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Influence of tetraalkylammonium chain length cation on molecular interactions of dioxane-DMSO-H_2O mixtures using ultrasonic technique at various temperatures

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Thermophysical properties provide a deep and meaningful picture of various interactions taking place in ternary and higher component liquid mixtures. Density (ρ), viscosity (η), and ultrasonic velocity (u) have been determined for the ternary liquid mixture of 1,4-dioxane-DMSO-water of different percentage compositions in the presence of quaternary alkyl ammonium iodide salts (R_4NI) of varying alkyl chain lengths at 303.15, 313.15 and 323.15 K. From the experimental data, the acoustical parameters such as adiabatic compressibility (β_{ad}), intermolecular free length (L_f), free volume (V_f), acoustic impedance (Z) and relaxation time (τ) have been evaluated. Studies at different temperatures have been carried out to check the validity of Frank's hypothesis as well as Eyring and Kincaid theory of model of propagation of sound velocity due to weak complex formation because of hydrogen bonds. The present investigation involves the study of nature of molecular interactions, molecular rearrangement and hydrogen bond making/breaking phenomena.

Keywords: Ultrasonic velocities, Acoustical parameters, Dielectric constants, Ternary liquid mixtures, Quaternary alkyl ammonium iodide salts, Molecular interactions, Hydrogen bonding

Ultrasonic velocity measurement finds wide applications in thousands of mixtures used in the process industry[1-4], hence knowledge of thermodynamic properties such as densities as well as thermo-acoustical parameters such as adiabatic compressibility (β_{ad}), intermolecular free length (L_f), free volume (V_f), acoustic impedance (Z) etc., of organic mixtures with water at various temperatures is of great importance. 1,4-Dioxane, DMSO and water have higher as well as lower values of dielectric constant (ε) which play a significant role in the studies of molecular interactions. The selection of ternary liquid systems for analysis is carried out in view of their ecological significance and industrial use[5-7]. Knowledge of thermophysical and thermo-acoustical properties of individual components and their mixtures is of great help in understanding the complex structure of liquids, which is the reason for selection of this ternary liquid system.

Adding tetraalkylammonium iodide salt of increasing alkyl chain lengths (i.e., from Et_4NI to Pen_4NI salt) to determine the molecular interactions involves the mixing of organic solvents at different temperatures[8-10], mixing of different compounds yields complex molecular structures that lead to various intermolecular interactions, resulting in non-ideal behaviour of mixtures[11]. Pathak *et al*. reported various molecular interactions by taking aqueous and non-aqueous binary solvent mixture and adding R_4NI salts (Et_4NI, Pr_4NI, Bu_4NI and Pen_4NI salts) using apparent molar volume measurements (ϕ_v), they showed the validity of Frank's hypothesis for these salt solutions[12]. Their observations confirmed that solute-solvent hating effect exists and the structure of any of the binary solvents is affected by the ion-solvent interactions.

A number of studies have been made on the intermolecular interactions in binary or ternary liquid mixtures at different temperatures using ultrasonic techniques[13-16]. The study of thermodynamic properties of ternary liquid containing electrolyte mixtures provides good measure of solute-solvent interactions. The present investigation is related to thermodynamic properties of ternary liquid mixtures of quadrupolar (dioxane), strongly dipolar (DMSO & water) and ionic species (salts), which play an important role in the development of molecular science.

In this paper, thermodynamic properties of ternary solution mixtures of 1,4-dioxane + DMSO + water containing Et_4NI to Pen_4NI salts (0.14 M) of different % compositions at 303.15, 313.15 and 323.15 K temperatures were investigated using ultrasonic and viscometric techniques. For this, measurement of ultrasonic velocity and acoustical parameters for ternary liquid mixture of DMSO and water along with 1,4-dioxane at 0.14 M of the components of the mixture at 2 MHz frequency and at different temperatures were carried out. These parameters play a significant role for above studies as they are highly sensitive towards molecular interactions in the liquid mixture[17].

Also, with the intention to present more general conclusions, systems of organic and aqueous solvent with tetraalkylammonium iodide salt of increasing alkyl chain lengths have been included in the analysis to see the effect of alkyl chain length size on molecular interactions.

In view of the aforementioned tasks, our previous results[18] have been extended with the experimental measurement of density and acoustical parameters of the ternary mixtures at atmospheric pressure over four % compositions (i.e., 0, 20, 40 & 60% 1,4-dioxane in DMSO-water) and at temperatures ranging from 303.15 to 323.15 K. Water has been taken as 40% constant in the selection of all ternary liquid mixtures. Molecular interactions between different molecules of the ternary liquid mixtures in the presence of R_4NI (tetraalkylammonium iodide) salt are investigated.

1,4-Dioxane has various applications. It is used as a stabilizer for chlorinated solvents such as TCA (1,1,1-trichloroethane), for impregnating cellulose acetate membrane filters, for wetting, as a dispersing agent in textile processes and as a laboratory cryoscopic solvent. It is also used as a non-polar solvent in organic chemical reactions and has high dielectric constant ($\varepsilon = 46.7$). DMSO is widely used topically to decrease pain and speed up healing of wounds, burns, muscle and skeletal injuries. It is also used to treat inflammation, osteoarthritis, rheumatoid arthritis etc. Tetraalkylammonium salts possess antimicrobial activity, and are used as phase transfer catalysts, fabric softeners, osmolytes and plant growth retardants.

The physiochemical properties such as density (ρ), viscosity (η) and ultrasonic velocity (u) of ternary liquid mixtures of 1,4-dioxane + dimethyl sulfoxide (DMSO) + water, containing tetraalkylammonium cation, are used to identify the behavior and nature of structure and making or breaking effect through molecular interactions. Many researchers have studied molecular interactions and structural properties of solution containing tetraalkylammonium salts in aqueous as well as non-aqueous binary solvent mixtures[19-20]. 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^+ (tetra alkyl ammonium cation) ions on account of water-hating influence of large alkyl chain[21]. So the formation of cavities occurs inside the enhanced water structure and the R_4N^+ ions are accommodated in it. The observations also confirm that such solute–solvent hating effect still exists and structure of any of the binary solvent is affected by the ion-solvent interactions.

According to Erying and Kincaid model[22] of sound propagation theory, if ultrasonic velocity decreases, intermolecular free length increases and vice versa, but in the present investigation for ternary liquid mixtures containing quaternary alkyl ammonium cation (R_4N^+), this is not applicable for lower tetra alkyl chain length cation due to specific type of molecular interactions which involve making/breaking of hydrogen bonds which does not accommodate the solvent molecules inside the cage of lower alkyl chain length cation, i.e., the Erying and Kincaid model for sound propagation failed in this case.

Materials and Methods

All the chemicals viz., 1,4-dioxane, dimethyl sulfoxide (DMSO) and quaternary alkyl ammonium iodide salts (R_4NI) such as tetraethylammonium iodide (Et_4NI), tetrapropylammonium iodide (Pr_4NI), tetrabutylammonium iodide (Bu_4NI) and tetrapentylammonium iodide (Pen_4NI) were obtained from E-Merck Chemicals Ltd, India. The R_4NI salts used in the present investigation, were purified by the method of Conway *et al.*[23] 1,4-Dioxane and DMSO (E-Merck, India) after being dried on freshly ignited quicklime, were 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. Also, the purity of the pure solvent was checked by comparing the measured densities and viscosities with those reported in literature. The densities and viscosities of the selected purified solvents, measured at 303.15, 313.15 and 323.15 K along with the literature values at the same temperatures are given in Table 1.

1, 4-Dioxane was used to prepare 0, 20, 40 and 60% (*v*/*v*) with binary solvent mixtures of 60, 40, 20 and 0% DMSO + water, in which water is taken to be 40% constant throughout the entire system of ternary liquid system. The values of dielectric constants (ϵ) for different % compositions of 1,4-dioxane + DMSO + water were measured with the help of BI-870 dielectric constant meter (absolute accuracy of ± 2%).

Ultrasonic velocities (u) of non-aqueous binary liquid mixtures were measured using a single crystal ultrasonic interferometer at lower frequency i.e., 2 MHz (Model-83S, supplied by Mittal enterprises, New Delhi, India. Calibration of the ultrasonic interferometer was done using the speed of sound of water at 298.15 K and its accuracy was found to be 0.4 ms^{-1}. The measuring cell was filled with 7–8 mL solution and was allowed to equilibrate for 30 min before taking the reading. The temperature was kept constant, using a water bath with an accuracy of ± 0.1 K. The densities and viscosities of these solutions were determined at different temperatures by magnetic float densitometer[37-38] and Ostwald viscometer respectively by using eqns 1 and 2.

$$\text{Density } (\rho) = (W+w+fI)/\ (V+w/\rho_{\text{pt}}) \qquad \ldots (1)$$

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, $\rho_{\text{pt},}$ density of pt and V, volume of float.

$$\eta_{\text{s}}\ /\ \eta_{\text{w}} = \rho_{\text{s}}/\ \rho_{\text{w}} \times t_{\text{s}}/\ t_{\text{w}} \qquad \ldots (2)$$

where $\eta_{\text{w},}$ ρ_{w} and t_{w} and η_{s}, ρ_{s} and t_{s} are the viscosity, density and time flow of water and unknown experimental solution respectively. Thermo-acoustical parameters such as adiabatic compressibility, β_{ad}, intermolecular free length, L_{f}, acoustic impedance, Z, relaxation time, τ, and free volume, V_{f}, were determined using standard equations[39-42].

Results and Discussion

The experimental values of density, viscosity and ultrasonic velocity for the ternary liquid system (1,4-dioxane + DMSO + water) containing tetra alkyl ammonium iodide (R_4NI) salts of 0.1 M have been calculated at 303.15 K, 313.15 K and 323.15 K. Thermo-acoustical behaviour of R_4NI in aqueous and non-aqueous solution have been measured over a range of temperatures. In the present investigation, studies were made with different % composition of 1,4-dioxane in binary system (DMSO + water) (*v*/*v*), in which water has been taken at a composition of 40% constant, while DMSO varies with 0, 20, 40 and 60% with dioxane for the entire range of selected compositions.

The dielectric constant (ϵ) of the selected pure 1,4-dioxane, DMSO and water are 2.25, 46.7 and 80.4 respectively. The dielectric constant of DMSO + water (ϵ = 66.4) can be gradually decreased by adding 1,4-dioxane (ϵ = 2.25) to it (Supplementary Data, Table S1). Thus four types of 1,4-dioxane + DMSO + water mixtures of varying dielectic constants were prepared, namely 0% dioxane (ϵ = 66.4), 20% dioxane (ϵ = 61.5), 40% dioxane (ϵ = 54.7) and 60% dioxane (ϵ = 48.5) in DMSO + water (*v*/*v*). Density measurements of some R_4NI salt solutions in these solvent mixtures were made and acoustical parameters were then calculated with 0.14 M concentration for each salt.

Ionized molecules interact strongly with solvent and the strength, ionic size, and nature of this interaction influence many thermophysical properties of the solvent like density and viscosity[43]. Hence,

Table 1 — Experimental and literature values of density and viscosity of purified solvents at different temperatures

Component	T (K)	ρ (g cm^{-3})		η (N s m^{-2})	
		experimental	literature	experimental	literature
DMSO	303.15	1.0908	1.0905[33], 1.0907[29]	1.8185	1.8034[33], 1.8102[23]
	313.15	1.0805	1.0804[34], 1.0806[35]	1.5203	1.5152[23]
	323.15	1.0709	1.0721[17]	1.2377	1.2351[17]
1, 4-Dioxane	303.15	1.0223	1.0225[29], 1.0224[28]	1.1125	1.1000[28], 1.0937[27]
	313.15	1.0120	1.0110[30]	0.9502	0.9425[30]
	323.15	0.9831	0.9834[25]	0.8091	0.8112[29]
Water	303.15	0.9957	0.9960[23], 0.9956[20]	0.8007	0.8005[18], 0.8075[20]
	313.15	0.9923	0.9922[20], 0.9922[24]	0.6460	0.6382[23], 0.6660[20]
	323.15	0.8904	0.8902[17]	0.4379	0.4298[20]

there is an increase in the number of solute ions with concentration, the trend of positive and negative deviation of acoustical parameters with different ionic size of solute at different % compositions of solvent confirms that the properties of liquid mixtures are affected by molecular interactions with changing concentration at various temperatures.

The structural changes occurring in the ternary liquid mixtures with increase in % composition of dioxane may cause a decrease in ultrasonic velocity at a particular temperature, as shown in Tables 2-5. The observed systematic change in the data of densities (ρ), viscosities (η) and ultrasonic velocities (u) follows Eyring and Kincaid theory for sound propagation in the ternary liquid system of 1,4-dioxane + DMSO + water, which gives some reliable information for the study of intermolecular interactions. The computed values of acoustical parameters of the selected four ternary liquid systems are given in Tables 2-5. It is observed that the ultrasonic velocity, density and viscosity decrease with increase in the % composition of dioxane in DMSO + water (40% constant). At all temperatures, the ultrasonic velocity, density and viscosity decreases. Such a decrease in velocity is an indication of molecular association between the components of the liquid mixture. Increasing trends of adiabatic compressibility is observed for Bu_4NI and Pen_4NI salt

Table 2 — Experimental values of density (ρ), ultrasonic velocity (u), viscosity (η) and derived acoustical parameters of 1,4-dioxane + DMSO + water + Et_4NI salt mixtures at different temperatures

% Compositions of solvents			ρ	$\eta \times 10^3$	u	$\beta_{ad} \times 10^{-10}$	$L_f \times 10^{-11}$	$Z \times 10^6$	$\tau \times 10^{-10}$	$V_f \times 10^{-7}$
Dioxane	DMSO	water	(g cm^{-3})	(N s m^{-2})	(m s^{-1})	(N^{-1} m^2)	(m)	(kg m^2 s^{-1})	(s)	(m^{3}mol^{-1})
303.15K										
0	60	40	1.0798	0.9562	1712	2.7143	2.816	1.8486	3.460	4.6979
20	40	40	1.0677	0.9029	1685	2.6592	2.758	1.7990	3.201	5.0475
40	20	40	1.0476	0.8304	1566	2.4535	2.545	1.6788	2.592	5.1764
60	0	40	1.0353	0.7579	1486	2.2218	2.305	1.5681	2.208	5.5398
313.15K										
0	60	40	1.0735	0.8969	1728	2.7815	2.941	1.8550	3.326	5.2441
20	40	40	1.0616	0.8399	1681	2.6617	2.814	1.7845	2.980	5.6059
40	20	40	1.0415	0.7809	1539	2.2741	2.404	1.6028	2.367	5.5302
60	0	40	1.0301	0.7229	1458	2.0636	2.182	1.5218	1.989	5.7797
323.15K										
0	60	40	1.0646	0.8515	1615	2.4499	2.639	1.7193	2.781	5.1222
20	40	40	1.0524	0.7728	1591	2.4052	2.591	1.6743	2.478	5.8485
40	20	40	1.0323	0.7225	1540	2.2973	2.475	1.5897	2.213	6.2201
60	0	40	1.0209	0.7155	1479	2.1426	2.308	1.5099	2.044	5.9969

Table 3 — Experimental values of density (ρ), ultrasonic velocity (u), viscosity (η) and the derived acoustical parameters of 1,4-dioxane + DMSO + water + Pr_4NI salt mixtures at different temperatures

% Compositions of solvents			ρ	$\eta \times 10^3$	u	$\beta_{ad} \times 10^{-10}$	$L_f \times 10^{-11}$	$Z \times 10^6$	$\tau \times 10^{-10}$	$V_f \times 10^{-7}$
Dioxane	DMSO	water	(g cm^{-3})	(N s m^{-2})	(m s^{-1})	(N^{-1} m^2)	(m)	(kg m^2 s^{-1})	(s)	(m^{3}mol^{-1})
303.15 K										
0	60	40	1.0787	0.8088	1683	2.6258	2.724	1.8154	2.832	6.5228
20	40	40	1.0563	0.7818	1637	2.5369	2.632	1.7291	2.644	6.8001
40	20	40	1.0473	0.7646	1603	2.3409	2.428	1.6405	2.501	6.4659
60	0	40	1.0344	0.7456	1516	2.1329	2.212	1.5384	2.155	6.4990
313.15 K										
0	60	40	1.0714	0.7651	1637	2.5011	2.644	1.7538	2.551	6.5228
20	40	40	1.0492	0.7493	1564	2.3313	2.465	1.6409	2.329	6.9169
40	20	40	1.0316	0.7293	1495	2.1665	2.291	1.5577	2.106	7.4030
60	0	40	1.0292	0.7149	1445	2.0287	2.145	1.5154	1.933	7.8891
323.15 K										
0	60	40	1.0632	0.7639	1601	2.4108	2.597	1.7021	2.455	5.4237
20	40	40	1.0413	0.7390	1526	2.2363	2.496	1.5890	2.203	6.2596
40	20	40	1.0232	0.7222	1502	2.2048	2.375	1.5368	2.123	6.8115
60	0	40	1.0198	0.7018	1420	1.9772	2.130	1.4481	1.850	7.0146

Table 4 — Experimental values of density (ρ), ultrasonic velocity (u), viscosity (η) and the derived acoustical parameters of 1,4-dioxane + DMSO + water + Bu_4NI salt mixtures at different temperatures

% Compositions of solvents			ρ	$\eta \times 10^3$	u	$\beta_{ad} \times 10^{-10}$	$L_f \times 10^{-11}$	$Z \times 10^6$	$\tau \times 10^{-10}$	$V_f \times 10^{-7}$
Dioxane	DMSO	water	(g cm^{-3})	(N s m^{-2})	(m s^{-1})	(N^{-1} m^2)	(m)	(kg m^2 s^{-1})	(s)	(m^3mol^{-1})
303.15 K										
0	60	40	1.0804	0.8224	1679	3.2833	3.406	1.8039	3.600	9.0777
20	40	40	1.0614	0.7845	1582	3.7645	3.905	1.6791	3.937	8.9746
40	20	40	1.0496	0.7720	1526	4.0913	4.244	1.6016	4.211	8.7711
60	0	40	1.0321	0.7507	1471	4.4776	4.645	1.5182	4.482	8.7178
313.15 K										
0	60	40	1.0739	0.8192	1594	3.6648	3.875	1.7117	4.002	8.4464
20	40	40	1.0573	0.7730	1527	4.0562	4.289	1.6144	4.180	8.7013
40	20	40	1.0434	0.7655	1493	4.2996	4.546	1.5422	4.388	8.5965
60	0	40	1.0251	0.7494	1478	4.4656	4.722	1.4871	4.462	8.8030
323.15 K										
0	60	40	1.0631	1.0477	1550	3.9152	4.218	1.6478	5.209	5.7997
20	40	40	1.0489	1.0187	1492	4.2828	4.614	1.5649	5.744	6.5549
40	20	40	1.0329	0.8851	1408	4.7835	5.061	1.4843	5.763	7.0323
60	0	40	1.0165	0.7351	1384	5.1359	5.533	1.4068	6.433	7.3106

Table 5 — Experimental values of density (ρ), ultrasonic velocity (u), viscosity (η) and the derived acoustical parameters of 1,4-dioxane + DMSO + water + Pen_4NI salt mixtures at different temperatures

% Compositions of solvents			ρ	$\eta \times 10^3$	u	$\beta_{ad} \times 10^{-10}$	$L_f \times 10^{-11}$	$Z \times 10^6$	$\tau \times 10^{-10}$	$V_f \times 10^{-7}$
Dioxane	DMSO	water	(g cm^{-3})	(N s m^{-2})	(m s^{-1})	($N^{-1}m^2$)	(m)	(kg m^2 s^{-1})	(s)	(m^3mol^{-1})
303.15 K										
0	60	40	1.0788	1.0501	1656	3.3801	3.506	1.7864	4.732	7.4273
20	40	40	1.0676	1.0264	1568	3.8097	3.952	1.6739	5.213	7.1171
40	20	40	1.0511	1.0184	1493	4.2685	4.428	1.5692	5.796	6.7406
60	0	40	1.0328	1.0095	1453	4.5862	4.758	1.5006	6.173	6.5980
313.15 K										
0	60	40	1.0724	1.0056	1540	3.9318	4.157	1.6514	5.272	7.1077
20	40	40	1.0604	0.9902	1502	4.1801	4.420	1.5927	5.518	7.6417
40	20	40	1.0423	0.8495	1465	4.4702	4.727	1.5269	5.463	8.0002
60	0	40	1.0255	0.8406	1378	5.1353	5.430	1.4131	5.755	8.5198
323.15 K										
0	60	40	1.0626	0.9982	1522	4.0625	4.377	1.6172	5.469	6.2133
20	40	40	1.0492	0.9902	1480	4.3512	4.688	1.5528	5.917	6.8876
40	20	40	1.0345	0.9656	1410	4.8621	5.238	1.4586	6.259	7.1007
60	0	40	1.0142	0.9478	1312	5.7280	6.172	1.3306	7.238	7.5230

solution while a decreasing trend is observed for Et_4NI and Pr_4NI salt solution upon adding 1,4-dioxane into the binary system of DMSO + water (Figs 1a-1c). When 1,4-dioxane content increases, molecular rearrangement takes place through the molecular interaction between the solute and solvent in the liquid mixture which causes structural change and hence increases the adiabatic compressibility.

Variation of adiabatic compressibility (β_{ad}) can be understood theoretically on the basis of change in the value of dielectric constant (ε). The nature of molecular interaction between the solute and solvent also depends on the values of dielectric constant. It is known that electrostatic force of attraction, F, between the ions, is inversely proportional to the dielectric constant of solvent medium (i.e., $F \propto 1/\varepsilon$), the increase in the value of dielectric constant of the solvent medium results in weak electrostatic force of attraction between the ions and hence ion-ion interactions become weaker as there is a gradual increase of dielectric constant of the medium. On moving from 0 to 60% 1,4-dioxane, the dielectric constant values of the ternary system decreases, hence force of attraction between the ions of the components gradually increases i.e., molecular association takes place forming a H-bonding network.

Adiabatic compressibility is greater for Et_4NI than Pr_4NI salt solution but is lower in case of Bu_4NI and

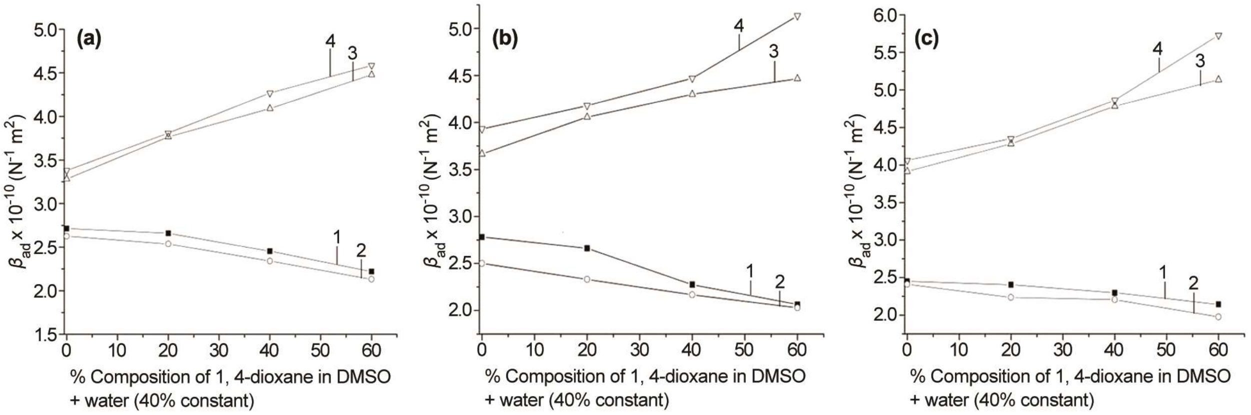

Fig. 1 — Adiabatic compressibility versus % composition of dioxane in DMSO + water (40 % constant) at (a) 303.15 K, (b) 313.15 K, and, (c) 323.15 K.

Pen_4NI salt solution (Figs 1a-1c). This can be understood on the basis of behaviour of solvent molecules with ionic size of salts. 3D molecular structure of tetraethylammonium iodide (Et_4NI), tetraproylammonium iodide (Pr_4NI), tetrabutylammonium iodide (Bu_4NI) and tetrapentylammonium iodide (Pen_4NI) salts are given in Supplementary Data, Fig. S1. A large vacant space is available in the molecular structure of Pr_4NI and Pen_4NI salt, while the molecular structures of Et_4NI and Pr_4NI have very little vacant space, therefore solvent molecules are able to penetrate into the vacant space of Bu_4NI and Pen_4NI salt but not in the molecular structure of Et_4NI and Pr_4NI salt.

Furthermore, some specific type of molecular interactions i.e., rearrangement occurred between the ions of binary liquid mixtures with dioxane due to low value of dielectric constant, when dioxane is converted from boat to chair conformation. Dioxane occupies the large void space of the alkyl chain in chair form, while in the boat form it could not penetrate into this void space, due to lower stability of boat form as compared to chair form. A systematic representation of hydrogen bonding, types of molecular interactions between the components of 1,4-dioxane, DMSO and water with large void space of alkyl chain length of tetrapentylammonium iodide (Pen_4NI) salt are given in Supplementary Data, Fig. S2.

1, 4-Dioxane and DMSO molecules form a strong hydrogen bonding with water molecules around the Et_4N^+ and Pr_4N^+ ions, while in the case of Bu_4N^+ and Pen_4N^+ ions, some solvent molecules penetrate into its large vacant space and are not able to form hydrogen bonding with the water molecules. Hence, only few molecules of 1,4-dioxane and DMSO are able to form hydrogen bonding with water. Therefore, adiabatic compressibility of Bu_4NI and Pen_4NI is greater than that of Et_4NI and Pr_4NI salt solution.

Due to the smaller size of Et_4N^+ ion, adiabatic compressibility of Et_4N^+ is greater than that of Pr_4N^+ ion, while it is lower than that of Bu_4N^+ and Pen_4N^+ ion. This is explained on the basis of penetration of solvent molecule into the vacant space of Bu_4N^+ and Pen_4N^+ ion and intermolecular hydrogen bonding.

According to Kannappan *et al.*[44], negative deviation in the curve of intermolecular free length (L_f) indicates that sound waves cover longer distance due to decrease in L_f, ascribing the dominant nature of hydrogen bond interaction between unlike molecules. Intermolecular free length (L_f) depends on adiabatic compressibility (β_{ad}) and shows a similar nature as that of compressibility. Hence free length also increases for Bu_4N^+ and Pen_4N^+ ions, while it decreases for Et_4N^+ and Pr_4N^+ ions at a slower rate as shown in Figs 2a-2c. Such type of variations causes penetration of solvent molecules that are not able to form hydrogen bonding in case of Bu_4N^+ and Pen_4N^+ ions while forming bonds in case of Et_4N^+ and Pr_4N^+ ions. On the basis of a model for sound propagation proposed by Eyring and Kincaid, ultrasonic velocity should decrease when the intermolecular free length increases and vice versa. It is reflected by the present investigation for Bu_4N^+ and Pen_4N^+ ions. But this theory is not applicable for Et_4N^+ and Pr_4N^+ ions due to presence of strong hydrogen bonding of 1,4-dioxane and DMSO with water molecules, thus showing negative deviations. On increasing the temperature, intermolecular free length increases for all the components of ternary liquid mixtures.

The decrease in the values of acoustic impedance (Z) on increasing dioxane content from 0 to 60% of Dioxane in DMSO + water solution can be

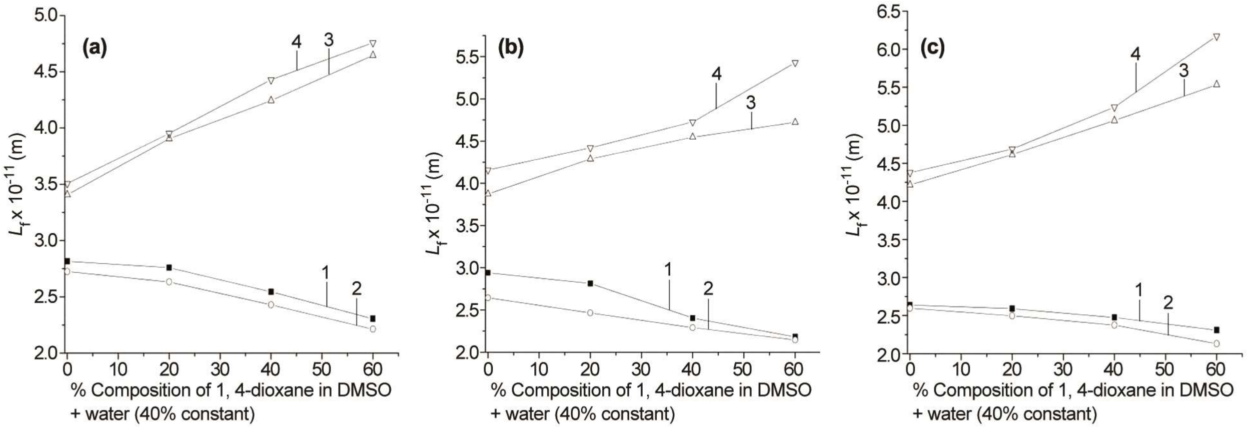

Fig. 2 — Intermolecular free length (L_f) versus % composition of 1, 4-dioxane in DMSO + water (40 % constant) at (a) 303.15 K, (b) 313.15 K, and, (c) 323.15 K.

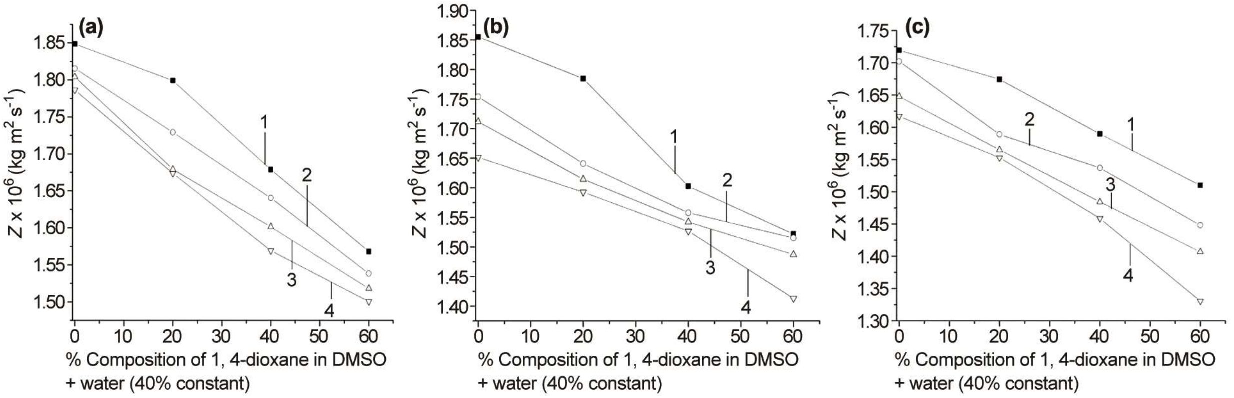

Fig. 3 — Acoustic impedance (Z) versus % composition of 1, 4-dioxane in DMSO + water (40 % constant) at (a) 303.15 K, (b) 313.15 K, and, (c) 323.15 K.

attributed to the effective solute-solvent interactions (Figs 3a-3c). Acoustic impedance (Z) is greater for Et_4N^+ and is lower for Pen_4N^+ ion, while Pr_4N^+ and Bu_4N^+ ions show intermediate values of Z at all the studied temperatures. All the solution mixtures show trends of linearity at all temperatures and acoustic impedance decreases with increasing temperature. The acoustic impedance is a measure of the internal and elastic properties of the medium and hence supports the possibilities of molecular interactions, it is also used for assessing the absorption of sound in the medium, therefore, Et_4N^+ and Pr_4N^+ ions show greater elastic property, as compared to Bu_4N^+ and Pen_4N^+ ions. The change in the values of Z can be understood on the basis of ionic size and longer alkyl chains which provide large number of cavities within the alkyl chains than those available in case of smaller size alkyl chains.

The relaxation time (τ) slowly increase with increase in dioxane content from 0 to 60% in DMSO + water for Bu_4N^+ and Pen_4N^+ ions while it slowly decreases for Et_4N^+ and Pr_4N^+ ions. The values of relaxation time are larger for all the systems and also show trends of linearity as shown in Figs 4a-4c. On increasing the temperature of the system, deviations increase between small and large alkyl chain cations and a similar behaviour is seen in Et_4N^+ and Pr_4N^+ ions, and, Bu_4N^+ and Pen_4N^+ ions, the value of τ is higher for Pen_4N^+ and lower for Et_4N^+ ion at all temperatures. The dispersion of ultrasonic velocity in the system contains information about the characteristics time (τ) of the relaxation process that causes dispersion in the liquid mixtures. The relaxation time (τ) increases with increase in the size of R_4N^+ ions from Bu_4N^+ to Pen_4N^+, while it decreases from Et_4N^+ to Pr_4N^+ ions. Such large variations in curves of τ indicates that there exists strong ionic interactions as well as hydrogen bonding between the components of the ternary liquid mixtures.

Free volume is the average volume in which the central molecule can move due to the repulsion of the

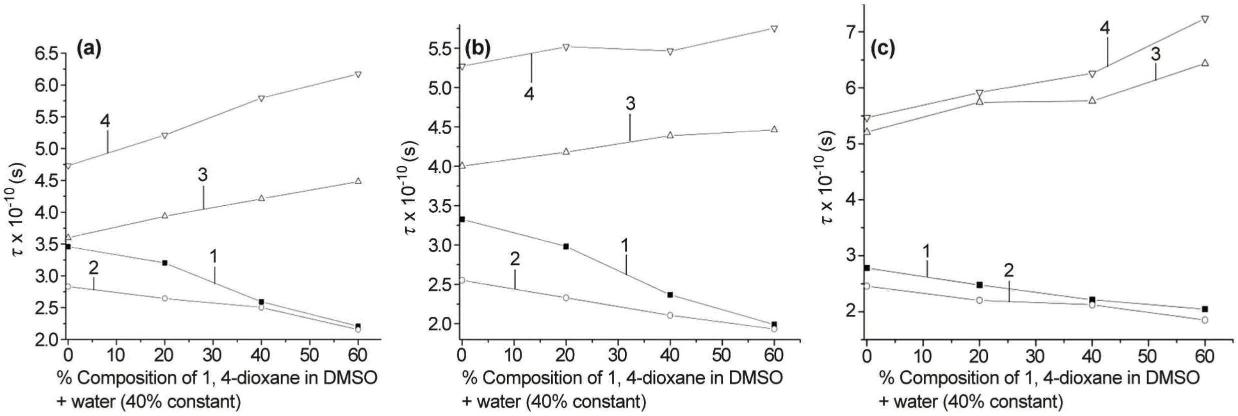

Fig. 4 — Relaxation time (τ) versus % composition of 1,4-dioxane in DMSO + water (40 % constant) at (a) 303.15 K, (b) 313.15 K, and, (c) 323.15 K.

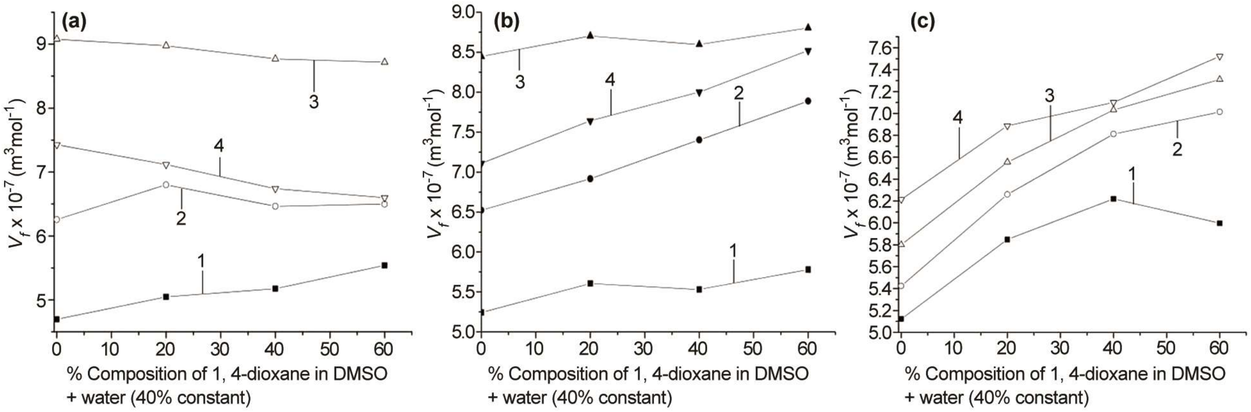

Fig. 5 — Free volume (V_f) versus % composition of 1,4-dioxane in DMSO + water (40 % constant) at (a) 303.15 K, (b) 313.15 K, and, (c) 323.15 K

surrounding molecules. At a constant concentration (0.14 M) of component liquid and constant temperature, the viscosity remains constant, hence,

$$V_f \propto U^{3/2} \qquad \ldots (3)$$

Since velocity decreases at a fixed frequency and free volume also decreases, at 303.15 K, Bu_4N^+ and Pen_4N^+ ions obey this equation, but Et_4N^+ and Pr_4N^+ do not follow this trend as shown in Fig. 5a. On raising the temperature, free volume of all the R_4N^+ cations shows a non-linear and slow increase (Figs 5b-5c). This is due to the increase in internal energy and strong repulsive forces occurring within the large vacant space of R_4N^+ cation, due to which solvent molecules are not able to hold within it, thus forming a weak type of hydrogen bonding around Bu_4N^+ and Pen_4N^+ cation. Hence, on increasing the % composition of dioxane, free volume of all the systems increases slowly in a non-linear manner at 313.15 and 323.15 K but it decreases for Bu_4N^+ and Pen_4N^+ ions, and increases for Et_4N^+ and Pr_4N^+ ion at 303.15 K. 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 increasing values of free volume after increasing the % composition of dioxane in DMSO + water system. These observations confirm the formation of strong hydrogen bonding among the aqueous and non-aqueous solvents and the non-polar, dioxane present in the chair conformation.

Fort *et al.*[45], noticed the negative deviation in the trend of free volume which tends to decrease as the strength of the interaction between unlike molecules increases. All the variation in the nature of curve can be explained in terms of molecular interaction, structural effect and interstitial accommodation along with changes in free volume, which are reflected in the present investigation. The molecules of 1,4-dioxane are inserted within the large void space of Bu_4N^+ and Pen_4N^+ cation by the conversion from boat (polar) to chair conformation (non-polar) and produces weak repulsive forces with tetraalkylammonium cation, which causes dipole-induced dipole interactions. A stronger molecular interaction occurs between DMSO and water at higher temperature, which becomes unstable due to increase in its energy. This energy can be reduced by the conversion of boat to chair form of 1,4-dioxane. Hence, the stability of solvent molecules is increased through weak hydrogen bonding. This leads to additional dipole-induced dipole type molecular interactions in the case of Bu_4N^+ and Pen_4N^+ cations.

Free volume (V_f) of Bu_4N^+ cation is greater at 303.15 and 313.15 K than Pen_4N^+ cation because very few molecules of the organic solvent penetrate into the void space of Bu_4N^+ cation whereas a large number of organic solvent molecules penetrate into the vacant space of Pen_4N^+ cation. At 323.15 K, Pen_4N^+ shows higher activity towards free volume because upon raising the temperature of liquid system, the internal energy increases and repulsive forces become dominant among the organic liquid molecules and quaternary alkyl chain length. Hence organic solvent molecules are held within the void space of higher alkyl chain length leading to greater free volume.

Thus, the present investigation proved that specific types of forces occurred between the molecules such as making/breaking of hydrogen bond, electrostatic forces between charged molecules of a permanent dipole, induced dipole or force of attraction or repulsion between non-polar molecules. Thermodynamic property of ternary liquid mixtures arises from the structural fitting of one component into another due to the difference in shape and size of the solute and solvent molecules.

Conclusions

Viscosities of ternary systems with water, 1,4-dioxane, and DMSO were experimentally measured at various temperatures and acoustical parameters were calculated using standard equations, and correlated by means of Eyring and Kincaid theory and, Frank's hypothesis. The viscosity prediction for the ternary system with the same models lead to best results in case of higher alkyl chain length cation. The observed trends and variations of thermophysical and acoustical parameters with different % composition of 1,4-dioxane in DMSO + water provide useful information about the structural interactions. It is seen that there exists molecular association between the component of the ternary liquid mixture due to dipole-dipole, dipole-induced dipole and hydrogen bonding interactions, which varies with change in dielectric constant and temperature. The present investigation shows that the model of propagation of ultrasonic velocity as given by Eyring and Kincaid theory, failed for lower alkyl chain length i.e., Et_4NI and Pr_4NI salt, while it is applicable for higher alkyl chain length i.e., Bu_4NI and Pen_4NI salts. This is due to the accommodation of solvent molecules in the large cavity in case of higher alkyl chain length and breaking of hydrogen bonding as well as formation of strong hydrogen bonding in case of lower alkyl chain length cation, that validated Frank's hypothesis.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(12)1454-1463_SupplData.pdf.

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References

1 Rajagopal K & Chenthilnath S, *Ind J Pure Appl Phys*, 48 (2010) 326.

2 Caro M N, Trenzado J L, Galván S, Romano E, González E, Alcalde R & Aparicio S, *J Chem Eng Data*, 58 (2013), 909.

3 Grande M C, Julia J A, Barrero C R & Marschoff C M, *Phys Chem Liq*, 51 (2013) 457.

4 Wang C, Li H, Zhu L & Han S, *Fluid Phase Equilib*, 189 (2001) 129.

5 Plechkova N V & Seddon K R, *Chem Soc Rev*, 37 (2008) 123.

6 Attri P, Reddy P M & Venkatesu P, *Ind J Chem*, 49 A (2010) 736.

7 Attri P, Reddy P M, Venkatesu P, Kumar A & Hofman T, *J Phys Chem B*, 114 (2010) 6126.

8 Gallego-Juarez J A, *Phys Procedia*, 3 (2010) 35.

9 Brigante M & Sumbatyan M A, *Russ J Nondestr Test*, 49 (2013) 100.

10 Ali A, & Nabi F, *J Disp Sci Techn*, 31 (2010) 1326.

11 Zade S D, *Rasayan J Chem*, 4 (2011) 620.

12 Pathak R N, Saxena I, Archna, Kumar R & Singh N, *Trans Farad Soc*, 3 (2014) 87.

13 Xu G, Li X, Hu Y, Wang Y, Fan G & Zhang M, *J Chem Eng Data*, 55 (2010) 2345.

14 Yadava S S & Yadav A, *Ind J Pure Appl Phys*, 42 (2004) 338.

15 Sarkar L & Roy M N, *J Chem Eng Data*, 340 (2009) 3307.

16 Roy M N, Sah R S & Pradhan P, *Int J Thermophys*, 31 (2010) 316.

17 Shinde B R & Jadhav K M, *Pharm Onli*, 2 (2010) 533.

18 Saxena I, Kumar V & Devi R, *IOSR- J App Chem*, 10 (2017) 26.

19 Pathak R N, Saxena I, Archna & Mishra A K, *Ind Counc Chem*, 26 (2009) 170.

20 Saxena I, Kumar V & Devi R, *Russ J Phys Chem B*, 90 (2018) 17.

21 Frank H S, *J Phys Chem*, 67 (1963) 1554.

22 Eyring & Kincaid J F, *J Chem Phys*, 6 (1938) 620.

23 Conway B E, Verrall R E & Desnoyers J E, *Trans Farad Soc*, 62 (1966) 2738.

24 Osval S L & Patel N B, *J Chem Eng Data*, 40 (1995) 845.

25 Aminabhavi T M & Patil V B, *J Chem Eng Data,* 43 (1998) 497.

26 Pacak P, *J Sol Chem,* 16 (1987) 71.

27 Aznarez S, Mussari L &. Postigo M A, *J Chem Eng Data*, 38 (1993) 270.

28 Palaiologou M M, Molinou I E & Tsierkezos N, *J Chem Eng Data*, 47 (2002) 1285.

29 Ottani S, Vitalini D, Comelli F & Castellari C, *J Chem Eng Data*, 47 (2002) 1197.

30 Contreras M, *J Chem Eng Data*, 46 (2001) 1149.

31 Kinart C M, Kinart W J & Wiklinska A, *J Chem Eng Data*, 47 (2002) 23.

32 Kapadi U R, Chavan S K & Yemul O S, *J Chem Eng Data*, 42 (1997) 548.

33 Tsierkezov N & Molinou I, *J Chem Eng Data*, 43 (1998) 989.

34 Baraldi P, Franchini G C, Marchetti A, Sanna G, Tassi L, Ulrici A & Vaccari G, *J Sol Chem*, 29 (2000) 489.

35 Papanatasiou G E & Ziogas I, *J Chem Eng Data*, 37 (1992) 167.

36 Dizechi M & Marschall E, *J Chem Eng Data*, 27 (1982) 358.

37 Pathak R N & Saxena I, *Ind J Eng Mat Sci*, 5 (1998) 278.

38 Saxena I, Mishra, A K, Kumar V, Gautam S & Tripathi J, *Int J Curr Res*, 8 (2016) 39800.

39 Nikam P S & Hasan M, *J Chem Eng Data*, 88 (1988) 165.

40 Nikam P S & Hasan M, *Asian J Chem*, 5 (1993) 319.

41 Kumar N V B, Rao S A & Rao C K, *J Acoust Soci Ind*, 28 (2000) 297.

42 Reddy R K, Rama M S & Moorthy R L, *J Acoust Soci Ind*, 19 (1991) 22.

43 Adreev M, Pable J De, Chremos A, Douglas J F, *J Phys Chem B*, 122 (2018) 4029.

44 Kannappan A N & Palani R, *Ind J Pure & Appl Phys*, 70B (1996) 59.

45 Fort R J & Moore W R, *Trans Farad Soc*, 61 (1965) 2102.