



Solvation studies of dimethylsulfoxide in non-aqueous solvents at high temperatures and at an atmospheric pressure

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Received 30 January 2021; revised and accepted 28 December 2021

Solvation studies of pure non aqueous liquids like dimethylsulfoxide, pyridine and nitromethane and their binary mixtures have been measured at 0, 20, 40, 60, 80 and 100 mol% of pyridine and nitromethane at 298 K, 308 K and 318 K temperatures. Density, viscosity and ultrasonic velocities of the solvents have been measured. From the measured data, the isentropic compressibility and acoustic parameters like acoustic impedance, free volume, intermolecular free length, internal pressure, Gibb's free energy, relaxation time, Rao's constant, absorption coefficient, Wada's constant, and entropy are calculated using experimental velocities, viscosities and densities at three different temperatures (298 K, 308 K and 318 K) and 1 atm pressure.

Keywords: Density, Viscosity, Ultrasonic Velocity, Non-aqueous solvents, Acoustic parameters

Dimethylsulfoxide (DMSO) is polar aprotic solvent which dissolve large variety of polar and non-polar solvents. Uses of DMSO in biological processes, chemical reactions and industries are very well known. All the three solvents used in the present studies, dimethylsulfoxide (DMSO), pyridine (Py) and nitromethane (NM) are polar aprotic solvent which have tendencies to associate through various kinds of interactions like dipole-dipole, intermolecular or solvent-solvent interactions. In order to study the type of interactions, there are many approaches, in which physico-chemical properties like densities, viscosities, ultrasonic velocities of pure solvents or their mixture can be measured and the data can be used to elucidate the nature of interactions. Owing to the physico-chemical behaviour concerning type of structure, nature of complex formation and extent of molecular interaction in liquids, these studies have found broad applications. The dielectric constants of DMSO, Py and NM are 46.7, 12.4 and 35.07, respectively. Similarly, the dipole moments of DMSO, Py and NM are 4.06 D, 2.26 D, and 3.95 D, respectively. Since both factors determine the extent of interactions in the solvents, so it is suggested that there can be strong intermolecular interaction in the liquid phase as dielectric constant and dipole moment is very high. Though lot of work has been done on DMSO with other polar solvents but no work has

been done in a mixed solvent of DMSO in Py and NM and at high temperatures. Saba *et al.*¹ interpreted the physical parameters of an ionic liquid in DMSO at 298 K. In a mixture of dioxane, acetone and DMSO, Syal *et al.*² studied the solvents ultrasonic velocity and excess parameters. Mishra *et al.*³ also reported physio-chemical properties in mixture of DMSO with propanoic acid and n-butyric acid. Ultrasonic studies in terms of molecular interactions for solvents DMSO, CCl₄ at 308.15 K were studied by Tiwari *et al.*⁴. Ultrasonic and transport behaviour of Cu and Na perchlorates in cyanobenzene (CB), pyridine (Py) and cyanomethane (CM) were studied by Gill *et al.*⁵. Rao *et al.*⁶ also studied ultrasonic velocities of mixtures of methanol and Py at variable temperatures. Ultrasonic study of 1-butanol, Py and benzene was reported by Arul and Palaniappan⁷. Sharma *et al.*⁸ studied the thermodynamic properties of surfactants in mixed solvents. Study of surfactant mediated reaction in cyclodextrin was done by Ghosh and co-workers⁹. Acoustic studies of Mn in alcohols were studies by Mehrotra *et al.*¹⁰. Das and co-worker¹¹ studied physicochemical properties on the micellization of cationic, anionic, and nonionic surfactants in water-polar organic solvent mixtures.

For the presented paper, density, viscosity and ultrasonic velocities of pure liquids like DMSO, Py and NM and their binary mixtures were measured

at 0, 20, 40, 60, 80 and 100 mol% of Py and NM at variable temperatures ranging from 298 K to 318 K. From the measured data, the isentropic compressibility (κ_s) and acoustic parameters like acoustic impedance (Z), free volume (V_f), absorption coefficient (Abs_{coeff}), intermolecular free length (L_f), Gibb's free energy (ΔG), relaxation time (τ), Rao's constant (R_m), internal pressure (π_i), Wada's constant (w), and entropy (H) were calculated using experimental velocities, viscosities and densities at three different temperatures (298 K, 308 K and 318 K) and 1 atm pressure.

Experimental Details

Materials

Table 1 shows the source, molecular mass, density, purity and water content of three solvents. Detailed method for solvent purity is reported in our previous paper¹².

Apparatus

Binary mixtures of three solvents were prepared by mixing a desired amount of the solvents. It was accomplished by first conversion of each solvent's required mass into volume at 298 K using calculated density. An electronic weighing balance (SAG 285, Mettler Toledo) with a precision of $\pm 10^{-6}$ kg was used for the mass measurements. Solvents were contained in air-tight glass stoppered bottles and treated carefully to prevent any form of evaporation or contamination in the solutions. The likely concentration error was found to be less than $\pm 1 \times 10^{-4}$ mol·dm⁻³.

For viscosity experiments with a vibrating frequency of 30 Hz, the A&D company's Sine wave vibro viscometer was used. The equipment calibration was done by estimating the viscosity of distilled water with an accuracy of ± 0.01 mPa.s at 298 K. The solvents were taken into a small container for the measurement and sensory plates of the apparatus were dipped into it, which measured the viscosity directly. In each case, the calculation was

repeated twice to achieve greater reproducibility of the results. Overall viscosity measurement accuracy was found to be ± 0.1 %.

For the detection of density and ultrasonic velocity, DSA 5000M (Anton Parr) was used. The sample was inserted into a long, borosilicate glass U-tube which oscillates at its 2 MHz frequency. The apparatus was cleaned with distilled water and air at the beginning of each series of readings. Calibration of apparatus was done by measurement of the density and ultrasonic velocity of known liquids such as water ($\rho = 0.99705$, $u = 1496.68$ m.s⁻¹) and acetonitrile ($\rho = 0.77687$, $u = 1280.9$ m.s⁻¹) were calculated at 298 K for calibration and were well compatible with literature values, ¹³ $\rho = 0.99707$, ¹⁴ $u = 1496.6$ m.s⁻¹ for water and $\rho = 0.77685$, $u = 1280.8$ m.s⁻¹ for acetonitrile¹⁵. In the DSA apparatus, the temperature regulation is ± 0.01 K. Accuracy in the density value was $\pm 1 \times 10^{-5}$ g.cm⁻³ and for ultrasonic velocity was ± 0.1 m.s⁻¹.

Theory

The isentropic compressibility (κ_s) and acoustic parameters like acoustic impedance (Z), free volume (V_f), absorption coefficient (Abs_{coeff}), internal pressure (π_i), Gibb's free energy (ΔG), relaxation time (τ), Rao's constant (R_m), intermolecular free length (L_f), Wada's constant (w), and entropy (H) were calculated using experimental velocities, viscosities and densities at three different temperatures (298 K, 308 K and 318 K) and 1 atm pressure.

1) Many researchers¹⁶ have studied the relationship between ultrasonic velocity (u) and isentropic compressibility (κ_s). From the Newton-Laplace equation, isentropic compressibility was determined. It is commonly used in studies related to liquid mixtures' physico-chemical activity, such as molecular interactions, dissociation and formation.

$$\kappa = 1 / \rho u^2 \quad \dots (1)$$

where ρ denotes density and u , ultrasonic velocity.

2) The acoustic impedance (Z) of a medium is calculated by a relation:

Table 1 — Procurement, Density, Water content and Purity of Solvents

Solvents Used	Procurement	CAS- No.	Molecular Formula	Molar Mass (g mol ⁻¹)	Grade	Density ^a (g cm ⁻³)	Mass Fraction Purity	Water Content
Dimethylsulfoxide (DMSO)	Merck	67-68-5	C ₂ H ₆ OS	78.13	ACS	1.0953	0.998 ^b	0.0002 ^c
Pyridine (Py)	Merck	110-86-1	C ₅ H ₅ N	79.1	ACS, Reag.	0.9786	0.995 ^b	0.0001 ^c
Nitromethane (NM)	Loba Chemie	75-52-5	CH ₃ NO ₂	61.04	LR	1.1295	0.98 ^b	0.0025 ^c

^adensity at 298 K by Anton Parr density meter (DSA 5000 M), ^bFrom Gas Chromatography Method, ^cKarl- Fischer Titration Method

$$z = \rho \cdot u \quad \dots (2)$$

3) A characteristic attribute of acoustic parameter is the intermolecular free length (L_f) between the molecules in the liquid state as the data provides information on attractive or repulsive forces¹⁷ between liquid mixtures. The free length of the intermolecular is determined by the relation

$$L_f = K \sqrt{\kappa_s} \quad \dots (3)$$

where K is constant whose value is taken as 1.995×10^{-6} at 298 K, 2.095×10^{-6} at 308 K and 2.115×10^{-6} at 318 K.

4) Relaxation time (τ) is the resistance offered by the viscosity of a solvent in the flow of a sound wave that is classically absorbed and measured using the following relationship:

$$\tau = \frac{4\eta}{3\kappa_s} \quad \dots (4)$$

where η is the viscosity coefficient.

5) Free Volume (V_f) has been calculated from the relation

$$V_f = \left(\frac{M_{eff} \cdot u}{\kappa \cdot \eta} \right)^{3/2} \quad \dots (5)$$

where, M_{eff} is the effective molecular mass, K is temperature dependent constant equals to 4.281×10^9 for all liquids at 298 K.

6) Absorption coefficient (Abs_{coeff}) of the medium was found by a relation

$$Abs_{coeff} = \frac{8\pi^2 \eta}{3\rho \cdot u^2} \quad \dots (6)$$

7) The internal pressure (π_i) is calculated by the relation

$$\pi_i = bRT \left(\frac{K \cdot \eta}{u} \right)^{1/2} \left(\frac{\rho^{2/3}}{M_{eff}^{7/6}} \right) \quad \dots (7)$$

where b refers to cubic packing of solvent taken to be equal to 2, K is dimensionless constant having a value

4.281×10^9 , T is absolute temperature, η is viscosity in $\text{N m}^{-2} \text{s}$, R is gas constant, u is ultrasonic velocity in m s^{-1} , M_{eff} is effective molecular weight and ρ is density in kg m^{-3} .

8) In accordance with Eyring rate processing theory, Gibbs free energy (ΔG) was determined from acoustic relaxation time (τ):

$$\Delta G = RT \ln \left(\frac{KT\tau}{h} \right) \quad \dots (8)$$

where K is Boltzmann constant, h is planck constant and τ is relaxation time.

9) Molar sound velocity or Rao's constant (R_m) has been evaluated from the relation

$$R_m = \frac{M_{eff} \cdot u^{1/3}}{\rho} \quad \dots (9)$$

10) Wada's constant (w) has been calculated using isentropic compressibility values

$$w = \left(\kappa_s \right)^{1/7} \frac{M_{eff}}{\rho} \quad \dots (10)$$

11) Enthalpy (H) has been calculated by the relation

$$H = \Pi_i \frac{M_{eff}}{\rho} \quad \dots (11)$$

Results and Discussions

DMSO, Py, and NM experimentally measured parameters at 298K are tabulated in Table 2. Density (ρ) is an estimation of the interactions between solvent-solvent and ion-solvent. These interactions occur as a result of some kind of bonding between solvent molecules that may be hydrogen like bonding, resulting in a reduction in the size of the solvent molecules and hence decrease in density. For the systems studied, ρ decreases with the increase in the mol% composition of Py in DMSO+Py mixture at all the three temperatures. Py has N-moiety which could be involved in the hydrogen bonding with DMSO which resulted in the decrease in the density. But for DMSO+NM mixtures, density increases as the mol% composition of NM increases at all the three temperatures. Viscosity (η) shows a linear decrease at

Table 2 — Density (ρ), viscosity (η), and ultrasonic velocity(u) for DMSO, Py, and NM at 298 K

Solvents	ρ ($\text{g}\cdot\text{cm}^{-3}$)		η (mPa.s)		u ($\text{m}\cdot\text{s}^{-1}$)	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
DMSO	1.0953	1.09530 ¹⁸ ; 1.09533 ¹⁹ ; 1.09537 ²⁰	1.99	1.99 ²¹ ; 2.00 ²²	1486.49	1486.74 ²³
Py	0.9786	0.9782 ²⁴	0.88	0.88 ¹⁵ ; 0.884 ²⁵	1418.14	1419.2 ¹⁵
NM	1.1295	1.12958 ²⁶ ; 1.1296 ²⁷	0.612	0.615 ^{28,29}	1321.38	1320.41 ³⁰

298 K, 308 K and 318 K for both systems, which may be attributable to both Py and NM's less viscous nature. The disparity in solvent molecule sizes when Py and NM are added to DMSO results in the loss of interaction between molecules of solvent. This resulted in a reduction in viscosity values and, relative to pure solvents, this loss in the molecular interaction resulted in higher mixture flow.

Ultrasonic velocity (u) values are resultant of forces acting between the solvent molecules. As evident from above reported Table 3, value of ultrasonic velocity falls at all three temperatures with a rise in the mole percentage composition of both Py and NM. The drop in value of u is due to an increased interaction between the molecules of the solvent. In addition, as temperature rises, velocity decreases, it has been found that this can be due to increased vibration or collision between solvent molecules. Ultrasonic velocity is correlated with κ_s and L_f . Ultrasonic velocity is inversely related to intermolecular free length in accordance with model proposed by Eyring and Kincaid³¹. This is also in line with the predicted molecular interaction between the solvent molecules, which, as shown in Fig. 1, results in increased compressibility. For both systems, this increase in κ_s and L_f with temperature indicates the breaking of any form of homo interaction at higher temperatures between the same solvent molecules³². The distance between the molecules is great in dilute solutions. Therefore, the extent of the non-covalent

interaction would be low. When in condensed liquids, the distance between the molecules is lesser because of bonding (hydrogen or intermolecular). Therefore, in both samples, as shown in Fig 1(e,f), the intermolecular free length (L_f) was found to increase. A parameter which determines the elastic properties of the medium is the acoustic impedance (Z). Table 4 reveals that as the mole percentage composition of Py and NM increases, Z decreases. Z is responsible for ultrasonic wave propagation. The increase in the value of Z indicates strong solvent interactions and weak solvent interactions imply a lesser value of Z . Therefore, as shown in Fig. 1(c,d), a linear decrease in the Z value with an increase in the mol percentage composition of co-solvent indicates a good solvent-solvent interaction in DMSO-rich regions as compared to Py and NM.

Free volume (V_f) is related to effective molecular mass. One of the key variables in explaining the disparity in the solvation behaviour of the solvent is free volume. Free volume and its dependable properties are closely related to the solvent molecular structure, and can depict compelling features about interactions. Structural behaviour in terms of shape and size of the solvent molecules, impact these molecular interactions between same and different solvent molecules. Fig. 2 (a,b) depicts that the V_f values rises with an increase in the mole percent composition of Py and NM, as well as with the increase in temperature, as shown in Table 5. In the

Table 3 — Density (ρ), Viscosity (η) and ultrasonic velocity (u) for DMSO+Py and DMSO+NM binary mixture at various temperatures

DMSO+Py									
Mol % Py	ρ (g.cm ⁻³)			η (mPa.s)			u (m.s ⁻¹)		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	1.0953	1.0852	1.0753	1.99	1.645	1.385	1486.49	1467.07	1434.18
20	1.0702	1.0633	1.0535	1.61	1.455	1.236	1471.21	1453.97	1419.78
40	1.0494	1.0441	1.0342	1.32	1.284	1.089	1457.83	1442.84	1408.32
60	1.0233	1.0197	1.0099	1.12	1.093	0.932	1444.98	1428.76	1392.62
80	1.0033	0.9972	0.9873	1.01	0.942	0.787	1432.41	1407.8	1370.3
100	0.9786	0.9695	0.9594	0.88	0.771	0.655	1418.14	1381.7	1341.87
DMSO+NM									
Mol % NM	ρ (g.cm ⁻³)			η (mPa.s)			u (m.s ⁻¹)		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	1.0953	1.0852	1.0753	1.99	1.645	1.385	1486.49	1467.07	1434.18
20	1.0997	1.0909	1.0805	1.254	1.426	1.203	1438.27	1432.1	1402.47
40	1.1054	1.0953	1.0841	1.04	1.201	1.031	1403.33	1385.32	1353.53
60	1.1124	1.1007	1.0887	0.912	0.997	0.847	1370.19	1340.46	1304.49
80	1.1209	1.1064	1.0935	0.78	0.775	0.673	1342.88	1311.78	1274.88
100	1.1295	1.1155	1.1018	0.612	0.564	0.51	1321.38	1285.63	1247.7

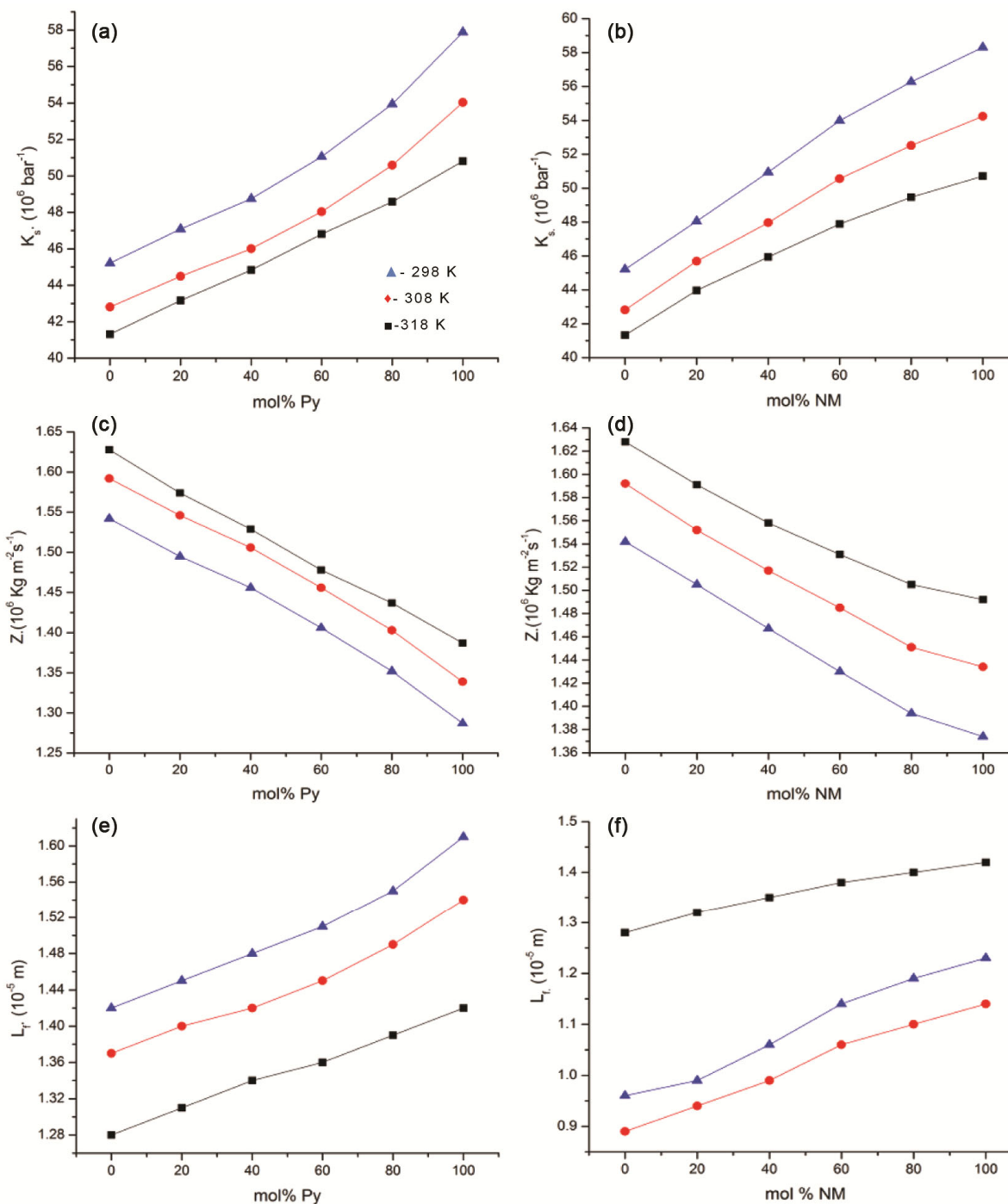


Fig. 1 — (a) Isentropic compressibility (κ_s) v/s mol% Py, (b) Isentropic compressibility (κ_s) v/s mol% NM, (c) Acoustic impedance (Z) v/s mol% Py, (d) Acoustic impedance (Z) v/s mol% NM, (e) Inter-molecular free length (L_r) v/s mol% Py, and (f) Inter-molecular free length (L_r) v/s mol% NM

two systems, i.e., DMSO+Py and NM+DMSO this implies strong interaction. Moreover, the solvent molecules get closer as the temperature increases, resulting in more available space. The viscosity, the density and the ultrasonic velocity were used to

measure the relaxation time. As compared to DMSO, the relaxation time (τ) value falls with rise in the mole percent composition of Py and NM. Ultrasonic velocity provides information on the duration of the dispersion-causing relaxation process. The relaxation

Table 4 — Isentropic compressibility (κ_s), Acoustic impedance (Z), Intermolecular free length (L_f) for DMSO+Py and DMSO+NM binary mixture at different temperatures

DMSO+Py									
Mol % Py	$\kappa_s \cdot 10^6 \text{ bar}^{-1}$			$Z \cdot 10^6 \text{ Kg m}^{-2}\text{s}^{-1}$			$L_f \cdot 10^{-5} \text{ m}$		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	41.32	42.81	45.21	1.628	1.592	1.542	1.28	1.37	1.42
20	43.17	44.49	47.09	1.574	1.546	1.495	1.31	1.40	1.45
40	44.84	46.01	48.75	1.529	1.506	1.456	1.34	1.42	1.48
60	46.81	48.04	51.06	1.478	1.456	1.406	1.36	1.45	1.51
80	48.58	50.59	53.94	1.437	1.403	1.352	1.39	1.49	1.55
100	50.81	54.03	57.89	1.387	1.339	1.287	1.42	1.54	1.61
DMSO+NM									
Mol % NM	$\kappa_s \cdot 10^6 \text{ bar}^{-1}$			$Z \cdot 10^6 \text{ Kg m}^{-2}\text{s}^{-1}$			$L_f \cdot 10^{-5} \text{ m}$		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	41.32	42.81	45.21	1.628	1.592	1.542	1.28	0.89	0.96
20	43.96	44.69	47.05	1.581	1.562	1.515	1.32	0.94	0.99
40	45.94	47.57	50.35	1.551	1.517	1.467	1.35	0.99	1.06
60	47.88	50.56	53.98	1.524	1.475	1.420	1.38	1.06	1.14
80	49.47	52.52	56.27	1.505	1.451	1.394	1.40	1.10	1.19
100	50.71	54.24	58.31	1.492	1.434	1.374	1.42	1.14	1.23

Table 5 — Free Volume (V_f), Relaxation time (τ), Absorption coefficient ($\text{Abs}_{\text{coeff}}$) for DMSO+Py and DMSO+NM binary mixture at different temperatures

DMSO+Py									
Mol % Py	$V_f \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$			$\tau \cdot 10^{-12} \text{ s}$			$\text{Abs}_{\text{coeff}} \cdot 10^{-8} \text{ Npm}^{-1}\text{s}^2$		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	5.03	6.56	8.22	10.96	9.39	8.35	2.16	1.85	1.65
20	6.83	7.81	9.63	9.27	8.63	7.76	1.83	1.69	1.53
40	9.11	9.35	11.54	7.89	7.88	7.08	1.56	1.55	1.37
60	11.54	11.77	14.39	6.99	7.00	6.34	1.39	1.38	1.25
80	13.35	14.45	18.17	6.54	6.36	5.66	1.29	1.25	1.12
100	16.25	19.05	23.36	5.96	5.56	5.04	1.18	1.09	0.99
DMSO+NM									
Mol % NM	$V_f \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$			$\tau \cdot 10^{-12} \text{ s}$			$\text{Abs}_{\text{coeff}} \cdot 10^{-8} \text{ Npm}^{-1}\text{s}^2$		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	5.03	6.56	8.22	10.96	9.39	8.35	2.16	1.85	1.65
20	7.81	8.21	9.03	9.35	8.49	7.55	1.45	1.68	1.49
40	9.39	10.21	9.97	8.37	7.62	6.92	1.26	1.25	1.16
60	11.34	11.60	11.77	7.82	6.72	6.09	1.15	1.14	1.13
80	12.98	12.65	15.98	6.15	5.43	5.05	1.01	1.00	0.99
100	17.08	18.52	20.60	5.14	4.08	3.96	0.82	0.81	0.78

time of 10^{-12} sec is due to the process of structural relaxation³³ and it is proposed that the molecules of solvents are repositioned due to co-operative effect³⁴ in such a case. The relaxation time in the present study decreases with temperature for both the solvent mixtures. The absorption coefficient ($\text{Abs}_{\text{coeff}}$) is correlated with the medium's velocity and viscosity. With a rise in the mol percentage composition of Py and NM, $\text{Abs}_{\text{coeff}}$ value decreases and compared to

DMSO+NM, it is more for DMSO+Py mixture and if the temperature of the system increases, the value decreases further. This trend suggests the extent of complexity with increase in the mol% composition of co-solvents Py and NM and also with temperature³⁵.

Table 6 indicates internal pressure (π_i) decreases as co-solvent composition increases (Fig. 3). The value decreases more with the rise in temperature. This may be due to the release of the binding forces that

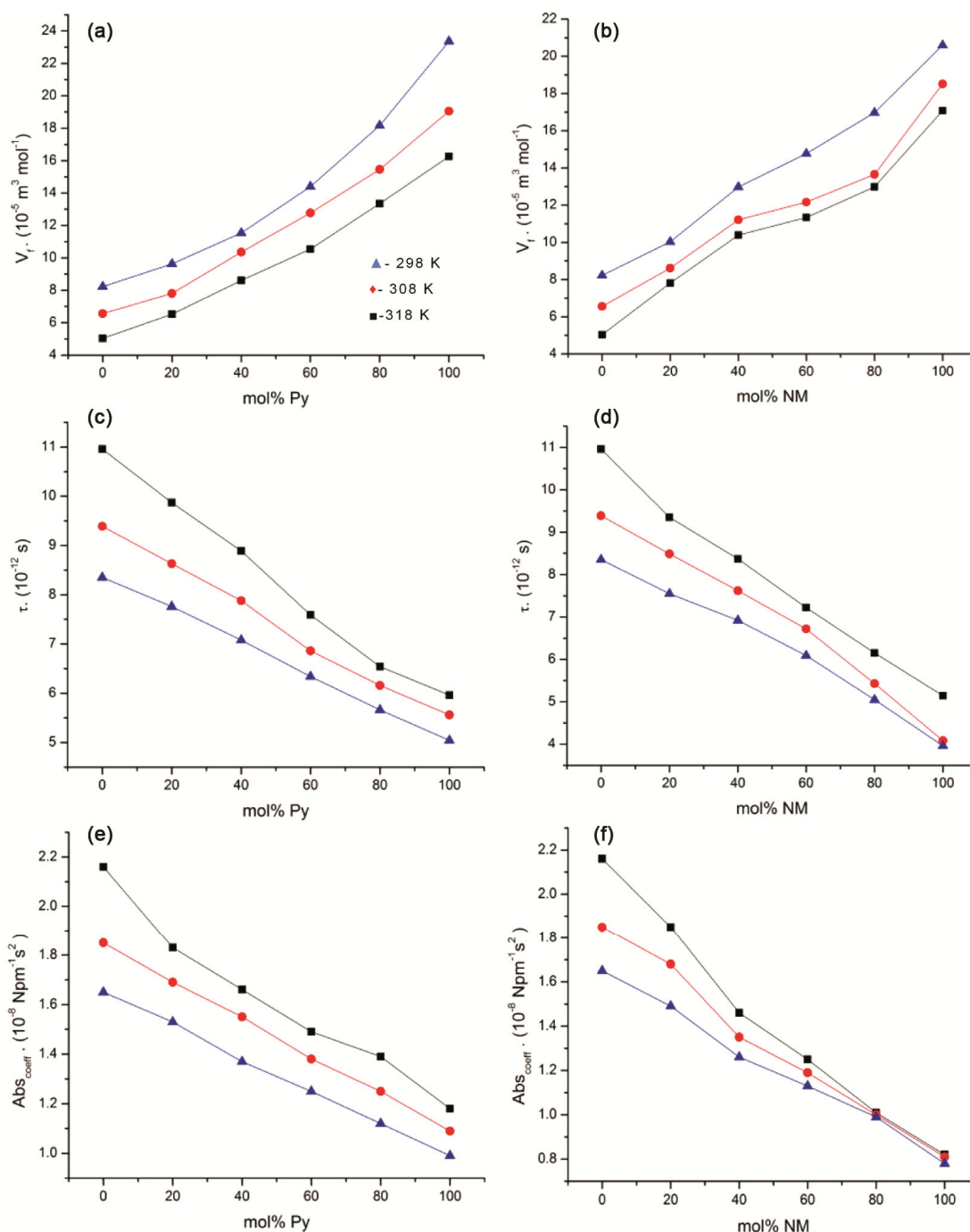


Fig. 2 — (a) Free Volume (V_f), v/s mol% Py, (b) Free Volume (V_f), v/s mol% NM, (c) Relaxation time (τ) v/s mol% Py, (d) Relaxation time (τ) v/s mol% NM, (e) Absorption coefficient (Abs_{coeff}) v/s mol% Py, and (f) Absorption coefficient (Abs_{coeff}) v/s mol% NM

contribute to the breaking up of structure of solvent. As the mol percentage composition of Py and NM increases, enthalpy (H) decreases and the same pattern is also seen with temperature rise. Gibbs's free energy increases as we move to Py and NM rich

region. This illustrates the strong interactions between the solvent molecules which rise with rise in temperature. Rao's constant (R_m) and the Wada's constant (w) shows an increasing trend for DMSO+Py binary mixture but the same decreases for

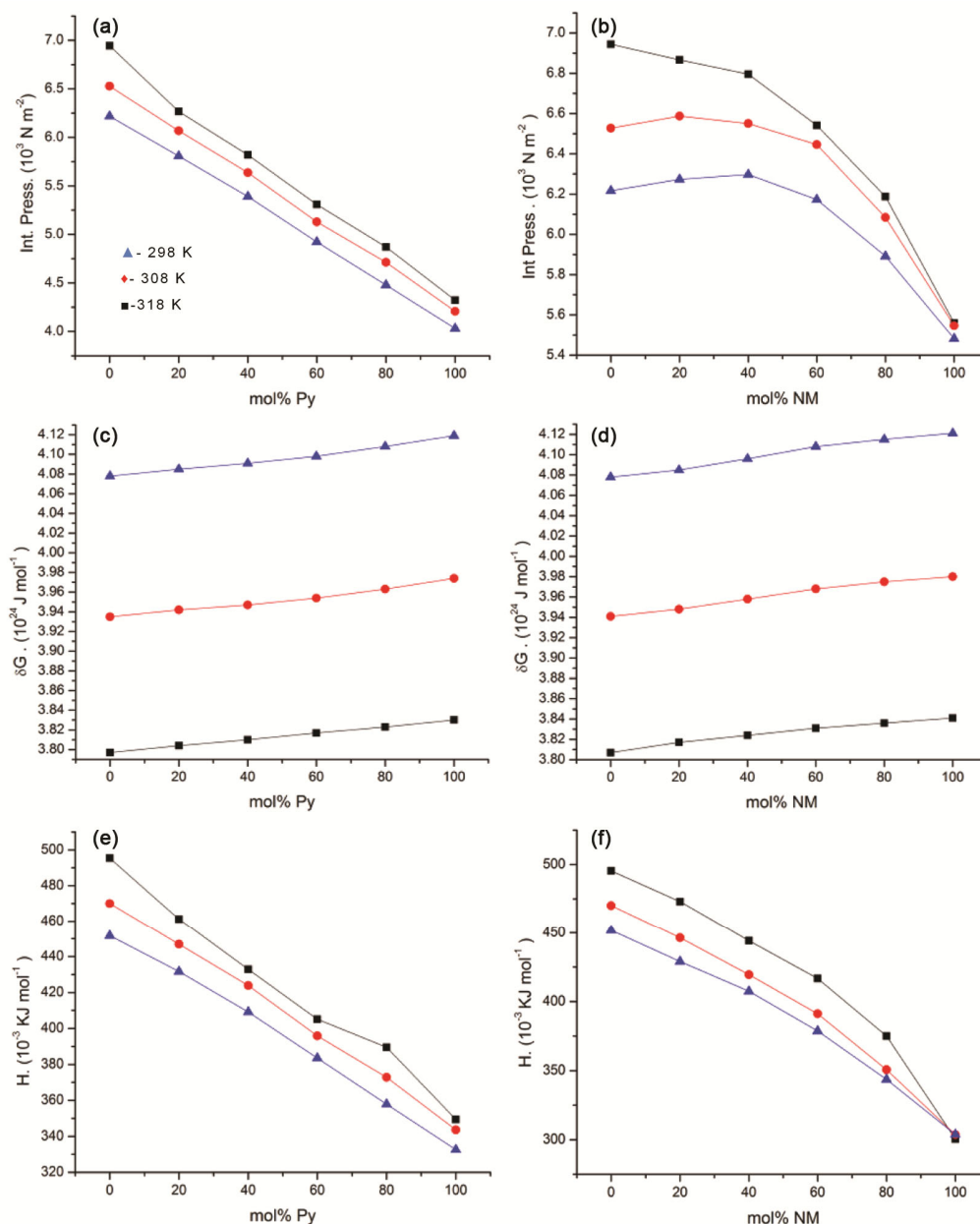


Fig. 3 — (a) Internal Pressure (π_i) v/s mol% Py, (b) Internal Pressure (π_i) v/s mol% NM, (c) Gibb's Free energy (ΔG) v/s mol% Py, (d) Gibb's Free energy (ΔG) v/s mol% NM, (e) Enthalpy (H) v/s mol% Py, and (f) Enthalpy (H) v/s mol% NM

Table 6 — Internal Pressure (π_i), Gibb's Free energy (ΔG), Enthalpy (H) for DMSO+Py and DMSO+NM binary mixture at different temperatures

Mol % Py	DMSO+Py			DMSO+NM			DMSO+Py		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	6.944	6.528	6.217	3.797	3.935	4.078	495.355	470.007	451.724
20	6.166	6.068	5.807	3.804	3.942	4.085	451.170	446.879	431.669
40	5.520	5.637	5.391	3.810	3.947	4.091	412.924	423.816	409.188
60	5.008	5.130	4.922	3.817	3.954	4.098	385.108	395.894	383.544
80	4.700	4.713	4.478	3.823	3.963	4.108	369.574	372.861	357.843
100	4.323	4.207	4.031	3.830	3.974	4.119	349.437	343.647	332.623

(Contd.)

Table 6 — Internal Pressure (π_i), Gibb's Free energy (ΔG), Enthalpy (H) for DMSO+Py and DMSO+NM binary mixture at different temperatures (Contd.)

Mol % NM	DMSO+NM								
	$\pi_i \cdot 10^3 \text{ N m}^{-2}$			$\Delta G \cdot 10^{24} \text{ J mol}^{-1}$			H. $10^{-3} \text{ KJ mol}^{-1}$		
	298 K	308 K	318 K	298 K	308 K	318 K	298 K	308 K	318 K
0	6.944	6.528	6.217	3.807	3.941	4.078	495.355	470.007	451.724
20	5.997	6.588	6.273	3.817	3.948	4.085	402.958	446.275	429.021
40	5.896	6.551	6.297	3.824	3.958	4.096	374.111	419.491	407.367
60	5.942	6.446	6.173	3.831	3.968	4.108	356.702	391.097	378.659
80	5.888	6.084	5.892	3.836	3.975	4.115	334.940	350.653	343.561
100	5.560	5.547	5.482	3.841	3.980	4.121	300.503	303.535	303.754

Table 7 — Rao's constant (R_m), Wada's constant (w) for DMSO+Py and DMSO+NM binary mixture at different temperatures

Mol %	DMSO+Py					
	R_m			W		
	298 K	308 K	318 K	298 K	308 K	318 K
0	814.089	818.072	819.387	41.918	42.094	42.152
20	832.181	834.297	835.405	42.729	42.822	42.871
40	848.083	849.456	850.693	43.442	43.502	43.557
60	869.286	869.079	870.050	44.387	44.378	44.421
80	886.320	886.606	887.473	45.148	45.162	45.199
100	908.122	909.708	910.724	46.117	46.187	46.231

Mol %	DMSO+NM					
	R_m			W		
	298 K	308 K	318 K	298 K	308 K	318 K
0	814.089	818.072	819.387	41.918	42.094	42.152
20	758.424	763.447	765.442	39.135	39.358	39.446
40	710.273	713.743	715.558	36.721	36.875	36.955
60	666.702	668.880	670.148	34.539	34.636	34.691
80	627.568	630.846	632.246	32.578	32.724	32.786
100	593.022	594.999	596.415	30.842	30.930	30.993

DMSO+NM binary mixture as shown in Table 7. This may be due to more compactness of the medium due to the more number of molecules in same region. This could be due to hydrogen bonding in case of DMSO+Py as compared to DMSO+NM. These follow same trend as the temperature rises.

Conclusions

Density, viscosity, ultrasonic velocities of pure liquids like DMSO, Py and NM and their binary mixtures were measured at 0, 20, 40, 60, 80 and 100 mol% of Py and NM at temperatures, 298 K, 308 K and 318 K. Results showed that there are stronger molecular interactions present between the solvent systems studied. Increased interaction of solvent molecules is due to the decrease in velocity values, and these interactions further increases with rise in temperature as the viscosity value falls. With an increase in the mol percentage composition of co-solvent, a linear decrease in the Z value shows that there is a good solvent-solvent interaction in DMSO compared to Py and NM. Moreover, increase in the values of V_f with temperature indicates strong

interaction in the two systems i.e. DMSO+Py and DMSO+NM. Gibbs's free energy also increases as we move to Py and NM rich region. The current study thus depicts strong molecular interactions between the two solvent mixtures and interactions seem to be more for DMSO+Py systems at higher temperatures.

Acknowledgement

Author thanks the DAV College, Sector-10, Chandigarh for financial support.

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