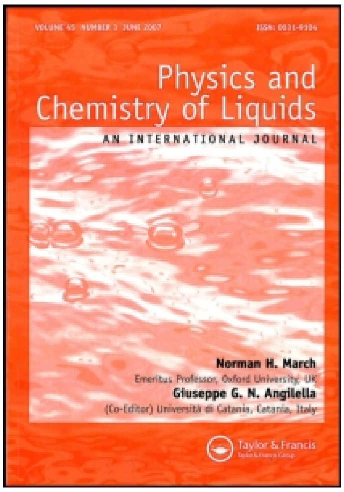

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# Thermodynamic studies of some 1,2,4-triazole derivatives in DMF and THF solutions at 308.15 K

Shipra Baluja[a]; Nikunj Kachhadia[a]; Asif Solanki[a]
[a] Department of Chemistry, Saurashtra University, Rajkot, Gujarat, India

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# Thermodynamic studies of some 1,2,4-triazole derivatives in DMF and THF solutions at 308.15 K

SHIPRA BALUJA*, NIKUNJ KACHHADIA and ASIF SOLANKI

Department of Chemistry, Saurashtra University, Rajkot – 360005, Gujarat, India

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Some new 1,2,4-triazole derivatives have been synthesized and characterized by TLC, IR, NMR and mass spectra. Densities, viscosities and ultrasonic velocities of these compounds have been measured over the wide composition range at 308.15 K in dimethyl formamide (DMF) and tetrahydro furan (THF). From these data, various acoustical and thermodynamic parameters (C.V. Suryanarayana, J. Kuppuswamy. *J. Acoust. Soc. Ind.*, **4**, 75 (1976); H. Erying, M.S. John, *Significance of Liquid Structures*, Wiley, New York (1969); G.K. Johri, R.C. Misra. *Acustica*, **56**, 66 (1989)) were evaluated. Some of these parameters are isentropic compressibility ($\kappa_s$), intermolecular free length ($L_f$), relaxation strength ($r$), relative association ($R_A$), Rao's molar constant ($R_m$), van der Waal's constant ($b$), molar compressibility ($W$), internal pressure ($\pi$), free volume ($V_f$), solvation number ($S_n$) etc. The behavior of solutions of these compounds in DMF and THF are explained from the evaluated parameters.

*Keywords*: Synthesis; Thermo dynamic properties; DMF; THF

## 1. Introduction

At present, ultrasonics is a subject of extensive research, and we find its usefulness in the fields of biology, biochemistry, engineering, geography, geology, medicine, polymer industry etc. It has also been applied to process monitoring and materials characterization [1]. Ultrasonic velocity ($U$) together with density ($\rho$) and viscosity ($\eta$) data furnishes a wealth of information about bulk properties and intermolecular forces [2–7], which find applications in several industries and technological processes [8,9].

A literature survey reveals that ultrasonic velocity of various organic, inorganic and biological compounds in various solvents have been studied [10–15]. Our research group has also studied acoustical studies of some Schiff bases in various solvents [16–19]. In continuation of our previous work, the present work deals with acoustical properties of some 1,2,4-triazole derivatives in dimethyl formamide (DMF) and tetrahydrofuran (THF).

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*Corresponding author. Email: shkundal_ad1@sancharnet.in; shipra_baluja@rediffmail.com

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The choice of 1,2,4-triazoles is due its multi-applicability in the field of medicine. They are known to be important moiety in the drug industry [20,21]. The applications of these compounds attract us to study their behavior in various solvents.

## 2. Experimental

The solvents used in the present work were of AR grade and were purified according to the standard procedure described in the literature [22]. The compounds were recrystalized before use.

The computation of ultrasonic and thermodynamic properties requires the measurements of $U$, $\eta$, and $\rho$.

The densities of pure solvents and their solutions were measured by using a Single Capillary Pycnometer made of borosil glass having a bulb capacity of 10 mL. The marks on the capillary were calibrated by using triple distilled water. The ultrasonic velocity of pure solvents and their solutions were measured by using Single Crystal Variable Path Ultrasonic Interferometer operating at 2 MHz. Viscosity of pure solvents and solutions were measured by an Ubbelohde viscometer with an accuracy of 0.06%. All the measurements were carried out at 308.15 K. The uncertainty of temperature is ±0.1 K and that of concentration is 0.0001 M.

The experimental data of $U$, $\eta$ and $\rho$ are given in table 1.

## 3. Theory

From the experimental data of density, viscosity and ultrasound velocity of pure solvent and solutions, various acoustical parameters were calculated using following standard equations:

(1) Isentropic compressibility ($\kappa_s$): $= \dfrac{1}{U^2\rho}$.

(2) Intermolecular length ($L_f$): $L_f = K\kappa_s^{1/2}$

where $K$ is Jacobson constant ($=6.0816 \times 10^4$).

(3) Relaxation strength ($r$): $r = 1 - \left(\dfrac{U}{U_\propto}\right)^2$

where $U_\propto = 1.6 \times 10^5\,\mathrm{cm\,s^{-1}}$.

(4) Relative association ($R_a$): $R_a = \dfrac{\rho}{\rho_0}\left(\dfrac{U_0}{U}\right)^{1/3}$.

(5) Rao's molar sound function ($R_m$): $R_m = \left(\dfrac{M}{\rho}\right)U^{1/3}$

where $M$ is the molecular weight of solution.

Table 1. The density ($\rho$), ultrasonic velocity ($U$) and viscosity ($\eta$) of triazole derivatives in DMF and THF at 308.15 K.

| | DMF | | | THF | | |
|---|---|---|---|---|---|---|
| Conc. ($M$) | Density ($\mathrm{g\,cm^{-3}}$) | Velocity ($\times 10^{-5}\,\mathrm{cm\,s^{-1}}$) | Viscosity ($\times 10^{3}$ poise) | Density ($\mathrm{g\,cm^{-3}}$) | Velocity ($\times 10^{-5}\,\mathrm{cm\,s^{-1}}$) | Viscosity ($\times 10^{3}$ poise) |
| | HAS-A | | | HAS-A | | |
| 0.00 | 0.9335 | 1.4568 | 7.1882 | 0.8713 | 1.2152 | 4.3830 |
| 0.01 | 0.9397 | 1.4378 | 7.8316 | 0.8714 | 1.2296 | 4.4839 |
| 0.02 | 0.9417 | 1.4405 | 8.1532 | 0.8734 | 1.2332 | 4.5378 |
| 0.04 | 0.9436 | 1.4440 | 8.3436 | 0.8769 | 1.2380 | 4.7650 |
| 0.06 | 0.9471 | 1.4491 | 8.4768 | 0.8803 | 1.2424 | 4.9232 |
| 0.08 | 0.9489 | 1.4523 | 8.6786 | 0.8825 | 1.2464 | 5.0122 |
| 0.10 | 0.9505 | 1.4584 | 8.8540 | 0.8850 | 1.2484 | 5.0991 |
| | HAS-B | | | HAS-B | | |
| 0.01 | 0.9359 | 1.4153 | 7.3944 | 0.8735 | 1.2194 | 4.4370 |
| 0.02 | 0.9381 | 1.4172 | 7.6075 | 0.8738 | 1.2237 | 4.4984 |
| 0.04 | 0.9404 | 1.4239 | 7.7662 | 0.8767 | 1.2258 | 4.5775 |
| 0.06 | 0.9425 | 1.4256 | 8.0083 | 0.8785 | 1.2279 | 4.6138 |
| 0.08 | 0.9446 | 1.4284 | 8.2551 | 0.8790 | 1.2300 | 4.6830 |
| 0.10 | 0.9480 | 1.4296 | 8.3551 | 0.8810 | 1.2340 | 4.7674 |
| | HAS-C | | | HAS-C | | |
| 0.01 | 0.9368 | 1.4248 | 7.4302 | 0.8708 | 1.2180 | 4.4002 |
| 0.02 | 0.9381 | 1.4272 | 7.6589 | 0.8721 | 1.2208 | 4.4671 |
| 0.04 | 0.9405 | 1.4300 | 7.7512 | 0.8742 | 1.2248 | 4.5194 |
| 0.06 | 0.9423 | 1.4332 | 7.9216 | 0.8785 | 1.2264 | 4.6145 |
| 0.08 | 0.9443 | 1.4364 | 8.1468 | 0.8789 | 1.2288 | 4.6655 |
| 0.10 | 0.9465 | 1.4388 | 8.6300 | 0.8817 | 1.2308 | 4.7435 |
| | HAS-D | | | HAS-D | | |
| 0.01 | 0.9364 | 1.4203 | 7.4413 | 0.8716 | 1.2224 | 4.4604 |
| 0.02 | 0.9376 | 1.4298 | 7.6095 | 0.8727 | 1.2272 | 4.5018 |
| 0.04 | 0.9400 | 1.4353 | 7.9007 | 0.8753 | 1.2296 | 4.6774 |
| 0.06 | 0.9435 | 1.4385 | 8.1725 | 0.8777 | 1.2324 | 4.7623 |
| 0.08 | 0.9463 | 1.4414 | 8.4925 | 0.8788 | 1.2356 | 4.8306 |
| 0.10 | 0.9484 | 1.4476 | 8.7581 | 0.8805 | 1.2396 | 4.9115 |
| | HAS-E | | | HAS-E | | |
| 0.01 | 0.9345 | 1.4070 | 7.3502 | 0.8717 | 1.2188 | 4.4468 |
| 0.02 | 0.9360 | 1.4103 | 7.4540 | 0.8740 | 1.2204 | 4.4818 |
| 0.04 | 0.9377 | 1.4132 | 7.5302 | 0.8758 | 1.2236 | 4.6018 |
| 0.06 | 0.9405 | 1.4156 | 7.7777 | 0.8773 | 1.2248 | 4.6683 |
| 0.08 | 0.9418 | 1.4189 | 7.8286 | 0.8795 | 1.2288 | 4.7437 |
| 0.10 | 0.9450 | 1.4232 | 7.9420 | 0.8816 | 1.2304 | 4.8530 |

(6) Van der Waal's constant (b): $b = \left(\frac{M}{\rho}\right)\left[\sqrt{1-\left(\frac{MU^2}{3RT}\right)-1}\,\right]$

where $R$ is gas constant and $T$ is absolute temperature.

(7) Molar compressibility ($W$): $W = \left(\frac{M}{\rho}\right)\kappa_s^{-1/7}$.

(8) Internal pressure $(\pi) = bRT\left(\frac{k\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M^{7/6}}\right)$

where $k$ is constant $(4.28 \times 10^9)$, $\eta$ is the viscosity of the solution and $b$ is packing fraction (=2).

(9) Free volume $(V_f)$: $V_f = \left[\frac{MU}{K\eta}\right]^{3/2}$.

(10) Solvation number $(S_n)$: $S_n = \frac{M_2}{M_1}\left[1 - \frac{\kappa_s}{\kappa_{s1}}\right]\left[\frac{(100 - X)}{X}\right]$

where $X$ is the number of grams of solute in 100 gm of the solution. $M_1$, $M_2$, $\kappa_{s1}$ and $\kappa_s$ are the molecular weights and isentropic compressibility of solvent and solute, respectively.

(11) Apparent molar volume $(\Phi_v) = \left[\frac{M}{\rho}\right] - \left[\frac{1000\{\rho - \rho_o\}}{\rho C}\right]$

where $M$ is the molecular weight of Schiff bases, $\rho$ and $\rho_o$ are the densities of solute and solvent, respectively and $C$ is the concentration of the solution in $M$.

(12) Apparent molar compressibility $(\Phi_k) = \left[(\rho_o\kappa_s - \rho\kappa_s^\circ)\left(\frac{1000}{C\rho_o}\right)\right] + \left[\frac{\kappa_s^\circ M_2}{\rho_o}\right]$

where $\kappa_s$ and $\kappa_s^\circ$ are the adiabatic compressibility of solvent and Schiff bases solution.

Some of these parameters are given in tables 2 and 3.

## 4. Results and discussion

Figure 1 shows the variation of ultrasound velocity with concentrations for both the solvents, DMF and THF. It is clear from figure 1 that increase in velocity with concentration is more in THF solutions than that in DMF. Ultrasonic velocity depends on intermolecular free length $(L_f)$ inversely. Increase in the $L_f$ causes a decrease in velocity or *vice versa*. Tables 2 and 3 show the regular decrease of $L_f$ values for both the solvents, causing thereby increase in velocity with concentration.

The isentropic compressibility of the solutions in both the solvents is also found to decrease with increase of concentration. This phenomenon can be explained by assuming that the solvated molecules are fully compressed by the electrical forces of the ions. The compressibility of the solution is mainly due to the free solvent molecules. Due to solute–solvent interactions in the system, compressibility of the solution decreases with the increase in solute concentration. This is further confirmed by decrease of $L_f$ and relaxation strength $(r)$ values. The increase in viscosity in both solvents also confirms the same. The association between solute and solvent molecules is further confirmed by relative association $(R_a)$ values, which are found to increase continuously with concentration for all the compounds in both the solvents.

Table 2. Variation of acoustical parameters with concentration of triazole derivatives in DMF at 308.15 K.

| Conc. ($M$) | $\kappa_s \times 10^{11}$ ($cm^2 dyn^{-1}$) | $L_f$ (Å) | $r$ | $Z \times 10^{-5}$ ($g cm^{-2}$) | $R_m \times 10^{-3}$ ($cm^{-8/3} s^{-1/3}$) | $b$ ($cm^3 mol^{-1}$) | $W \times 10^{-3}$ ($cm^{-1} dyn^{-1}$) | $\pi$ | $V_f$ ($cm^3$) |
|---|---|---|---|---|---|---|---|---|---|
| HAS-A | | | | | | | | | |
| 0.00 | 5.0476 | 0.4321 | 0.1710 | 1.3599 | 4.1198 | 73.6390 | 2315.9617 | 544.6836 | 0.1356 |
| 0.01 | 5.1477 | 0.4363 | 0.1925 | 1.3511 | 4.1334 | 74.1835 | 2327.2419 | 493.6951 | 0.1793 |
| 0.02 | 5.1177 | 0.4351 | 0.1895 | 1.3565 | 4.1854 | 75.1044 | 2357.0637 | 495.7954 | 0.1729 |
| 0.04 | 5.0825 | 0.4336 | 0.1855 | 1.3626 | 4.2966 | 77.0979 | 2420.0896 | 485.8237 | 0.1747 |
| 0.06 | 5.0280 | 0.4312 | 0.1797 | 1.3725 | 4.4007 | 78.9360 | 2479.5809 | 475.1384 | 0.1784 |
| 0.08 | 4.9964 | 0.4299 | 0.1761 | 1.3781 | 4.5102 | 80.9012 | 2541.7521 | 466.6030 | 0.1796 |
| 0.1 | 4.9465 | 0.4277 | 0.1692 | 1.3862 | 4.6233 | 82.8797 | 2605.5656 | 457.2802 | 0.1821 |
| HAS-B | | | | | | | | | |
| 0.01 | 5.3341 | 0.4442 | 0.2175 | 1.3245 | 4.1294 | 74.4446 | 2.3254 | 482.0700 | 0.1909 |
| 0.02 | 5.3075 | 0.4431 | 0.2154 | 1.3295 | 4.1807 | 75.3677 | 2.3549 | 481.3400 | 0.1873 |
| 0.04 | 5.2449 | 0.4404 | 0.2080 | 1.3390 | 4.2949 | 77.3769 | 2.4196 | 470.4600 | 0.1907 |
| 0.06 | 5.2206 | 0.4394 | 0.2061 | 1.3436 | 4.4042 | 79.3721 | 2.4818 | 463.3500 | 0.1900 |
| 0.08 | 5.1886 | 0.4381 | 0.2030 | 1.3493 | 4.5138 | 81.3529 | 2.5441 | 456.5300 | 0.1894 |
| 0.1 | 5.1613 | 0.4369 | 0.2017 | 1.3553 | 4.6136 | 83.1832 | 2.6016 | 446.8700 | 0.1934 |
| HAS-C | | | | | | | | | |
| 0.01 | 5.2583 | 0.4410 | 0.2070 | 1.3348 | 4.1305 | 74.3212 | 2.3256 | 482.5011 | 0.1912 |
| 0.02 | 5.2334 | 0.4399 | 0.2043 | 1.3389 | 4.1823 | 75.2413 | 2.3551 | 482.3658 | 0.1869 |
| 0.04 | 5.1996 | 0.4385 | 0.2012 | 1.3449 | 4.2843 | 77.0844 | 2.4131 | 471.1123 | 0.1914 |
| 0.06 | 5.1665 | 0.4371 | 0.1976 | 1.3505 | 4.3887 | 78.9622 | 2.4724 | 462.5101 | 0.1931 |
| 0.08 | 5.1326 | 0.4357 | 0.1940 | 1.3564 | 4.4914 | 80.8074 | 2.5307 | 455.9490 | 0.1927 |
| 0.1 | 5.1036 | 0.4345 | 0.1914 | 1.3618 | 4.5915 | 82.6157 | 2.5878 | 456.7510 | 0.1836 |
| HAS-D | | | | | | | | | |
| 0.01 | 5.2938 | 0.4425 | 0.2120 | 1.3300 | 4.1215 | 74.2237 | 2320.7613 | 484.3583 | 0.1895 |
| 0.02 | 5.2168 | 0.4393 | 0.2014 | 1.3406 | 4.1744 | 75.0559 | 2350.2202 | 481.9011 | 0.1884 |
| 0.04 | 5.1639 | 0.4370 | 0.1953 | 1.3492 | 4.2665 | 76.6727 | 2402.5210 | 477.8765 | 0.1854 |
| 0.06 | 5.1221 | 0.4353 | 0.1917 | 1.3572 | 4.3502 | 78.1696 | 2450.6554 | 474.1468 | 0.1828 |
| 0.08 | 5.0863 | 0.4337 | 0.1884 | 1.3640 | 4.4359 | 79.7068 | 2499.7799 | 471.6505 | 0.1789 |
| 0.1 | 5.0317 | 0.4314 | 0.1814 | 1.3729 | 4.5278 | 81.3008 | 2551.8666 | 466.9023 | 0.1775 |
| HAS-E | | | | | | | | | |
| 0.01 | 5.4052 | 0.4471 | 0.2267 | 1.3149 | 4.1117 | 74.2421 | 2.3156 | 483.7173 | 0.1899 |
| 0.02 | 5.3714 | 0.4457 | 0.2230 | 1.3201 | 4.1519 | 74.9377 | 2.3385 | 481.1159 | 0.1846 |
| 0.04 | 5.3398 | 0.4444 | 0.2199 | 1.3252 | 4.2340 | 76.4158 | 2.3852 | 472.1064 | 0.1932 |
| 0.06 | 5.3059 | 0.4430 | 0.2172 | 1.3314 | 4.3098 | 77.7855 | 2.4287 | 469.1805 | 0.1918 |
| 0.08 | 5.2738 | 0.4417 | 0.2135 | 1.3363 | 4.3933 | 79.2770 | 2.4759 | 459.8652 | 0.1947 |
| 0.1 | 5.2244 | 0.4396 | 0.2088 | 1.3449 | 4.4675 | 80.5852 | 2.5186 | 453.2950 | 0.1970 |

In both the solvents, the Rao's molar sound function ($R_m$), van der Waal's constant ($b$) and molar compressibility ($W$) for all the solutions are observed to increase linearly (correlation coefficient $\gamma = 0.9993$–$0.9999$), which suggest that no complex or aggregate formation takes place in these solutions.

The internal pressure ($\pi$) is the resultant of forces of attraction and repulsion between the molecules in a solution. Tables 2 and 3 show that it decreases with concentration in both the solvents. The decrease in internal pressure indicates the decrease in cohesive forces. Although decrease in compressibility, internal molecular free length, relaxation strength and increase of velocity, viscosity suggest predominance of solute–solvent interaction, the decrease in internal pressure indicates the existence of solute–solute interactions in these solutions. This is further supported by free volume. The free volume ($V_f$) of a solute molecule at a particular temperature and pressure depends on the internal pressure of a liquid, in which it is dissolved. The decrease in molecular

Table 3. Variation of acoustical parameters with concentration of triazole derivatives in THF at 308.15 K.

| Conc. ($M$) | $\kappa_s \times 10^{11}$ ($cm^2\,dyn^{-1}$) | $L_f$ (Å) | $r$ | $Z \times 10^{-5}$ ($g\,cm^{-2}$) | $R_m \times 10^{-3}$ ($cm^{-8/3}\,s^{-1/3}$) | $b$ ($cm^3\,mol^{-1}$) | $W \times 10^{-3}$ ($cm^{-1}\,dyn^{-1}$) | $\pi$ | $V_f$ ($cm^3$) |
|---|---|---|---|---|---|---|---|---|---|
| HAS-A | | | | | | | | | |
| 0.00 | 7.7721 | 0.5362 | 0.4232 | 1.0588 | 4.0993 | 77.0792 | 2.3016 | 394.5863 | 0.3925 |
| 0.01 | 7.5902 | 0.5298 | 0.4094 | 1.0715 | 4.1867 | 78.5011 | 2.3494 | 388.8659 | 0.3223 |
| 0.02 | 7.5287 | 0.5277 | 0.4059 | 1.0771 | 4.2525 | 79.7062 | 2.3868 | 383.5784 | 0.3261 |
| 0.04 | 7.4406 | 0.5246 | 0.4013 | 1.0856 | 4.3825 | 82.1248 | 2.4607 | 378.5788 | 0.3202 |
| 0.06 | 7.3595 | 0.5217 | 0.3970 | 1.0937 | 4.5107 | 84.5143 | 2.5337 | 371.2120 | 0.3214 |
| 0.08 | 7.2502 | 0.5194 | 0.3932 | 1.0999 | 4.6437 | 86.9983 | 2.6089 | 361.4834 | 0.3291 |
| 0.1 | 7.1721 | 0.5178 | 0.3912 | 1.1048 | 4.7713 | 89.4166 | 2.6815 | 352.6926 | 0.3359 |
| HAS-B | | | | | | | | | |
| 0.01 | 7.6987 | 0.5336 | 0.4191 | 1.0652 | 4.1590 | 78.1593 | 2.3356 | 389.7258 | 0.3227 |
| 0.02 | 7.6423 | 0.5317 | 0.4150 | 1.0693 | 4.2277 | 79.4064 | 2.3739 | 384.7643 | 0.3252 |
| 0.04 | 7.5912 | 0.5299 | 0.4131 | 1.0747 | 4.3455 | 81.6462 | 2.4410 | 375.1974 | 0.3324 |
| 0.06 | 7.5495 | 0.5284 | 0.4110 | 1.0787 | 4.4679 | 83.9712 | 2.5103 | 364.2244 | 0.3441 |
| 0.08 | 7.5197 | 0.5274 | 0.4090 | 1.0812 | 4.5969 | 86.4205 | 2.5828 | 354.7882 | 0.3521 |
| 0.1 | 7.4541 | 0.5251 | 0.4052 | 1.0872 | 4.7191 | 88.7006 | 2.6519 | 346.6631 | 0.3589 |
| HAS-C | | | | | | | | | |
| 0.01 | 7.7408 | 0.5351 | 0.4205 | 1.0606 | 4.1659 | 78.3135 | 2.3386 | 387.9996 | 0.3256 |
| 0.02 | 7.6939 | 0.5334 | 0.4178 | 1.0647 | 4.2238 | 79.3821 | 2.3713 | 384.3124 | 0.3265 |
| 0.04 | 7.6253 | 0.5311 | 0.4140 | 1.0707 | 4.3395 | 81.5446 | 2.4368 | 373.9707 | 0.3364 |
| 0.06 | 7.5682 | 0.5291 | 0.4125 | 1.0774 | 4.4394 | 83.4516 | 2.4944 | 367.0306 | 0.3303 |
| 0.08 | 7.5353 | 0.5279 | 0.4102 | 1.0800 | 4.5605 | 85.7418 | 2.5624 | 357.4845 | 0.3495 |
| 0.1 | 7.4869 | 0.5262 | 0.4083 | 1.0852 | 4.6661 | 87.7567 | 2.6230 | 350.2944 | 0.3551 |
| HAS-D | | | | | | | | | |
| 0.01 | 7.6781 | 0.5329 | 0.4163 | 1.0654 | 4.1602 | 78.1203 | 2.3352 | 390.9554 | 0.3200 |
| 0.02 | 7.6086 | 0.5305 | 0.4117 | 1.0710 | 4.2142 | 79.0777 | 2.3656 | 386.4777 | 0.3236 |
| 0.04 | 7.5564 | 0.5287 | 0.4094 | 1.0763 | 4.3115 | 80.9148 | 2.4210 | 382.9311 | 0.3183 |
| 0.06 | 7.5015 | 0.5267 | 0.4067 | 1.0817 | 4.4093 | 82.7519 | 2.4766 | 375.7999 | 0.3224 |
| 0.08 | 7.4534 | 0.5250 | 0.4036 | 1.0858 | 4.5140 | 84.7079 | 2.5354 | 367.9300 | 0.3284 |
| 0.1 | 7.3911 | 0.5228 | 0.3998 | 1.0915 | 4.6157 | 86.5921 | 2.5930 | 360.9955 | 0.3332 |
| HAS-E | | | | | | | | | |
| 0.01 | 7.7227 | 0.5344 | 0.4197 | 1.0624 | 4.1496 | 77.9850 | 2.3297 | 391.6160 | 0.3193 |
| 0.02 | 7.6822 | 0.5330 | 0.4182 | 1.0666 | 4.1882 | 78.7071 | 2.3521 | 388.3541 | 0.3217 |
| 0.04 | 7.6263 | 0.5311 | 0.4152 | 1.0716 | 4.2785 | 80.3943 | 2.4032 | 383.3381 | 0.3211 |
| 0.06 | 7.5984 | 0.5301 | 0.4140 | 1.0745 | 4.3675 | 82.0910 | 2.4537 | 376.5802 | 0.3253 |
| 0.08 | 7.5301 | 0.5277 | 0.4102 | 1.0807 | 4.4553 | 83.7143 | 2.5036 | 370.2903 | 0.3295 |
| 0.1 | 7.4927 | 0.5264 | 0.4086 | 1.0847 | 4.5401 | 85.3236 | 2.5519 | 365.8943 | 0.3291 |

association causes an increase in free volume. Thus, free volume is an inverse function of internal pressure. Hence, increase in free volume causes internal pressure to decrease or *vice versa*. However, tables 2 and 3 show that although internal pressure decreases linearly, free volume varies irregularly for different compounds in both DMF and THF. This again confirms the existence of both solute–solute and solute–solvent interactions in these systems.

Further, the apparent molar compressibility ($\phi_k$) and apparent molar volume ($\phi_v$) of the solutions are fitted to Gucker's relation [23] and Masson's equation [24], respectively.

$$\phi_k = \phi_k^\circ + S_k\sqrt{C} \tag{13}$$

$$\phi_v = \phi_v^\circ + S_v\sqrt{C} \tag{14}$$

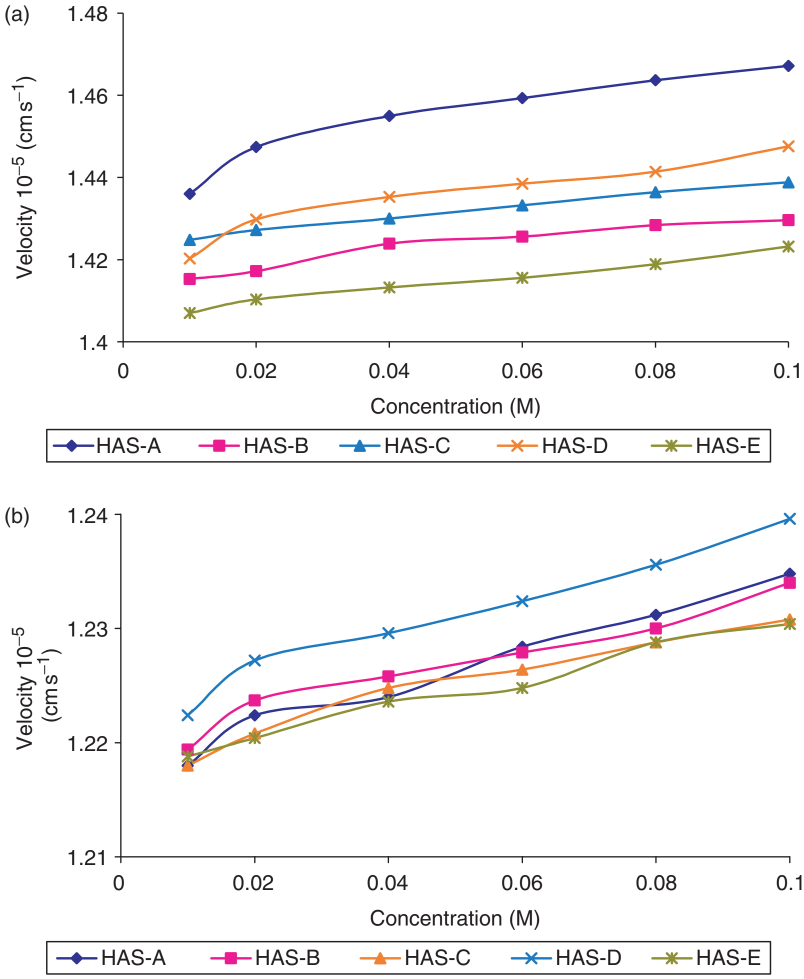

Figure 1. Variation of ultrasonic velocity ($U$) against concentration in DMF (A) and THF (B) at 308.15 K.

From the plot of $\Phi_v$ *versus* $\sqrt{C}$, $\Phi_v^\circ$ and $S_v$ values were calculated from the intercept and slope, respectively. $S_v$ is the measure of solute–solvent interaction. These values of $\Phi_v^\circ$ and $S_v$, along with the Gucker's constants $\Phi_k^\circ$ and $S_k$ are reported in table 4.

Table 4 shows that in $\Phi_k^\circ$ values are positive (except HAS-A) for DMF solutions whereas it is negative for THF solutions. The $S_k$ values are negative (except HAS-A) for DMF solutions whereas it is positive for THF. Positive $\Phi_k^\circ$ values and negative $S_k$ suggest solute–solute interactions as in DMF solutions and negative $\varphi_k^\circ$ and positive $S_k$ indicate solute–solvent interactions.

Thus, in DMF solutions both solute–solvent and solute–solute interactions exist. The predominance of any of these interactions appears in any of the calculated parameters in DMF solutions, as observed in $\Phi_v^\circ$ and $S_v$ values. Whereas in THF solutions, solute–solvent interactions exists. In both DMF and THF solutions, $\varphi_v^\circ$ values are negative and $S_v$ values are positive. The negative $\varphi_v^\circ$ and positive $S_v$ suggest electrostrictive solvation of ions.

Table 4. Various constants of Gucker's and Masson's equations.

| | $\Phi_k^\circ \times 10^8$ | $S_k \times 10^8$ | $\Phi_v^\circ$ | $S_v$ |
|---|---|---|---|---|
| DMF | | | | |
| HAS-A | −1.02 | 0.85 | −462.53 | 1133.10 |
| HAS-B | 9.8 | −40.00 | −111.95 | 158.82 |
| HAS-C | 5.8 | −19.59 | −365.14 | 862.00 |
| HAS-D | 9.1 | −10.00 | −481.99 | 1207.80 |
| HAS-E | 10.6 | 32.13 | −244.74 | 463.66 |
| THF | | | | |
| HAS-A | −3.7 | 5.48 | −171.33 | 574.65 |
| HAS-B | −19.8 | 30.00 | −153.24 | 1122.45 |
| HAS-C | −5.8 | 12.96 | −20.00 | 722.22 |
| HAS-D | −4.95 | 11.75 | −21.77 | 812.58 |
| HAS-E | −8.55 | 14.62 | −60.42 | 307.69 |

The degree of interaction is also measured in terms of solvation number ($S_n$). The solvation number is a measure of structure forming or structure breaking tendency of solute in a solution. The positive $S_n$ values are due to structure forming tendency of solute or *vice versa*. In DMF solutions, for all the Schiff bases, $S_n$ values either decreases or are irregular whereas in THF solutions, $S_n$ values are observed to increase with concentration continuously for all the Schiff bases. These further suggest that solute–solute interactions are also present in DMF solutions.

Thus, both solute–solute and solute–solvent interactions exist in DMF solutions. The velocity, compressibility, intermolecular free length and relaxation strength showed solute–solvent interactions whereas internal pressure, solvation number and $\Phi_k^\circ$ suggest solute–solute interactions. For the evaluation of previous parameters, only density was considered whereas for latter's calculations, molecular weight and viscosity are also considered.

In DMF, there are two lone pair of electrons which may interact differently with different solute molecules. Thus, the dipole–dipole interactions between solute and solvent molecules play an important role in DMF solutions due to which predominance of type of interaction is affected. Thus, overall structure-breaking tendency of triazole derivatives is observed in DMF solutions whereas in THF, structure-forming tendency is observed.

In THF, most of the properties suggest existence of solute–solvent interactions. The solvation number also indicates structure-forming tendency of these triazole derivatives.

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