Thermodynamic and physiochemical properties and the excess functions of binary mixtures of Dimethylsulfoxide with Pyridine and Nitromethane at variable temperatures - 298 to 318K.

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ABSTRACT

The density ($\rho$), viscosity ($\eta$), relative permittivity ($\varepsilon$), and ultrasonic velocity ($u$) in the binary mixture of Dimethylsulfoxide with Pyridine and Nitromethane have been measured at all composition and temperatures 298 K, 308 K, and 318 K. From the experimentally measured values, the excess molar volumes ($V^E$) and the deviation in the viscosities ($\Delta\eta$), relative permittivity ($\Delta\varepsilon$), and ultrasonic velocity ($\delta u$) have been correlated. The negative and the positive deviations in the excess functions have been discussed in terms of molecular interactions.

KEYWORDS
dimethylsulfoxide, pyridine, nitromethane, density, viscosity, relative permittivity, ultrasonic velocity, excess parameters.

1. INTRODUCTION

Knowledge of the thermodynamic and physiochemical properties of binary solvents makes it useful for industrial and non-industrial point of view. Binary solvents rather than pure liquids have industrial applications, as mixing the solvents gives flexibility to the solution by altering their properties, either by varying the composition or by varying the concentration of solvents or both. Moreover, the mixing of liquids introduces some extra degree of freedom and results in a new phenomenon that is not present in pure liquids, such as complex formation, association, dissociation, etc. One of the fundamental importance of physiochemical studies is that it provides the relevant information regarding the nature of solvents and the extent of interactions which can be, ion-ion or ion-solvent or solvent-solvent which makes it imperative for the interpretation of data. μ

Dimethylsulfoxide (DMSO), Pyridine (Py), and Nitromethane (NM) all being polar solvents are widely used solvents that have a wide range of applications like solvent extractions, as a solvent in many condensation reactions, in biological processes, etc. The dielectric constant of DMSO (46.7), Py (12.4), and NM (35.07), and the dipole moments of DMSO (4.06 D), Py (2.26 D), and NM (3.95 D), is quite high, suggesting strong intermolecular interaction in the liquid phase. They can dissolve a wide range of solvents and are miscible with many other solvents. In the present paper, thermodynamic and physiochemical properties of DMSO with Py and NM were studied over the whole range of solvent composition at 298K, 308K, and 318K. Thermodynamic property like density ($\rho$), viscosity ($\eta$), relative permittivity ($\varepsilon$), and ultrasonic velocity ($u$) for the two mixtures i.e. DMSO+Py and DMSO+NM have been measured and the experimental data were used to calculate excess molar volume, excess viscosity, excess relative permittivity, and excess ultrasonic velocity.

H. Saba et. al [1] studied the physical and solubility properties of 1-ethyl-3-methyl imidazolium liquids in DMSO mixtures at 298.15K. Ultrasonic velocity and excess parameters of a binary mixture of dioxane and acetone with DMSO were studied by Syal et.al [2]. Cerdeirina et al [3]. reported on the thermodynamics properties of nitromethane with 1-Butanol, while Piekarski and Somsen [4] have measured heat capacities and volumes of methanol with
nitromethane. Cwiklinska and Kinart [5] studied the thermodynamic and physiochemical properties for the mixtures of nitromethane with 2- methoxy ethanol and 2-butoxy ethanol. Dimethylsulfoxide is a polar solvent that does not form a H-bonds network but aligns toward the self-association [6-8] process but the molecular dynamics (MD) simulations [9,10] demonstrate that weak H-bonds occur in liquid DMSO forming C-H⋯O bonds. With an increase in pressure [11], the strong molecular aggregates are formed in DMSO resulting in more structural order of the liquid. Such molecular aggregate formation can be due to either the intermolecular distance shortening or vibrational motions of neighboring molecules or both. It was supposed that the liquid DMSO structure was similar to the solid one [12]. Moreover, the DMSO molecule strongly reveals the solvophobic effects in systems with a H-bond network [13]. On the other hand, Py and NM do not show self- association which makes it interesting to study these systems in detail. The interactions occurring in the dissimilar solvent molecules and their contributions to the excess functions explain the properties of the binary solvents and also explain the type of interactions.

2. EXPERIMENTAL

2.1 Materials and Method

Dimethylsulfoxide (DMSO), Pyridine (Py) and Nitromethane (NM) have been used in the present studies and their source and purity is mentioned in Table 1. Dimethylsulfoxide (DMSO), (Merck) with boiling point 71-72 °C was purified by repeated crystallization. The crystallized solvent was further kept over 4Å molecular sieves for 2-3 days with occasional shaking. The solvent was fractionated through a long vertical column under reduced pressure. The middle fraction with specific conductance 2-8 x 10⁻⁸ S cm⁻¹, density 1.0953 g cm⁻³, and viscosity 1.990 cP was collected and stored under dry conditions. Pyridine (Py), (Merck) with a boiling point of 114-115 °C was refluxed over KOH for 3 hours and was distilled at atmospheric pressure and middle fraction with conductance 0.7-1.0 x 10⁻⁸ S cm⁻¹, density 0.9786 g cm⁻³, and viscosity 0.881 cP was collected and stored. Nitromethane (NM), (Loba Chemie) with a boiling point of 100-110 °C was distilled over P₂O₅ and was distilled at atmospheric pressure and middle fraction with conductance 0.5-0.8 x 10⁻⁸ S cm⁻¹, density 1.1295 g cm⁻³, and viscosity 0.612 cP was collected and stored.

TABLE1: Source and Purity of Solvents

| Solvent          | Provenance     | CAS-Number | Molecular Formula | Molar Mass (g mol⁻¹) | Grade | Density (g cm⁻³) | Mass Fraction Purity | Water Content |
|------------------|----------------|------------|-------------------|----------------------|-------|------------------|----------------------|--------------|
| Dimethylsulfoxide| E.Merck        | 67-68-5    | C₅H₆OS            | 78.13                | ACS   | 1.0953           | 0.998²              | 0.0002³       |
| Pyridine         | E.Merck        | 110-86-1   | C₅H₅N            | 79.1                 | ACS, Reag. | 0.9786         | 0.995²              | 0.0001³       |
| Nitromethane     | Loba Chemie    | 75-52-5    | CH₃NO₂           | 61.04                | LR    | 1.1295           | 0.98²               | 0.0025³       |

¹density at 298 K by Anton Parr density meter (DSA 5000 M) with a precision of 0.0004 g cm⁻³  
²From Gas Chromatography Analysis  
³Karl-Fischer Titration Method

2.2 Apparatus

Preparation of Binary mixtures of the solvents (DMSO, Py, and NM in the present case) was done by mixing a required volume of the solvents. It was done by converting the required mass of each solvent into volume first at 298K using measured densities. The density (ρ) was measured by Anton Parr density meter (DSA 5000 M) with a
precision of 0.0004 g cm\(^{-3}\). DSA was calibrated by doubly distilled water and dry air.

Sine wave Vibro viscometer (SV-10 Vibro viscometer) from A and D company limited, was used for viscosity studies. A series of concentration of each salt was measured by adding stock solutions of appropriate concentrations from a weight pipette into a known quantity of pure solvent or binary mixture taken in a small container in which sensory plates of SV-10 viscometer is immersed. The measurement in each case was repeated with two different stock solutions to get better reproducibility of results. The overall accuracy of the viscosity measurement was found to be ±1 %. Dielectric constants were measured with Dielectric constant meter (Model DCL-01) from SES Instruments Pvt. Ltd. (Roorkee, India) at 1 Mhz frequency with an accuracy of ± 1%.

DSA 5000M from Anton Parr was used to detect density and sound velocity. The sample is inserted in a long U-tube made of borosilicate glass that is excited to oscillate at its characteristic frequency. A piezoelectric actuator sends out ultrasonic pulses that travel through the sample. As the sample is filled in a cell with a known length, the travel distance is also known. A second piezoelectric element detects the sound pulse so that the time the ultrasonic waves need to travel through the samples can be measured. The sound velocity (m/s) is then simply calculated by the relation of distance (m) to time (s). Calibration is done by measuring the density and sound velocity of known liquids like water (1497.7 ms\(^{-1}\)) and acetonitrile (1279.9 ms\(^{-1}\)) which agreed well with literature values of 1497.5 ms\(^{-1}\) and 1280.8 ms\(^{-1}\) respectively [14,15] at 298 K. The temperature control in DSA apparatus is ±0.01K.

3. RESULTS AND DISCUSSIONS

The experimental densities (\(\rho\)), viscosity (\(\eta\)), relative permittivity (\(\varepsilon\)), and ultrasonic velocity (\(u\)) of DMSO, Py, and NM were measured and reported in Table 2 at 298K.

Table 2: Density (\(\rho\)), viscosity (\(\eta\)), relative permittivity (\(\varepsilon\)), and ultrasonic velocity(u) for DMSO, Py, and NM at 298K.

| Solvents | \(\rho/(\text{g cm}^{-3})\) | \(\eta/(\text{mPa s})\) | \(\varepsilon\) | \(u/(\text{m s}^{-1})\) |
|----------|-----------------|-----------------|-------------|-----------------|
|          | Expt.            | Lit.             | Expt.        | Lit.             | Expt.            | Lit.             |
| DMSO     | 1.0953           | 1.0953016; 1.0953317; 1.0953718 | 1.99        | 2.01221; 1.9920; 2.0021 | 46.7             | 46.720; 46.722; 46.7123 | 1486.49          | 1486.7424       |
| Py       | 0.9786           | 0.978215.25     | 0.88        | 0.8815; 0.88426; 0.8927 | 12.4             | 12.4825; 12.4278    | 1418.14          | 1419.215        |
| NM       | 1.1295           | 1.1295838; 1.129630 | 0.612      | 0.61511.32    | 35.07            | 36.033            | 1321.38          | 1320.415        |

3.1 Density properties

Densities, \(\rho\) for the binary systems of DMSO+Py and DMSO+NM in the whole range of composition at three different temperatures are displayed in Table 3 and 4. Perusal of Table 3 and 4 shows that density of pure components followed
the order: NM > DMSO > Py. For binary solutions the ρ varied as: DMSO+NM > DMSO+Py. By using the below equation, the excess molar volume \( V^E \) at any composition was calculated from the measured densities (ρ).

\[
V^E = X_1 \cdot M_1 (\rho^{-1} - \rho_1^{-1}) + X_2 \cdot M_2 (\rho^{-1} - \rho_2^{-1})
\]

(1)

In the above equation, \( M_1 \) and \( M_2 \) represent the molar masses of the pure components. \( \rho_1, \rho_2, \) and \( \rho \) are the densities of the pure components 1 and 2 and that of the mixtures at different temperatures, respectively.

Table 3: Density (ρ/ g. cm\(^{-3}\)) and excess molar volume (\( V^E / \text{cm}^3. \text{mol}^{-1} \)) for DMSO (1) and Py (2) at T= 298 K, 308 K, and 318 K.

| \( X_2 \) | 298 K | 308 K | 318 K |
|-------|-------|-------|-------|
| 0     | 1.0953 | 1.0753 |
| 0.1   | 1.0832 | 0.0634 | 1.0641 |
| 0.2   | 1.0702 | -0.0452 | 1.0535 |
| 0.3   | 1.0595 | -0.1643 | 1.0436 |
| 0.4   | 1.0494 | -0.3093 | 1.0342 |
| 0.5   | 1.0369 | -0.2635 | 1.0227 |
| 0.6   | 1.0233 | -0.1109 | 1.0099 |
| 0.7   | 1.0117 | -0.0828 | 0.9986 |
| 0.8   | 1.0033 | -0.2837 | 0.9873 |
| 0.9   | 0.9914 | -0.1916 | 0.9735 |
| 1     | 0.9786 | 0      | 0.9594 |

Table 4: Density (ρ/ g. cm\(^{-3}\)) and excess molar volume (\( V^E / \text{cm}^3. \text{mol}^{-1} \)) for DMSO (1) and NM (2) at T= 298 K, 308 K, and 318 K.

| \( X_2 \) | 298 K | 308 K | 318 K |
|-------|-------|-------|-------|
| 0     | 1.0953 | 1.0753 |
| 0.1   | 1.0978 | 0.0098 | 1.0779 |
| 0.2   | 1.0997 | 0.0645 | 1.0805 |
| 0.3   | 1.1022 | 0.0889 | 1.1023 |
| 0.4   | 1.1054 | 0.0802 | 1.0841 |
| 0.5   | 1.1089 | 0.0645 | 1.0866 |
| 0.6   | 1.1124 | 0.0598 | 1.1087 |
| 0.7   | 1.1161 | 0.0553 | 1.1091 |
| 0.8   | 1.1209 | 0.0058 | 1.0935 |
| 0.9   | 1.1251 | 0.0013 | 1.0972 |
| 1     | 1.1295 | 0      | 1.1018 |

Excess molar volume is negative for mixtures of DMSO with Py over the whole range of composition of Pyridine with...
two minima lying near $X_2 \approx 0.2$ and $X_2 \approx 0.6$ at all temperatures as shown in Fig 1. The excess molar volume value becomes more negative with an increase in temperature in the binary mixtures of DMSO+Py. Tresczanowicz, et. al [34] and Roux and Desnoyers [35] interpreted that excess molar volume, $V^E$ is the resultant contribution from several opposing factors which were primarily divided into three types: chemical, physical and structural. A physical contribution which is a specific interaction between the solvent molecules present in the mixture contributes to the negative value of $V^E$. The chemical factor also termed as specific intermolecular interactions result in a decrease in volume which includes charge transfer type forces and other complex-forming interactions. This also contributes to the negative values of $V^E$. The structural contributions are mostly negative. It can arise from several effects especially from a change in free volume and interstitial accommodation. In other words, structural contributions arising from the geometrical filling of one component lead to a negative contribution to $V^E$.

While in case of DMSO+NM binary mixture, excess molar volume values are positive over the whole range of mole fraction of NM at 298K but at 308 K and 318 K, the $V^E$ values are negative from the mole fraction $X_2 = 0.1$ to 0.3 and then all the values are positive with maxima at $X_2 = 0.7$ at 298 K and maxima and minima at $X_2 = 0.2$ and $X_2 = 0.8$ respectively at 308 K and 318 K as shown in Fig 2. It shows a sigmoid change from positive to negative excess volume values. The initial negative deviation in the DMSO+NM mixture is possibly due to interstitial accommodation of solvated NM in the bigger H-bonded structure of DMSO. Similar sigmoid changes in excess properties have also been reported by other authors [36]. $V^E$ value gives information about the net destruction of interaction and packing phenomenon that appears in the mixing process [37]. The positive values of $V^E$ indicate that the packing degree in these mixed liquids is lower than in the pure species and in their deal mixtures. $V^E$ values increase with an increase in temperature because it is expected that any kind of interaction whether H-bond or any kind of interstitial accommodation breaks at high temperatures.

### 3.2 Viscosity and related properties

Viscosities, $\eta$ for DMSO+Py and DMSO+NM at temperatures 298 K, 308 K, and 318 K have been reported in Tables 5 and 6. Fig 3 and 4 represent the $\eta$ as a function of mole fraction of Py and NM, respectively. And $\eta$ follows the order DMSO > Py > NM. Fig 3 and 4 clearly show that the viscous behavior of both the binary mixtures is the same i.e. all the $\eta$ versus $X_2$ curves fall rapidly in Py and NM rich regions showing less viscous nature of Py and NM. When Py and
NM are added in the solvent, the difference in the size of solvent molecule results in loss of association between pure solvent molecule which results in the fall of viscosity values. This disruption in molecular association resulted in greater fluidity of mixture as compared to pure solvents.

The viscosity deviation can be calculated as:

$$\Delta \eta = \eta_{12} - (\eta_1 \times X_1 + \eta_2 \times X_2)$$

where $\eta_{12}$ is the viscosity of the mixture and $\eta_1$ and $\eta_2$ are viscosities of pure components. The values of $\Delta \eta$ for the binary mixtures, DMSO+Py, and DMSO+NM are all negative at all three temperatures. These values are more negative at low temperatures. The negative deviation of viscosity values for both the binary mixtures suggests that the viscosities of associates formed between dissimilar molecules are relatively less than those of pure components.

Table 5: Viscosity, $\eta$ and deviation in viscosity, $\Delta \eta$ for DMSO+Py at 298 K, 308 K, and 318 K.

| $X_2$ | 298 K | 308 K | 318 K |
|-------|-------|-------|-------|
|       | $\eta$ | $\Delta \eta$ | $\Delta \eta$ | $\eta$ | $\Delta \eta$ |
| 0     | 1.99   | 0      | 1.645 | 0      | 1.385 |
| 0.1   | 1.79   | -0.089 | 1.553 | -0.005 | 1.312 |
| 0.2   | 1.61   | -0.158 | 1.455 | -0.015 | 1.236 |
| 0.3   | 1.45   | -0.207 | 1.368 | -0.015 | 1.165 |
| 0.4   | 1.32   | -0.226 | 1.284 | -0.011 | 1.089 |
| 0.5   | 1.21   | -0.225 | 1.196 | -0.012 | 1.006 |
| 0.6   | 1.12   | -0.204 | 1.093 | -0.027 | 0.932 |
| 0.7   | 1.08   | -0.133 | 1.007 | -0.026 | 0.859 |
| 0.8   | 1.01   | -0.092 | 0.942 | -0.004 | 0.787 |
| 0.9   | 0.95   | -0.041 | 0.856 | -0.002 | 0.713 |
| 1     | 0.88   | 0      | 0.771 | 0      | 0.655 |
Table 6: Viscosity, $\eta$ and deviation in viscosity, $\Delta\eta$ for DMSO+NM at 298 K, 308 K, and 318 K.

| $X_2$ | $298$ K |          |          | $308$ K |          | $318$ K |
|-------|---------|----------|----------|---------|----------|---------|
|       | $\eta$  | $\Delta\eta$ | $H$ | $\Delta\eta$ | $\eta$ | $\Delta\eta$ |
| 0     | 1.99    | -0.2922  | 0.0011  | 1.297   | -0.0005  |
| 0.1   | 1.560   | -0.4604  | 0.0028  | 1.203   | -0.0071  |
| 0.2   | 1.146   | -0.4306  | 0.0087  | 1.114   | -0.0085  |
| 0.3   | 1.040   | -0.3988  | 0.0116  | 1.031   | -0.0040  |
| 0.4   | 0.976   | -0.3251  | 0.0005  | 0.942   | -0.0055  |
| 0.5   | 0.912   | -0.2512  | 0.0006  | 0.847   | -0.0130  |
| 0.6   | 0.859   | -0.1664  | 0.0103  | 0.765   | -0.0075  |
| 0.7   | 0.780   | -0.1076  | 0.0052  | 0.673   | -0.0120  |
| 0.8   | 0.705   | -0.0448  | 0.0009  | 0.589   | -0.0085  |
| 1     | 0.612   | 0        | 0.564   | 0.510   | 0        |

Fig 5 and 6 shows a plot of deviation in viscosity for the binary mixtures DMSO+Py and DMSO+NM at three temperatures. Figure shows that $\Delta\eta$ decreases negatively in magnitude and approach minimum at around $X_2 = 0.5$ for DMSO+Py and $X_2 = 0.8$ for DMSO+NM binary mixture. DMSO, Py and NM being non-hydrogen bonded solvents, structural changes because of H-bond is not reflected by viscosity deviations. Further, literature studies reveals that relatively large negative values of viscosity excess function for non H-bond systems like AN-DMSO, BN-AN [38] mixtures have been attributed to dipole-dipole interactions. The disruption of molecular association leads to close packing in DMSO+Py mixtures. This can also be stated as the cause behind the newly observed change in compressibility and volume. Fig 1 and 2 represent an increase in the negative values of $V^E$. Hence, the above stands accounted for. The negative value of $\Delta\eta$ and $V^E$ is seen to be inversely proportional to each other with $\Delta\eta$ being less...
negative and $\eta^E$ more, with an increase in temperature. Similar observations have been reported in DMSO+PC, DMSO+MeOH mixtures [39]. Less negative $\Delta \eta$ in the above system can be attributed to thermal effect. The resultant of this thermal effect is a weakened association between solvent molecules and stronger intermolecular interaction leading to excess viscosity with an increase in temperature. The weakened association between the two solvent molecules causes a negative deviation in viscosity, of which the outcome is greater fluidity of the molecule with regard to the ideal mixture. A correlation between $\Delta \eta$ and $V^E$ values for some binary solvents systems was reported by Prolongo et al [40]. and by Dewan et. al [41]. suggesting dispersion and dipole interactions rather than H-bond formation for negative values for $\Delta \eta$.

3.3 Relative permittivity and related properties

By the use of the under mentioned equation

$$\Delta \varepsilon = \varepsilon_{12} - (\varepsilon_1 \cdot X_1 + \varepsilon_2 \cdot X_2)$$

(3)

More information on the binary mixture studied in terms of intermolecular interaction and internal structure was obtained where $\varepsilon_{12}$, $\varepsilon_1$, and $\varepsilon_2$ are the relative permittivity of the mixture and those of pure solvents 1 and 2 respectively. Tables 7 and 8 exhibits the deviation in the relative permittivity, positive for DMSO+Py binary mixture, and negative for DMSO+NM mixture. The unique tool of the thermodynamic parameter for investigating the coming together of intermolecular complexes in binary liquid systems provides a valuable aid for determining their stoichiometry and their relative thermostability [42]. The negative value in the deviation of relative permittivity suggests the decrease in the effective number of parallel aligned dipoles in the mixtures, which might be due to some break in the structures.

Table 7: Relative permittivity ($\varepsilon$) and deviation in relative permittivity ($\Delta \varepsilon$) for DMSO+Py at 298 K, 308 K, and 318K.

| $X_2$ | 298 K | 308 K | 318 K |
|-------|-------|-------|-------|
|       | $\varepsilon$ | $\Delta \varepsilon$ | $\varepsilon$ | $\Delta \varepsilon$ | $\varepsilon$ | $\Delta \varepsilon$ |
| 0     | 46.7  | 0     | 44.70 | 0     | 43.30 | 0     |
| 0.1   | 43.2  | -0.07 | 41.21 | -0.08 | 40.02 | 0.15  |
| 0.2   | 39.9  | 0.06  | 37.84 | -0.04 | 36.67 | 0.23  |
| 0.3   | 36.6  | 0.19  | 34.63 | 0.16  | 33.14 | 0.13  |
| 0.4   | 33.1  | 0.12  | 31.09 | 0.03  | 29.39 | -0.19 |
| 0.5   | 29.9  | 0.35  | 27.96 | 0.31  | 25.53 | -0.62 |
| 0.6   | 26.2  | 0.08  | 24.61 | 0.37  | 22.19 | -0.53 |
| 0.7   | 22.5  | -0.19 | 21.15 | 0.32  | 18.78 | -0.51 |
| 0.8   | 19.3  | 0.04  | 17.87 | 0.45  | 15.36 | -0.50 |
| 0.9   | 15.7  | -0.13 | 14.44 | 0.43  | 12.05 | -0.38 |
| 1     | 12.4  | 0     | 10.60 | 0     | 9.00  | 0     |

Table 8: Relative permittivity ($\varepsilon$) and deviation in relative permittivity ($\Delta \varepsilon$) for DMSO+NM at 298 K, 308 K, and 318K.

| $X_2$ | 298 K | 308 K | 318 K |
|-------|-------|-------|-------|
|       | $\varepsilon$ | $\Delta \varepsilon$ | $\varepsilon$ | $\Delta \varepsilon$ | $\varepsilon$ | $\Delta \varepsilon$ |
| 0     | 46.7  | 0     | 44.70 | 0     | 43.30 | 0     |
| 0.1   | 43.2  | -0.07 | 41.21 | -0.08 | 40.02 | 0.15  |
| 0.2   | 39.9  | 0.06  | 37.84 | -0.04 | 36.67 | 0.23  |
| 0.3   | 36.6  | 0.19  | 34.63 | 0.16  | 33.14 | 0.13  |
| 0.4   | 33.1  | 0.12  | 31.09 | 0.03  | 29.39 | -0.19 |
| 0.5   | 29.9  | 0.35  | 27.96 | 0.31  | 25.53 | -0.62 |
| 0.6   | 26.2  | 0.08  | 24.61 | 0.37  | 22.19 | -0.53 |
| 0.7   | 22.5  | -0.19 | 21.15 | 0.32  | 18.78 | -0.51 |
| 0.8   | 19.3  | 0.04  | 17.87 | 0.45  | 15.36 | -0.50 |
| 0.9   | 15.7  | -0.13 | 14.44 | 0.43  | 12.05 | -0.38 |
| 1     | 12.4  | 0     | 10.60 | 0     | 9.00  | 0     |
3.4 Ultrasonic velocity and related properties

The ultrasonic velocity (speed of sound), \( u \) for the binary mixtures DMSO+Py and DMSO+NM at temperature 298 K, 308 K, 318 K was measured and reported in Table 9 and 10. From the experimental measured data of the ultrasonic velocity, the deviation in ultrasonic velocity, \( \delta u \) obtained from the mole fraction additivity has been estimated from the relationship.

\[
\Delta u = u - (u_1X_1 + u_2X_2)
\]

Where \( u \) is the ultrasonic velocity of the mixture and \( u_1 \) and \( u_2 \) is the ultrasonic velocity of solvents 1 and 2.

Ultrasonic velocity, \( u \) decreases with an increase in temperature for both binary mixtures. The ultrasonic excess function, \( \delta u \) is negative for DMSO+Py at 298 K up to \( X_2 = 0.5 \), but the value is positive at 308 K and 318 K. whereas, the value of \( \delta u \) is negative for DMSO+NM binary mixture at all three temperatures.

Table 9: Ultrasonic velocity (\( u \)) and deviation in velocity (\( \delta u \)) for DMSO+Py at 298 K, 308 K, and 318 K.

| \( X_2 \) | 298 K | 308 K | 318 K |
| --- | --- | --- | --- |
| \( \varepsilon \) | \( \Delta \varepsilon \) | \( E \) | \( \Delta \varepsilon \) | \( \varepsilon \) | \( \Delta \varepsilon \) | \( \varepsilon \) | \( \Delta \varepsilon \) |
| 0 | 46.7 | 0 | 44.70 | 0 | 43.30 | 0 |
| 0.1 | 45.3 | -0.237 | 43.61 | -0.115 | 42.37 | 0.015 |
| 0.2 | 44.1 | -0.274 | 42.76 | 0.010 | 41.49 | 0.080 |
| 0.3 | 43.2 | -0.011 | 41.81 | 0.035 | 40.71 | 0.245 |
| 0.4 | 41.9 | -0.148 | 40.58 | -0.220 | 39.58 | 0.060 |
| 0.5 | 40.7 | -0.165 | 39.77 | -0.055 | 38.28 | -0.295 |
| 0.6 | 39.7 | -0.022 | 38.64 | -0.210 | 37.66 | 0.030 |
| 0.7 | 38.3 | -0.259 | 37.39 | -0.485 | 36.94 | 0.255 |
| 0.8 | 37.5 | 0.104 | 36.75 | -0.150 | 35.75 | 0.010 |
| 0.9 | 36.46 | 0.227 | 35.43 | -0.495 | 34.57 | -0.225 |
| 1 | 35.07 | 0 | 34.95 | 0 | 33.85 | 0 |

Table 10: Ultrasonic velocity (\( u \)) and deviation in velocity (\( \delta u \)) for DMSO+NM at 298 K, 308 K, and 318 K.
Ultrasonic velocity, \( u \), is a measure of strong forces acting between the solvent molecules. The sign and the magnitude of \( \delta u \) provide a major role in molecular rearrangement which might lead to molecular interactions between solvents. The negative value of \( \delta u \) indicates the presence of weak interactions, while the positive values of \( \delta u \) indicate the strong attractive forces between the unlike molecules [43]. The weak interactions between the molecules increase the intermolecular distance between them resulting in less wave propagation thus accounting for negative values in DMSO+NM. Fig7 and 8 clearly show that \( \delta u \) values are positive for DMSO+Py and negative for DMSO+NM at 308 K and 318 K with maxima and minima at \( X_2 = 0.6 \) respectively. Greater positive values of \( \delta u \) are also responsible for more negative VE.

| \( X_2 \) | \( 298 \text{ K} \) | \( 308 \text{ K} \) | \( 318 \text{ K} \) |
|---|---|---|---|
| 0 | 1486.49 | 1467.07 | 1434.18 |
| 0.1 | 1462.65 | 1450.92 | 1417.96 |
| 0.2 | 1438.27 | 1432.10 | 1402.47 |
| 0.3 | 1419.86 | 1409.28 | 1379.41 |
| 0.4 | 1403.33 | 1385.32 | 1353.53 |
| 0.5 | 1386.58 | 1362.67 | 1329.85 |
| 0.6 | 1370.19 | 1340.46 | 1304.49 |
| 0.7 | 1355.42 | 1322.85 | 1286.21 |
| 0.8 | 1342.88 | 1311.78 | 1274.88 |
| 0.9 | 1330.76 | 1301.32 | 1261.09 |
| 1 | 1321.38 | 1285.63 | 1247.70 |

Fig 7: Plot of deviation in velocities \( \delta u \) for the mixture DMSO+Py against mole fraction of Py. ♦ - 298 K; ■ - 308 K; ▲ - 318 K.

Fig 8: Plot of deviation in velocities \( \delta u \) for the mixture DMSO+NM against mole fraction of NM. ♦ - 298 K; ■ - 308 K; ▲ - 318 K.
4. CONCLUSIONS

In the present paper, the excess molar volumes ($V^E$) and the deviation in the viscosities ($\Delta\eta$), relative permittivity ($\Delta\varepsilon$), and ultrasonic velocity ($\delta u$) have been correlated at three different temperatures. The plots of deviation of all the thermodynamic parameters were plotted against a mole fraction of co-solvent. Results show that structural contributions arising from the geometrical filling of one component lead to a negative contribution to $V^E$. The $V^E$ shows a sigmoid change from positive to negative excess volume values for the DMSO+NM mixture. Further, the effect of temperature increase in molar volume and viscosity were also studied. The deviation in viscosity ($\Delta\eta$) tends to become less negative with an increase in temperature but $V^E$ becomes more negative with a rise in temperature. Greater positive values of $\delta u$ are also responsible for negative trend in $V^E$. Thus above interpretation show a stronger interaction in the DMSO+Py mixture and weak interactions in the DMSO+NM mixture.

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I want to thank you all for your constructive feedback in this review process. The reviewer’s comments provided valuable insights to refine the contents and analyze the paper thoroughly. In this document, I have tried to address the issues raised as best as possible.

Comments of reviewers

----------------------- REVIEW 1 ---------------------

SUBMISSION: 70
TITLE: Thermodynamic and physiochemical properties and the excess functions of binary mixtures of Dimethylsulfoxide with Pyridine and Nitromethane at variable temperatures - 298 to 318K.

----- TEXT:
1. The manuscript has been well written. The authors have addressed the technical aspects very well.

Comment: Thank you very much for appreciating my work.

2. The plagiarism report of this research article is 33% need to be reduced.

Comment- I have tried my best to make the required changes in the paper, Sir/Madam. Thank you.

----------------------- REVIEW 2 ---------------------

----- TEXT:
1) Abstract and conclusion content is almost same, thus need re-framing.

Comments- Thank you so much for critically analyzing this point. I have reframed the abstract and the conclusion part in the paper and have made few changes in the conclusion section.

2) Introduction is little weak especially missing the background of relevance of the study and rational approach of the research peace chosen by authors.

Comment: The study gives the knowledge about the changes occurring in the structure in terms of molecular association between different solvent molecules and self dissociation between the similar molecules in terms of the excess function like viscosity, ultrasonic velocity, density and relative permittivity.

3) Appropriate abbreviation of the full forms ought to be given at their very first instance (viz NO ). Full forms should have been described before the usage of the abbreviation.

Comment: I have corrected it and tried to explain the full form of abbreviation before using it.

4) Candidate has described the procedure under the head material , needs revision as no separate heading’s for methodology or procedure adopted , so either place them under different heads and give proper details or club them

Comment: Thank you so much for pointing out this. I have made the required changes and have changed the heading
from materials to materials and methods.

5) Quite variation in the decimal places wide variation ranging from 2 to 6
Comment: I have corrected this and a uniform pattern is followed.

6) No uniform pattern has been followed for some common words (fig, Fig), abbreviations
Comment: I have analyzed the inaccuracy in the paper and have corrected it and have followed a unique pattern.

7) Reviewers couldn’t make out the significance of study done, authors must have concluded in 1-2 lines
Comment: Thank you so much for pointing out this. I have added a line in conclusion part which shows the outcome of the study done. It shows a stronger interaction in the DMSO+Py mixture and weak interactions in the DMSO+NM mixture which can be attributed to structural changes occurring in solvent molecules on mixing. The Py molecule show a stronger type of intermolecular interactions with DMSO as compared to NM showing less packing forces of molecules in it.

8) There are many instances of language discrepancies in the manuscript and grammatical mistakes. Authors are advised to fix the grammatical, scientific and typographical errors, get the manuscript critically checked and edited along with other suggested modifications
Comment: I have tried to modify the paper and have thoroughly proof read the paper for any kind of grammatical mistake.

----------------------- REVIEW 3 ---------------------

----- TEXT:

1) The excess molar volume $V^E$ against mole fraction show first decreases then increases for DMSO+Py binary mixture while the excess molar volume $V^E$ against mole fraction for DMSO+NM binary mixture show first increase then decreases and become negative. Why?

Comment: I would like to appreciate the reviewer for analyzing the paper and raising this query. The excess molar volume $V^E$ for the DMSO+Py mixtures first increases indicating that pyridine molecules might have undergone some structural changes and occupied the interstitial sites of DMSO arising from structural factors and then decreases indicating interactions between two dissimilar molecules DMSO and Py starts to occur. But for DMSO+NM binary mixtures the initial negative value of $V^E$ is due to the interstitial accommodation of NM molecules in the bigger structure of DMSO. But the molar volume values start to become positive indicating the dissociation of self associated DMSO molecules by the further addition of NM which is not compensated by interactions occurring in DMSO and NM resulting in a sudden increase in the values till it reaches maxima. Further, the packing forces of the mixed liquid must be lower than the pure species which resulted in a decrease in the values of $V^E$. 
2) Why the Experimental viscosities $\eta$ and versus mole fraction decreases for the mixture DMSO+Py and DMSO+NM?

Comment: For this, I would like to address the less viscous nature of both Py and NM as compared to DMSO resulting in a decrease in experimental viscosity values. When Py and NM are added in the solvent, the difference in the size of solvent molecule results in loss of association between pure solvent molecule which result in the fall of viscosity values. This disruption in molecular association resulted in greater fluidity of mixture as compared to pure solvents.

3) Why the deviations in viscosities $\Delta\eta$ versus mole fraction show negative value for DMSO+Py and DMSO+NM?

Comment: The negative deviations in the values of viscosity for both binary mixtures suggest that the viscosities of associates formed between dissimilar molecules are relatively less than the pure solvents which are the result of thermal effect. It causes the weak association between the molecules thus, responsible for the negative values of $\Delta\eta$.

Once again, I would like to thank all the reviewers for the time they have put in reviewing my paper and look forward to meeting your expectations. Since your inputs have been precious, in the eventuality of a publication, I would like to acknowledge your contribution explicitly.