
0	**100**	**0.9373**	**0.5748**	**1379**	**5.610**	**2.3866**	**4742.40**	**4.299**	**129.25**
20	**80**	**0.9551**	**0.6273**	**1366**	**5.651**	**2.2089**	**5005.80**	**4.726**	**130.46**
40	**60**	**0.9750**	**0.6625**	**1342**	**5.694**	**2.0920**	**5225.39**	**5.029**	**130.84**
60	**40**	**0.9925**	**0.7052**	**1320**	**5.782**	**1.9462**	**5462.74**	**5.436**	**131.01**
80	**20**	**1.0050**	**0.7425**	**1294**	**5.942**	**1.7982**	**5669.60**	**5.882**	**131.77**
100	**0**	**1.0198**	**0.7931**	**1266**	**6.118**	**1.6197**	**5941.21**	**6.469**	**132.13**
At 323.15K									
0	**100**	**0.9283**	**0.5217**	**1347**	**5.385**	**2.6716**	**4687.20**	**3.740**	**125.04**
20	**80**	**0.9402**	**0.5625**	**1321**	**5.499**	**2.4824**	**4922.40**	**4.124**	**125.40**
40	**60**	**0.9625**	**0.5957**	**1289**	**5.937**	**2.2230**	**5172.63**	**4.715**	**125.89**
60	**40**	**0.9875**	**0.6551**	**1257**	**6.095**	**1.9877**	**5549.11**	**5.324**	**126.35**
80	**20**	**1.0030**	**0.6732**	**1235**	**6.435**	**1.8299**	**5694.96**	**5.776**	**126.94**
100	**0**	**1.0112**	**0.7013**	**1219**	**6.655**	**1.6859**	**5842.30**	**6.222**	**127.45**

However as the % composition of Dioxane increases in the DMF content, β_{ad} value increases in a slightly nonlinear manner as shown in Fig. 2 and departure from their linearity increases on increasing the temperature of the system, the value of adiabatic compressibility (β_{ad}) is greater for Pr_4NI salt solution at 303.15K while it is found higher for Pen_4NI at 323.15K. Such type of variations in the above curve of the β_{ad} depends on the size of the solute and solvent molecules and types of molecular interactions such as dipole - dipole, dipole - induced dipole etc. as well as molecular rearrangement between the components of the binary liquid mixtures as shown in Scheme 2. This is in agreement with the observations made by Syal et al. and Kalyanasundaram for alkali bromides in DMSO + Dioxane and poly methylacrylate (PMMA) in DMF mixture respectively at different temperatures [28-30]. Therefore, the present investigation prove that the constituent of component present in different shapes and size, involve specific molecular interactions between them, where as Bu_4N^+ and Pen_4N^+ ions present larger in size than ions (Et_4N^+, Pr_4N^+) have lower value of adiabatic compressibility (β_{ad}). Also, this can be understood on the basis of accommodation of solvent molecules inside the void space of large bulky group as Bu_4N^+ and Pen_4N^+ ions as compared to Et_4N^+ and Pr_4N^+ ions [18], causes very weak repulsive forces between them and thus the system becomes compact like structure. So, solvent

molecules could not be able to penetrate in to the vacant space of the Et_4N^+ and Pr_4N^+ ions, causes expansion of the system and having higher value of adiabatic compressibility as shown in Scheme 3.

Free energy (ΔG) decreases with increasing % composition of Dioxane in DMF for all the system. At 303.15K, Et_4NI salt solution has larger value of free energy while Pen_4NI salt solution has greater value of free energy at 323.15K as shown in Fig. 3 & 4. At all temperatures, Pr_4N^+ shows lower activity towards ΔG when % composition of DMF is higher while at 323.15K, Pen_4N^+ has higher activity at higher % composition of Dioxane. At 323.15K, Et_4N^+ and Pr_4N^+ have lower and higher activity of ΔG respectively as shown in Fig. 4. This trend of positive and negative deviations confirms that the properties of ILs mixture are affected by molecular rearrangement, molecular interactions and size of the ions at various temperatures.

The decrease in free energy suggests shorter time for rearrangement of molecules. This is attributed to hydrogen bonding charge transfer between molecules of the solution mixture. As the mixture consists of polar and non-polar liquids, in addition to dipole-dipole interactions there is a dipole-induced dipole interaction, which leads to decreasing values of ΔG after increasing the % composition of Dioxane in DMF. This observation confirms that the formation of hydrogen bonding is strong with DMF and very weak with Dioxane in the binary liquid mixtures. Dioxane present in chair conformation, which is non-polar molecule shown in Scheme 3.

The internal pressure (π_i) slowly increases on increasing the % of Dioxane in DMF liquid but decreases on increasing the temperatures for all the system. The values of internal pressure are higher for Et_4NI salt solution at 303.15K as well as at 323.15K and also showed trends of linearity at all temperatures as shown in Fig. 5 & 6. The internal pressure may give information regarding the nature and strength of force existing between the molecules. On increasing 20 to 80 % of Dioxane in DMF, the increase in the values of internal pressure indicates the presence of some specific molecular interactions between unlike molecules in the components. The structure of liquid is determined by strong attractive forces in the liquid with the relatively weak repulsive forces providing the internal pressure which leads to repulsive liquid molecules together [31]. On increasing the temperature from 303.15K to 323.15K of the system, the internal pressure is more sensitive to attractive forces.

The relaxation time (τ) slowly increases with increasing 20 to 80 % Dioxane in DMF content for all the system. The values of relaxation time are larger for Pr_4NI and lowered for Et_4NI and also showed trends of linearity at 303.15K as shown in Fig. 7. But deviations increases on increasing the temperature of the system and the value of τ is higher for Et_4NI and lowered for Pen_4NI at 323.15K as shown in Fig. 8 and 303.15K, Pr_4NI has higher activity towards relaxation time. The dispersion of ultrasonic velocity in the system should contain information about the characteristics time (τ) of the relaxation process that causes dispersion [32].

The relaxation time (τ) decreases with increase in the size of R_4N^+ ions from Et_4N^+ ion to Pen_4N^+ ion. Also, the value of τ decreases with rise in temperature is shown in Fig. 7 & 8. This trend of non – linearity curve of τ indicates that there are weak as a well as strong ionic interaction involves between the components of the binary liquid mixtures. The increase in acoustic impedance (z) values on increasing 20 to 80 % of Dioxane in DMF content can be attributed to the effective solute-solvent interactions.

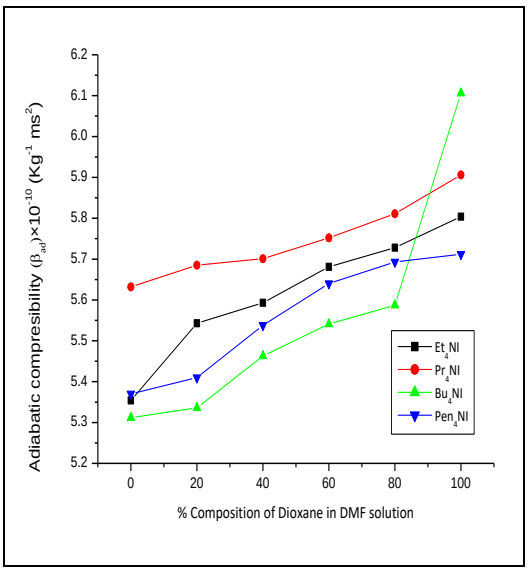


Fig. 1: Adiabatic compressibility (β_{ad}) vs % compositions of binary liquid mixture with different salts at 303.15K.

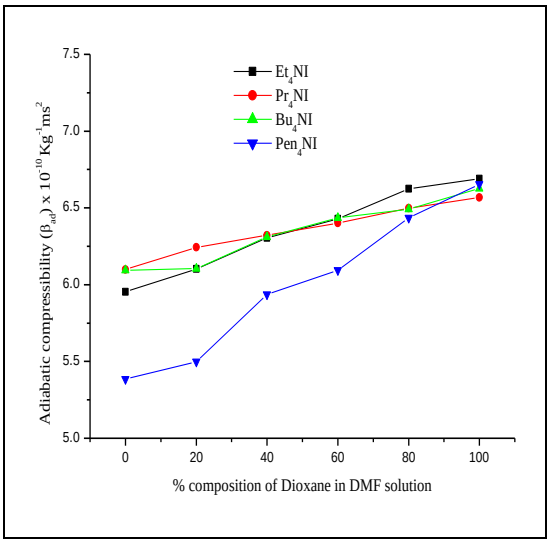


Fig. 2: Adiabatic compressibility (β_{ad}) vs % compositions of binary liquid mixture with different salts at 323.15K.

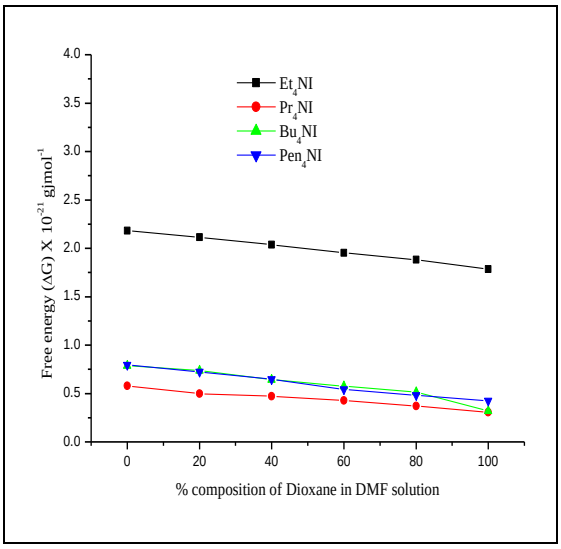


Fig. 3: Free energy (ΔG) vs % compositions of binary liquid mixture with different salts at 303.15K.

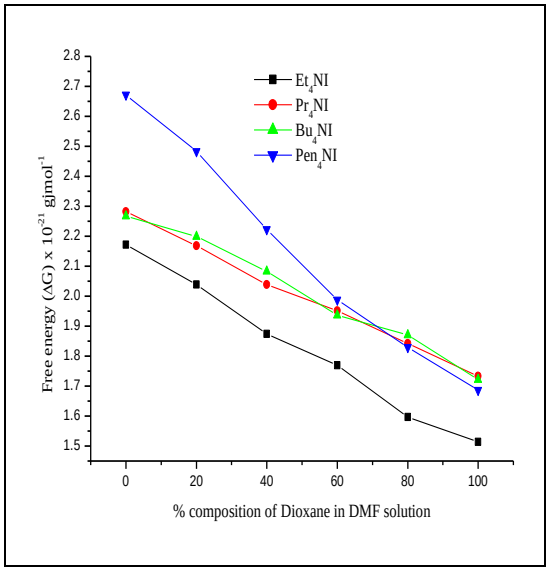


Fig. 4: Free energy (ΔG) vs % compositions of binary liquid mixture with different salts at 323.15K.

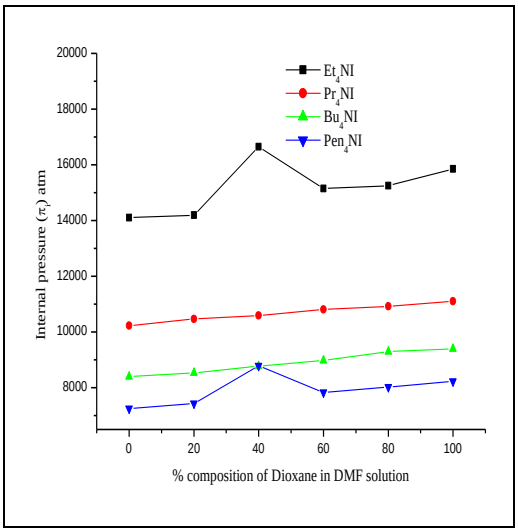


Fig. 5: Internal pressure (π_i) vs % compositions of binary liquid mixture with different salts at 303.15K.

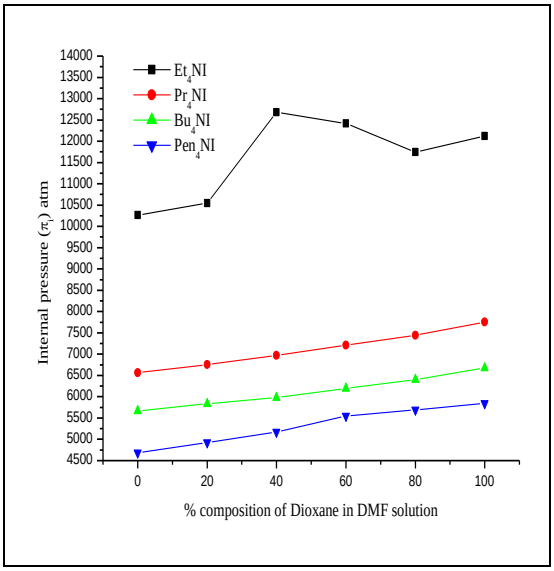


Fig. 6: Internal pressure (π_i) vs % compositions binary liquid mixture with different salts at 323.15K.

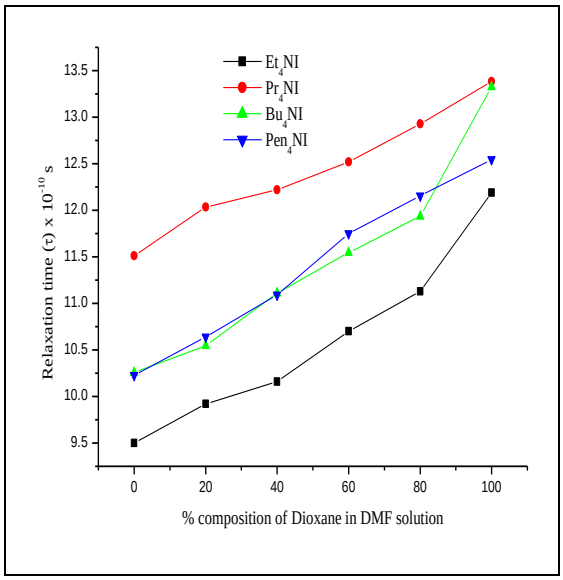


Fig. 7: Relaxation time (τ) vs % compositions of binary liquid mixture with different salts at 303.15K.

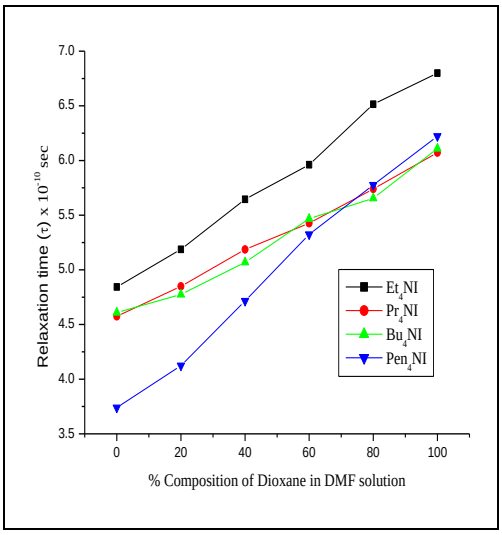


Fig. 8: Relaxation time (τ) vs % compositions of binary liquid mixture with different salts at 323.15K.

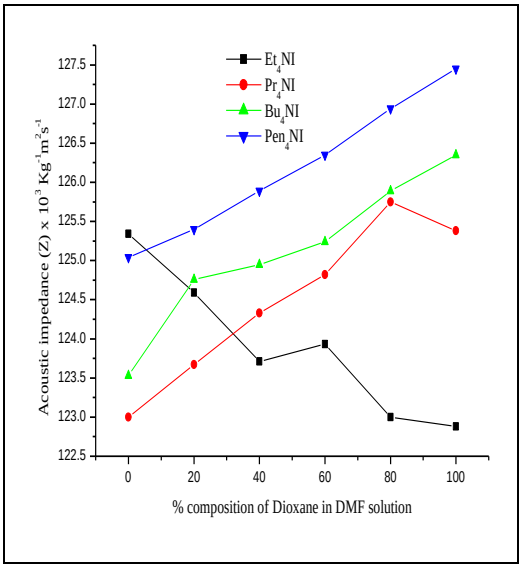


Fig. 9: Acoustic impedance (Z) vs % compositions binary liquid mixture with different salts at 303.15K.

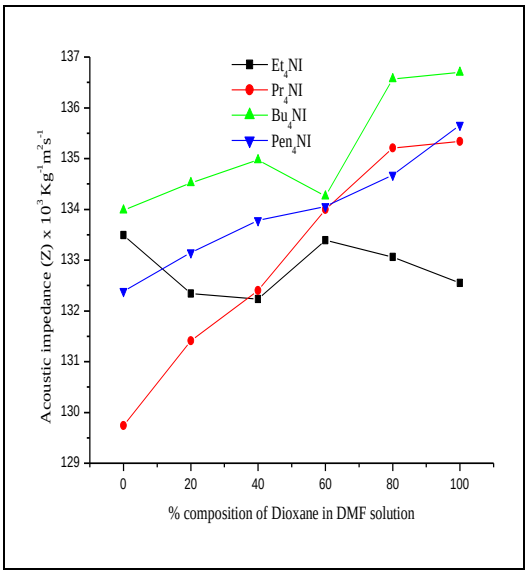


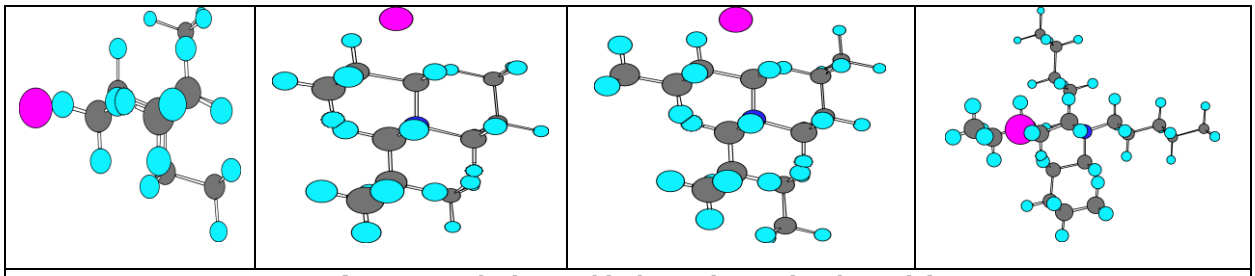
Fig. 10: Acoustic impedance (Z) vs % compositions of binary liquid mixture with different salts at 323.15K.

A similar type of behaviour except Et_4N^+ cation has been obtained for various salts studied in different systems. All the solution mixtures showed departure from the trends of linearity at 303.15K but it showed linear trends at 323.15K are shown in Fig. 9 & 10. The acoustic impedance is a measure of the resistance offered by the liquid medium, i.e., the bulk modulus of elasticity, which depends on the structural changes of the solution [33]. The change in the values of z can be understood on the basis of ionic size and bigger size alkyl chains which provide large number of cavities inside the alkyl chains than those available in smaller size alkyl chains. The molecules of solvent mixtures are accommodated inside these void spaces of alkyl chain of R_4NI.

IV. Conclusion

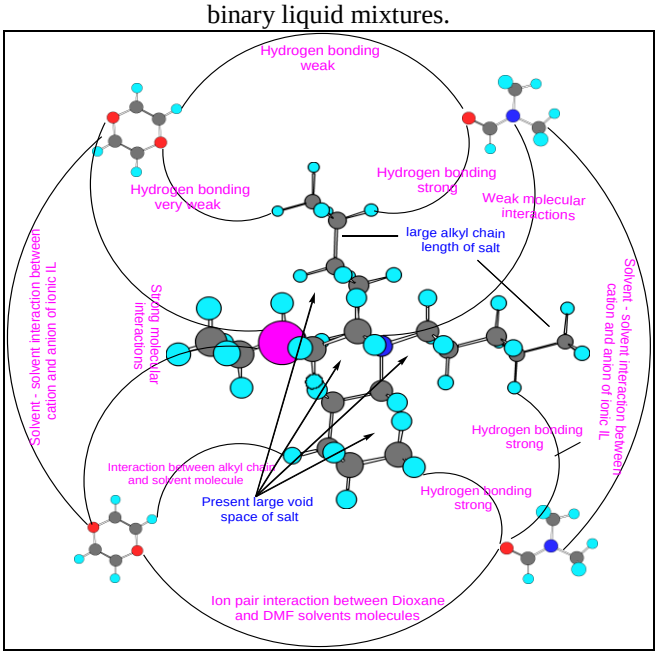
The work performed intends to map the thermo-physical behavior of two important families of DMF and Dioxane based on ammonium families (i.e. Et_4N^+, Pr_4N^+, Bu_4N^+, Pen_4N^+). All of them have the same cations of different size and having small as well as large void space, which showed specific behavior with binary liquid mixture at different temperatures. Obviously, fascinating results are obtained for structure and temperature dependent properties of unique kinds of DMF with Dioxane solvent and showes the nature of liquid with small void space to large void space with increasing alkyl chain length of R_4NI salt. The obtained theoretical and experimental result data; are helpful in understanding mixing effect and other existing molecular interactions during the ions transporting process. Furthermore; some specific type of molecular interactions of with Dioxane are obtained, when Dioxane is converted from boat to chair confirmation. Dioxane present within the large void space of alky chain in the chair form while boats form present away from cation. At every time DMF molecule present in polar form and formed hydrogen bonding with the molecules of Dioxane and very few molecules are able to penetrate into the void space of higher alky chain length because it created stronger dipole interactions with the alkyl chain as compared to Dioxane liquid mixture.

Scheme 1: 3D - molecular structure of Tetraethyl ammonium iodide (Et_4NI), Tetraproylammonium iodide (Pr_4NI), Tetrabutylammonium iodide (Bu_4NI) and Tetrapentyl ammonium iodide (Pen_4NI) salts molecules.



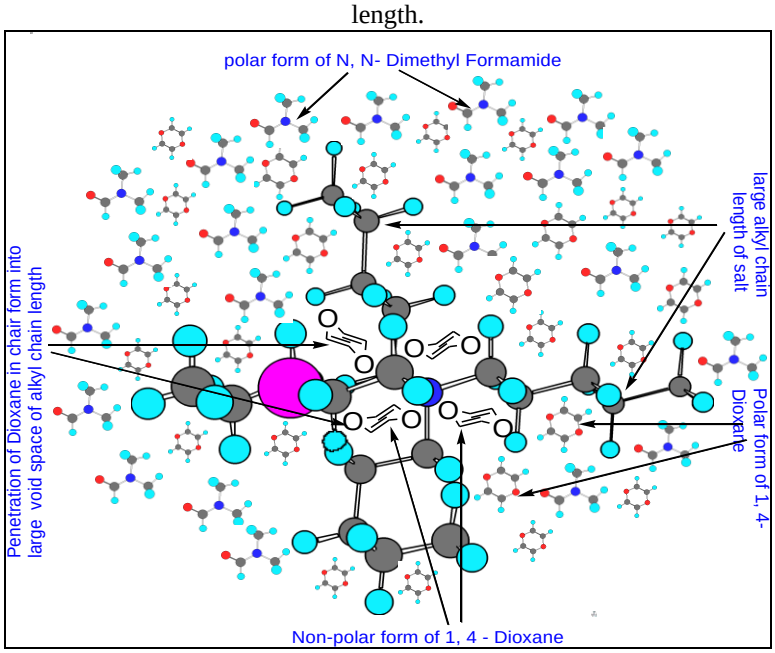
Colors: cyan = hydrogen, black = carbon and pink = iodide

Scheme 2: Showing hydrogen bonding, Types of molecular interactions occurred between the components of binary liquid mixtures.



Colours: blue = nitrogen, cyan = hydrogen, black = carbon, red = oxygen and pink = iodide

Scheme 3: Penetration of 1, 4 – Dioxane (chair form) within the large void space of alkyl chain length and planar form of Dioxane as well as N, N – Dimethyl Formamide (DMF) present away from the alkyl chain length.



Colours: blue = nitrogen, cyan = hydrogen, black = carbon, red = oxygen and pink = iodide

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Supporting Information

Dielectric constants of 1, 4 - Dioxane and N, N – Dimetyl Formamide and molecular structure of tetraethylammoniun iodide, tetrapropylammoniun iodide, tetrabutylammoniun iodide, tetrapentylammoniun iodide, Dioxane and DMF are available free charge on the internet at http:// pubs.acs.org.

Footnotes

Molecular interactions; Effect of large bulky group (R_4N^+) on the molecular structural and thermo-dynamical properties of binary liquid mixtures at different temperatures

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