Thermo-acoustical properties of carbamide and N, N-dimethylformamide binary mixture at different temperatures

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Density, viscosity and ultrasonic velocity of binary mixture of carbamide with N, N-dimethylformamide have been measured at temperatures of 10 °C, 20 °C, 30 °C and 40 °C and at atmospheric pressure. From these experimental measurements the thermo-acoustical parameters such as acoustic impedance (Z), adiabatic compressibility (β), relaxation time (τ), intermolecular free length (L_f) and Gibb's free energy of activation (ΔG) have been calculated. The variations in these parameters have been correlated to derive the intermolecular interactions taking place between the species of present binary mixture.

Keywords: Carbamide, DMF, Viscosity, Ultrasonic velocity, Thermo-acoustical, Compressibility, Molecular free length

1 Introduction

Chemical compounds with specific physical, chemical, thermodynamical properties decide their role and action in any application. Huge amount of research work has been carried in the field of thermo-acoustical studies, and still researchers found these studies very useful to understand the intermolecular interactions with some basic parameters such as ultrasonic velocity, density and viscosity[1-3]. The studies related to the gas treating units design[4], low-temperature fluidity[5], biodiesels applications[6], electrolyte solutions[7,8], pharmaceuticals[9] etc. are the area where these parameters play important role. Majority of the studies giving the solute-solute, solute-solvent and solvent-solvent interactions have been reported in liquid-liquid mixtures in past[1-6]. Present study deals with the measurements of density, viscosity and ultrasonic velocity of the solid-liquid binary mixtures. These are very essential parameters for understanding the behaviour of solutions[10], information about nature of molecular interactions[11] and structural aspects[12]. However, so far best of our knowledge, no thermo-acoustical studies of solid + liquid binary mixtures have been reported yet.

N, N –Dimethylformamide (DMF) is a versatile, non-aqueous polar solvent having wide range of applications[13]. It is used in pharmaceutical as well as in substitution and other reactions[14]. Carbamide, also known as urea, has practical applications as a fertilizer in agriculture. It is main nitrogenous compound of protein metabolism[15]. Along with this, urea and its derivatives have many applications in biological activities, pharmaceuticals and medicinal chemistry[16-19]. Based on these useful applications of both of the compounds, we decided to have productive data and knowledge of their binary mixtures based on thermo-acoustical study.

2 Experimental Details

2.1 Materials

DMF having purity ≥99 % of HPLC grade and Carbamide (Urea) of (≥99 % pure, AR grade) have been obtained commercially from Moly-Chem. Pvt Ltd, Mumbai. Also, the purity of DMF was ascertained by comparing its density, viscosity and ultrasonic velocity with literature values at different temperature (Table 1). Both materials were used without further purification. The binary mixture solutions were prepared with different weight of solid compound (x_1 of urea) in 0.0 gm to 1.0 gm range with the steps of 0.1 gm, added in 10 ml DMF, under the solubility limit of urea in DMF. The weight of the samples before and after preparation was recorded to calculate weight fraction of samples.

2.2 Measurements

The density measurements of binary mixtures were carried out by using vibrating U-tube operated digital density meter (DMA-35, Anton Paar) with the accuracy of ±0.1 kg/m³. Brookfield viscometer (LV-DV-II+Pro, Brookfield) were used to measure

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Table 1 — Comparison of experimental ultrasonic velocity, density and viscosity or pure DMF with literature values at different temperature.

	Ultrasonic velocity (U) (m·s^{-1})				Density (ρ) (Kg·m^{-3})				Viscosity ($\eta \times 10^{-10}$) (N·s·m^{-2})			
	10°C	20°C	30 °C	40 °C	10 °C	20 °C	30 °C	40 °C	10 °C	20 °C	30 °C	40 °C
Expt.	1509	1469	1437	1398	958.1	949.4	939.1	929.5	1.05	0.90	0.76	0.63
Lit.	—	—	1442[23] 1444[24]	1402[23]	—	—	939.5[24] 936.5[25]	933.6[23] 929.4[25]	—	—	0.7588[23]	0.6353[23]

Standard uncertainties: u(U)=0.2 m·s^{-1} ; u(ρ)=0.1 Kg·m^{-3}; u(η) =0.01 N·s·m^{-2}

Table 2 — Ultrasonic velocity (U), density (ρ), and viscosity (η) of urea + DMF binary mixtures at 10 °C, 20 °C, 30 °C and 40 °C.

Weight of Urea (gm)	Weight fraction of Urea (X$_1$)	Ultrasonic velocity (U) (m·s^{-1})				Density (ρ) (Kg·m^{-3})				Viscosity ($\eta \times 10^{-10}$) (N·s·m^{-2})			
		10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C
0.0	0.0000	1509	1469	1437	1398	958.1	949.4	939.1	929.5	1.05	0.90	0.76	0.63
0.1	0.0105	1516	1474	1446	1406	961.9	952.7	943.2	933.0	1.15	0.97	0.84	0.70
0.2	0.0207	1523	1480	1453	1413	965.1	956.5	946.1	936.4	1.21	1.03	0.88	0.74
0.3	0.0308	1529	1487	1459	1420	968.4	959.4	948.9	939.3	1.28	1.09	0.92	0.76
0.4	0.0406	1535	1493	1464	1427	971.9	962.3	951.9	942.2	1.35	1.15	0.97	0.80
0.5	0.0503	1541	1498	1470	1434	975.3	965.6	954.4	945.5	1.43	1.21	1.01	0.83
0.6	0.0597	1546	1502	1475	1439	979.0	968.6	957.7	949.3	1.51	1.28	1.06	0.87
0.7	0.0690	1550	1506	1478	1444	981.9	971.3	961.4	952.0	1.60	1.35	1.11	0.91
0.8	0.0781	1554	1509	1481	1448	984.8	974.5	964.1	955.1	1.71	1.43	1.17	0.95
0.9	0.0870	1556	1513	1484	1451	987.9	978.1	967.5	958.2	1.83	1.51	1.23	0.99
1.0	0.0958	1558	1515	1487	1455	991.2	980.5	970.7	961.4	1.97	1.61	1.30	1.05

the viscosities of the binary mixture, accuracy of the instrument was ±0.01 cP. Ultrasonic velocity measurements were performed using Ultrasonic interferometer for liquids (F-05, Mittal Enterprises). The measurement accuracy of the instrument is ±1 m/s. All the measurements were carried out at 10 °C to 40 °C with 10 °C intervals. Doubly walled sample cells of viscometer and interferometer assured the temperature maintenance under limit with accuracy of ±0.1 °C using refrigerated water circulating bath. The calibrations of each instrument were performed prior to actual measurements. Three measurements were performed for density and viscosity to avoid uncertainties in measurements.

3 Results and Discussion

For DMF measured data at different temperatures and the literature values were compared and found to be in good agreement (Table 1). The values of ultrasonic velocities, density and viscosity of binary mixtures are listed in Table 2

These measured data was then used to calculate the thermo-acoustical parameters viz. values of Z, β, τ, L$_f$, and ΔG are tabulated in Table 3. The standard relations given in literature[20-22] are used to calculate these parameters. The respective graphs of studied

parameters are used to interpret the intermolecular interactions between solute and solvent.

3.1 Ultrasonic velocity

Variation in ultrasonic velocity in solutions indicates the molecular association in the molecules present in it. Figure 1 shows the variation of ultrasonic velocity in the present binary mixture with weight fraction of urea in DMF. Ultrasonic velocity increases with the increase in Urea content in DMF. This increase suggests structure making capacity of urea[26]. Due to increase in molecular association the mixture becomes stiffer and hence, ultrasonic waves pass through the medium rapidly[27]. Minimum velocity indicates weaker interactions[28]. It has also been observed that with increase in temperature, ultrasonic velocity decreases as illustrated in Fig. 1. At higher temperature homo molecular clusters may break, leading to decrease in value of ultrasonic velocity[26]. This decrease in ultrasonic velocity indicates that the interaction between solute and solvent is becoming less dominant at higher temperatures.

3.2 Density

Figure 2 illustrates variation of density of mixture with weight fraction of urea in DMF. It has been observed that the density of mixture increases with

Table 3 — Derived thermo-acoustical parameters of Urea + DMF at different temperatures

Weight of urea (gm)	Weight fraction of urea (X_1)	Acoustic impedance ($Z \times 10^6$) (Kg·m^{-2}·s^{-1})				Adiabatic compressibility ($\beta \times 10^{-10}$) (m^2·N^{-1})				Relaxation time ($\tau \times 10^{-10}$) (s)			
		10 °C	20 °C	30 °C	40 °C	10 °C	20 °C	30 °C	40 °C	10 °C	20 °C	30 °C	40 °C
0.0	0.0000	1.445	1.393	1.350	1.299	4.583	4.887	5.149	5.504	6.417	5.865	5.218	4.624
0.1	0.0105	1.458	1.404	1.363	1.311	4.523	4.831	5.070	5.429	6.936	6.243	5.679	5.060
0.2	0.0207	1.469	1.415	1.374	1.323	4.467	4.773	5.006	5.348	7.207	6.554	5.874	5.277
0.3	0.0308	1.480	1.426	1.384	1.333	4.417	4.713	4.950	5.279	7.538	6.850	6.073	5.350
0.4	0.0406	1.491	1.436	1.393	1.344	4.366	4.662	4.901	5.212	7.861	7.148	6.339	5.559
0.5	0.0503	1.502	1.446	1.403	1.355	4.317	4.615	4.848	5.143	8.232	7.445	6.529	5.692
0.6	0.0597	1.513	1.454	1.412	1.366	4.273	4.576	4.799	5.087	8.604	7.810	6.783	5.901
0.7	0.0690	1.521	1.462	1.420	1.374	4.239	4.539	4.761	5.037	9.043	8.170	7.047	6.112
0.8	0.0781	1.530	1.470	1.427	1.382	4.204	4.506	4.729	4.994	9.587	8.592	7.377	6.326
0.9	0.0870	1.537	1.479	1.435	1.390	4.180	4.466	4.693	4.956	10.202	8.992	7.697	6.543
1.0	0.0958	1.544	1.485	1.443	1.398	4.156	4.443	4.659	4.913	10.917	9.538	8.076	6.878

Weight of urea (gm)	Weight fraction of Urea (X_1)	Molecular free length ($L_f \times 10^{-11}$) (m)				Gibb's free energy of activation ($\Delta G \times 10^{-20}$) (kJ·mol^{-1})			
		10 °C	20 °C	30 °C	40 °C	10 °C	20 °C	30 °C	40 °C
0.0	0.0000	4.283	4.506	4.710	4.958	3.221	3.313	3.392	3.465
0.1	0.0105	4.255	4.480	4.674	4.920	3.252	3.339	3.427	3.504
0.2	0.0207	4.228	4.453	4.644	4.887	3.267	3.358	3.441	3.522
0.3	0.0308	4.205	4.425	4.618	4.855	3.285	3.376	3.455	3.528
0.4	0.0406	4.181	4.401	4.595	4.824	3.301	3.393	3.473	3.544
0.5	0.0503	4.157	4.378	4.570	4.792	3.319	3.410	3.485	3.555
0.6	0.0597	4.136	4.360	4.547	4.766	3.336	3.429	3.501	3.570
0.7	0.0690	4.119	4.342	4.529	4.743	3.356	3.447	3.517	3.585
0.8	0.0781	4.102	4.327	4.514	4.722	3.379	3.468	3.536	3.600
0.9	0.0870	4.091	4.307	4.497	4.705	3.403	3.486	3.554	3.615
1.0	0.0958	4.079	4.296	4.480	4.684	3.429	3.510	3.574	3.637

Fig. 1 — Variation of ultrasonic velocity of mixture with weight fraction of urea in DMF.

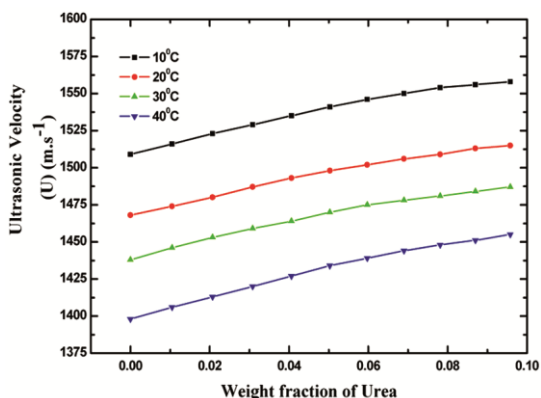Fig. 2 — Variation of density of mixture with weight fraction of urea in DMF.

concentration of urea and decreases with temperature. The increase in density with increase in concentration of urea proves the existence of solute – solvent molecular interaction. This increased density can be attributed to the presence of strong molecular interactions such as dipole-dipole and hydrogen bonding[26]. This molecular association brings the solute and solvent molecules close together by decreasing the volume and hence, increase in the density of solution.
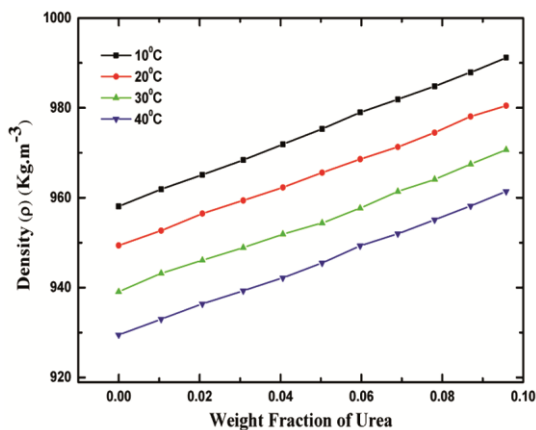
The decrease in density with increase in temperature indicates the decrease in intermolecular forces due to increase in thermal energy inside the medium.

3.3 Viscosity

The molecular interaction through the formation of hydrogen bonding, dipole-dipole interactions, and complex formation makes the contribution to the

changes in structural configuration of the molecules. This also results in geometric fitting of molecules in to each other's structures of different molecular sizes. The strength of molecular geometrical fittings affects the viscosity of the solution. For present case the increase in viscosity with increase in weight fraction of Urea in DMF is illustrated in Fig. 3. This increase thus conform the presence of strong molecular forces between the solute and solvent[29,30]. As temperature is raised, viscosities decreases as expected due to increases in thermal energy and hence decrease in molecular interacting forces.

3.4 Acoustic impedance

Figure 4 contains the information about variation of acoustic impedance (Z) with concentration of urea in DMF. The increase in Z values with concentration of urea at all temperatures can be attributed to the effective solute-solvent interactions[31]. This can also be attributed to the increase in pressure and cohesive energy of the binary systems due to presence of strong molecular interaction[32]. With increase in temperature
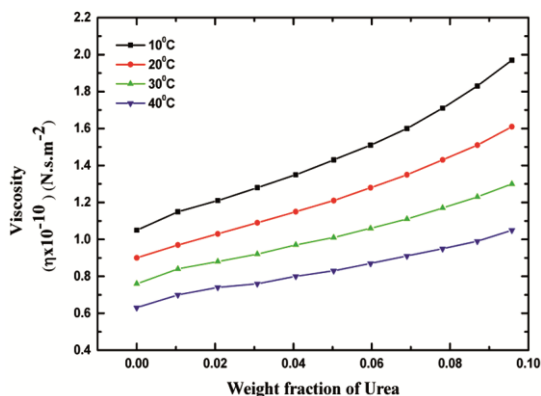
Z values decreases indicating the weakening of molecular forces, which is in good agreement with all other measured and derived parameters.

3.5 Adiabatic compressibility

Figure 5 shows the variation of adiabatic compressibility versus concentration of urea. It is observed that adiabatic compressibility decreases with increase in concentration of urea in DMF indicating the strong intermolecular interaction between solute and solvent molecules[33,34]. The self-associating tendency may be because of dipole-dipole interaction and hydrogen bonding as discussed in density variation. Adiabatic compressibility increases with increase in temperature. This trend supports the strong molecular interactions[35].

3.6 Relaxation time

The chemical contributions involved in making and breaking up of the associates present in the pure liquids, resulting in variation in the viscous relaxation time. From Fig. 6, it can reveal that the relaxation

Fig. 3 — Variation of Viscosity of mixture with weight fraction of Urea in DMF.

Fig. 5 — Variation of adiabatic compressibility of mixture with weight fraction of urea in DMF.
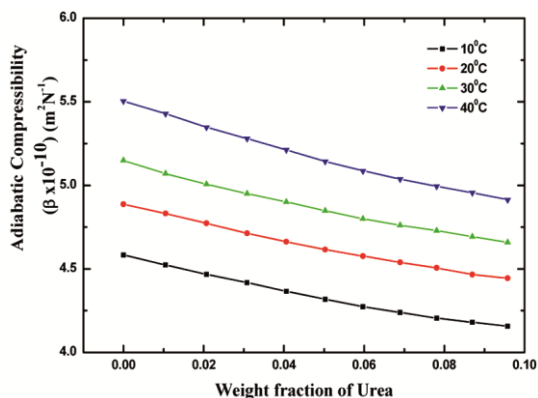

Fig. 4 — Variation of acoustic impedance of mixture with weight fraction of Urea in DMF.
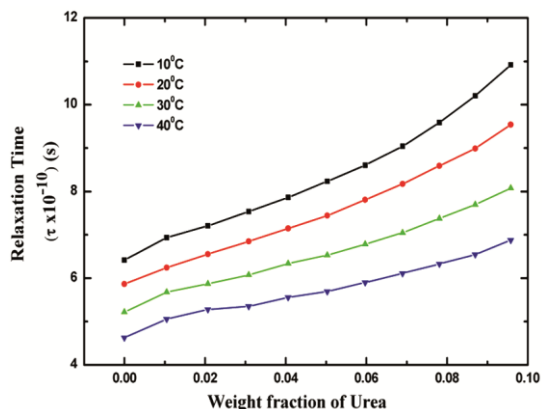

Fig. 6 — Variation of viscous relaxation time of mixture with weight fraction of urea in DMF.

time τ increases with increase in concentration of urea in DMF for all studied temperatures. The increase in relaxation time supports the view that viscous forces plays dominant role in relaxation process. Due to strong interaction between solute and solvent molecules, viscosity increases and hence relaxation time increases. This suggests the rearrangement of molecules via co-operation process and reinforcement of hydrogen bonds[31,36]. The non-linear variation of the relaxation time with weight fraction strongly supports to the presence of intermolecular interaction between solute and solvent[37]. As temperature is raised strength of hydrogen bonds decreases due to thermal energy resulting in structure braking effect. Hence, τ deceases with increase in temperature.

3.7 Intermolecular free length

Intermolecular forces play an important role in deciding the value of intermolecular free length. Due to increase in concentration of solute, the number of molecules increases in a given volume leading to attractive forces and hence decrease in intermolecular free length as shown in the Fig. 7. The interdependence of the intermolecular free length and ultrasonic velocity has been proposed by Kincaid and Eyring[38]. The decrease in compressibility brings the molecules closer together so as to decrease the molecular free length[32]. With increase in temperature, compressibility also increases thereby reducing the strength of molecular forces and increase in molecular free length. Due to increase in thermal energy, the structure becomes less ordered and molecules move apart, this results into increase in intermolecular free length (L_f) values suggesting solute-solvent interactions[3,27,31,39]. The result in thermal expansion of the liquid caused due to increase in temperature causes the free length to increase[28].

3.8 Gibb's free energy of activation of viscous flow

Figure 8 shows variation of Gibb's free energy with concentration of urea in DMF at all temperatures. It is observed that Gibb's free Energy (ΔG) increases with increase in weight fractions of urea. Due to strong interaction between solute and solvent molecules, the solution changes its initial structural ordering and rearrangement is done in shorter time[18,21].

With rise in temperature kinetic energy of molecules increases and it takes longer time for rearrangement of molecules for a given concentration. Thus Gibb's energy must decrease. However, in present case we found that, the Gibb's free energy
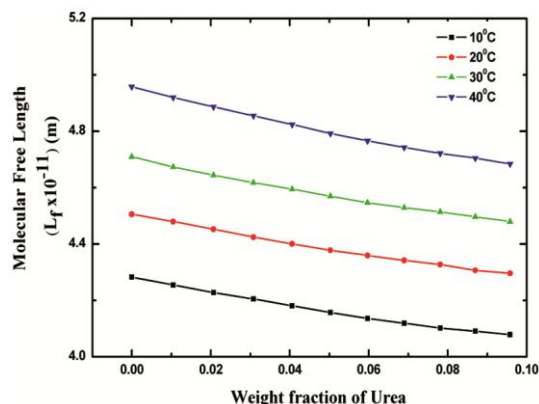

Fig. 7 — Variation of molecular free length of mixture with weight fraction of urea in DMF.
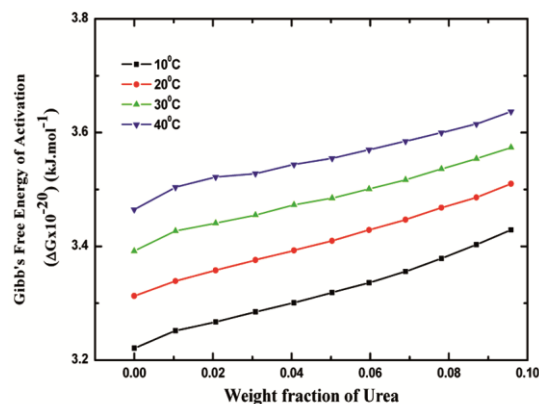

Fig. 8 — Variation of Gibb's free energy of activation of mixture with weight fraction of urea in DMF.

increases with increase in temperature also. Similar results of binary mixture of increasing ΔG with weight fraction and with temperature were observed by Anil Kumar et al.[40], which supports to the conclusion of intermolecular interactions in the present binary mixtures.

4 Conclusions

The study of solute solvent interaction has been carried out using thermo-acoustical properties of Carbamide and N, N-Dimethylformamide binary mixture. This study has been carried out at different temperatures of 10 °C, 20 °C, 30 °C and 40 °C and at atmospheric temperatures. Diverse measurable parameters like density, viscosity and ultrasonic velocity were used for the calculations of thermo-acoustical parameters namely acoustical impedance, adiabatic compressibility, relaxation time, intermolecular free length, Gibb's free energy of activation of viscous flow of the solution. These parameters were used to interpret the possible

intermolecular interactions. The variation of all these parameters with increasing concentration of urea supports the fact that strong intermolecular interaction exists between the solute and solvent molecules. Weakening of these interactions takes place when temperature rises.

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