International Journal of Engineering Research and General Science Volume 5, Issue 4, July-August, 2017
ISSN 2091-2730

Densitometric and Viscometric studies of 2, 4 dioxo pyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO at 298.15 K

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Abstract: Density, Viscosity of 2, 4 dioxo pyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile have been measured in 60% aqueous dimethyl sulphoxide (DMSO) at 298.15 K. From the experimental data the related parameters such as apparent molar volume, limiting apparent molar volume, semi-empirical parameter, Falkenhagen coefficient and Jones Dole coefficient were evaluated. Such parameters gives identification of molecular interactions such as ion-ion, ion-solvent and solvent-solvent.

Keywords: 2, 4 dioxo pyrimidine carbonitrile, 4-oxo-2-thioxo pyrimidine carbonitrile, density, viscosity, aqueous DMSO.

INTRODUCTION: Heterocyclic compounds contains heteroatoms such as oxygen, nitrogen and sulphur. These compounds may be aliphatic or aromatic in nature. Pyrimidine ring system belongs to the most important heterocycles in nature due to many biological significant compounds including nucleosides, nucleotides and biological activity[1-3] such as antiviral, antibacterial, anticancer, antifungal, antioxidant, antimalarial, anti HIV, sedatives, anticonvulsant, antihistamic agent, antihypertensive, anti-inflammatory, anticancer and calcium channel blockers. They are important component of nucleic acids and have been used as building blocks in pharmaceuticals. The study of ion-solvent interactions is very important to understand the nature of different solvents. The parameters like apparent molar volume, density, viscosity, 'A' and 'B' parameters of Jones Dole equation are useful to focus the solute solvent interactions and to understand different biochemical aspects at 298.15 K. The results are interpreted in terms of solute-solvent and solute-solute molecular interactions in these systems. Dimethyl sulphoxide (DMSO) is aprotic and is strongly associated due to highly polar S=O group. It has high miscibility in water and used for dissolving many organic as well as inorganic compounds. The study of DMSO is important because of its application in medicine.[4] It easily penetrates the biological membrane, facilitates chemical transport into biological tissues and is well known to have protective effects in biological systems.[5] It is also used as an inflammatory agent and for cancer treatment.[6] Therefore the unique property of DMSO gives rise to wide use as solvent. Also the drug water molecule interactions and its temperature dependence plays an important role in understanding

drug action[7] i.e. drug reaching the blood stream, its extend of distribution, its binding to the receptor and producing the physiological action.

MATERIAL: 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile were synthesized and purified by recrystallization technique in laboratory.[8-10] Triple distilled deionised water was used for preparation of solution at room temperature in a molar range of 2 x 10^{-3} to 1 x 10^{-3} mol L^{-1}. DMSO used is of analytical reagent grade (AR) of minimum assay of 99.9% obtained from SD Fine Chemicals, Mumbai.

Density measurements: The pycknometer was calibrated by measuring the densities of triple distilled water. The densities of distilled organic liquids like acetone, toluene and carbon tetrachloride were evaluated with respect to density of water.

Viscosity measurement: The solution viscosities were measured by using Ubbelohde viscometer at 298.15 K. The temperature of thermostat was maintained to desired temperature by using demerstat. The flow time was recorded by using digital stop watch. The different concentrations of solution were prepared in 60 % aqueous DMSO.

Data evaluation: The apparent molar volumes, $Ø_v$ were obtained from the following equation[11-14]

$$\Phi V = \frac{1000\ (\ \rho_0 - \rho\ )}{C\ \rho_0} + \frac{M2}{\rho_0}$$

where M_2, C, , ρ_0 and ρ are the molar mass of 2, 4 dioxo pyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile derivatives, concentration (mol. L^{-1}) and densities of the solvent and the solution respectively.

The apparent molar volumes Φv were plotted against the square root of concentration ($C^{1/2}$) in accordance with the Masson's equation[15]

$$\Phi V = \Phi^o_V + S_v\ C^{1/2}$$

where Φ^o_V is the limiting apparent molar volume and S_v is semi empirical parameter or associated constant which depends on the nature of solvent, solute and temperature.

The viscosity results for the aqueous solutions of 2, 4 dioxo pyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile were plotted in accordance with John Dole equation[16]

$$\frac{\eta_r - 1}{C^{1/2}} = A + B\ C^{1/2}$$

Where $\eta_r = (\eta/\eta_o)$ and η, η_o are viscosities of the solution and solvent respectively. C is the molar concentration. The linear plot for $(\eta_r\text{-}1)/C^{1/2}$ vs $C^{1/2}$ were obtained. The intercept (A) coefficient shows solute-solute interaction and the slope (B) reflect the solute-solvent interaction.

Table 1: Densities, molar volumes, viscosities and relative viscosities of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 298.15 K temperature

Densities (ρ) ($g.cm^{-3}$), Apparent molar volumes (Φv) ($cm^3.mol^{-1}$), Viscosities (η) (cP) and Relative Viscosities (η_r)

Compound	Conc mol L^{-1}	ρ	Φv	η	η_r
A-1	**0.002**	1.08925	-2907.7287	3.73009	1.106657
	0.004	1.08968	-1207.8968	3.72981	1.106576
	0.006	1.08978	-898.4166	3.74318	1.110542
	0.008	1.08982	-621.2701	3.74777	1.111902
	0.010	1.08994	-462.3727	3.75297	1.113446
A-2	**0.002**	1.08736	-2112.3182	3.70793	1.100084
	0.004	1.08772	-971.3985	3.71368	1.101791
	0.006	1.08815	-632.6639	3.72071	1.103874
	0.008	1.08893	-503.7138	3.7255	1.105296
	0.010	1.08912	-371.8382	3.73232	1.10732

Table 2: $(\eta_r-1)/C^{1/2}$ and $C^{1/2}$ values of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 298.15 K temperature.

Compound	$C^{1/2}$ mol L^{-1}	$(\eta_r-1)/C^{1/2}$
A-1	**0.04472**	2.38493
	0.06325	1.68513
	0.07746	1.42709
	0.08944	1.25110
	0.10000	1.13446
A-2	**0.04472**	2.23794
	0.06325	1.60945
	0.07746	1.34100
	0.08944	1.17725

	0.10000	1.07320

Table 3: Masson's and Jones-Dole parameters of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 298.15 K temperature.

Compound	Φ^{o}_{V}	S_v	A ($dm^{3/2}mole^{-1/2}$)	B ($dm^{3}mole^{-1}$)
A-1	-4359.2	41876	3.2336	-22.101
A-2	-3179.1	30154	3.0451	-20.772

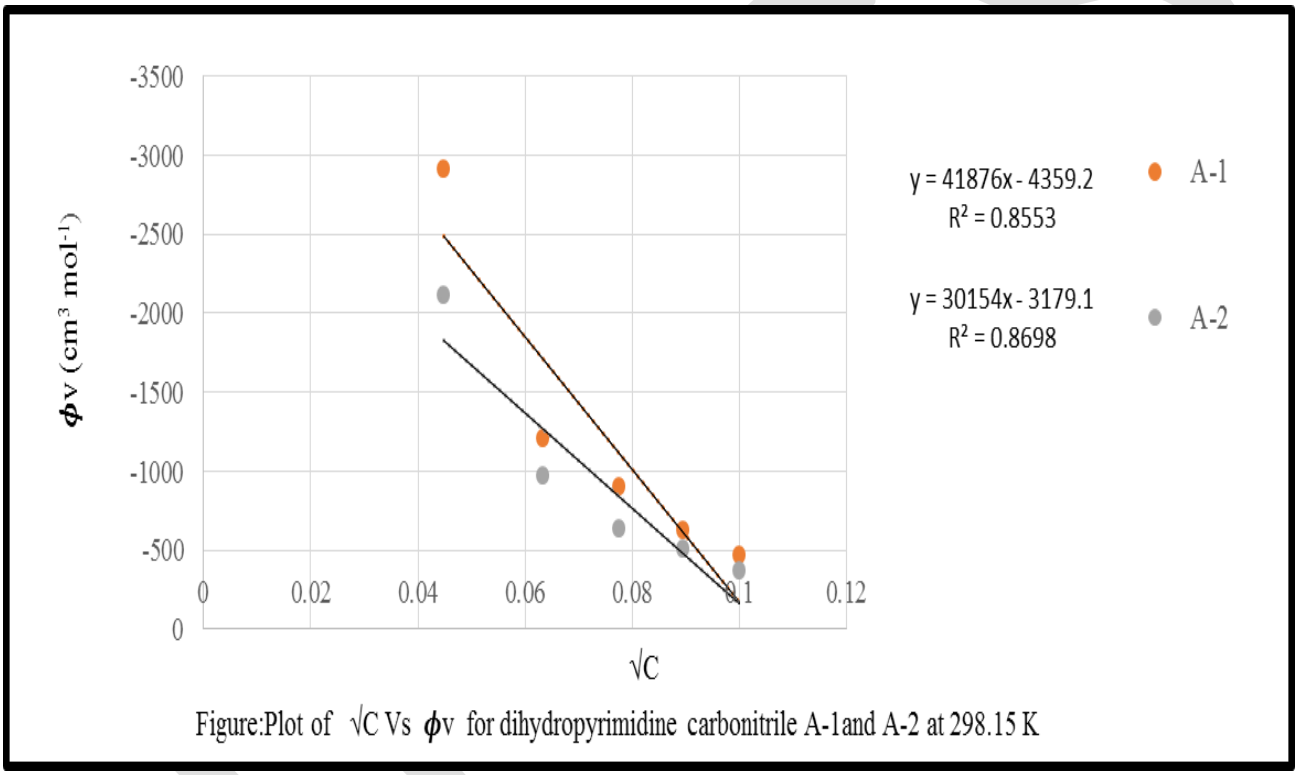
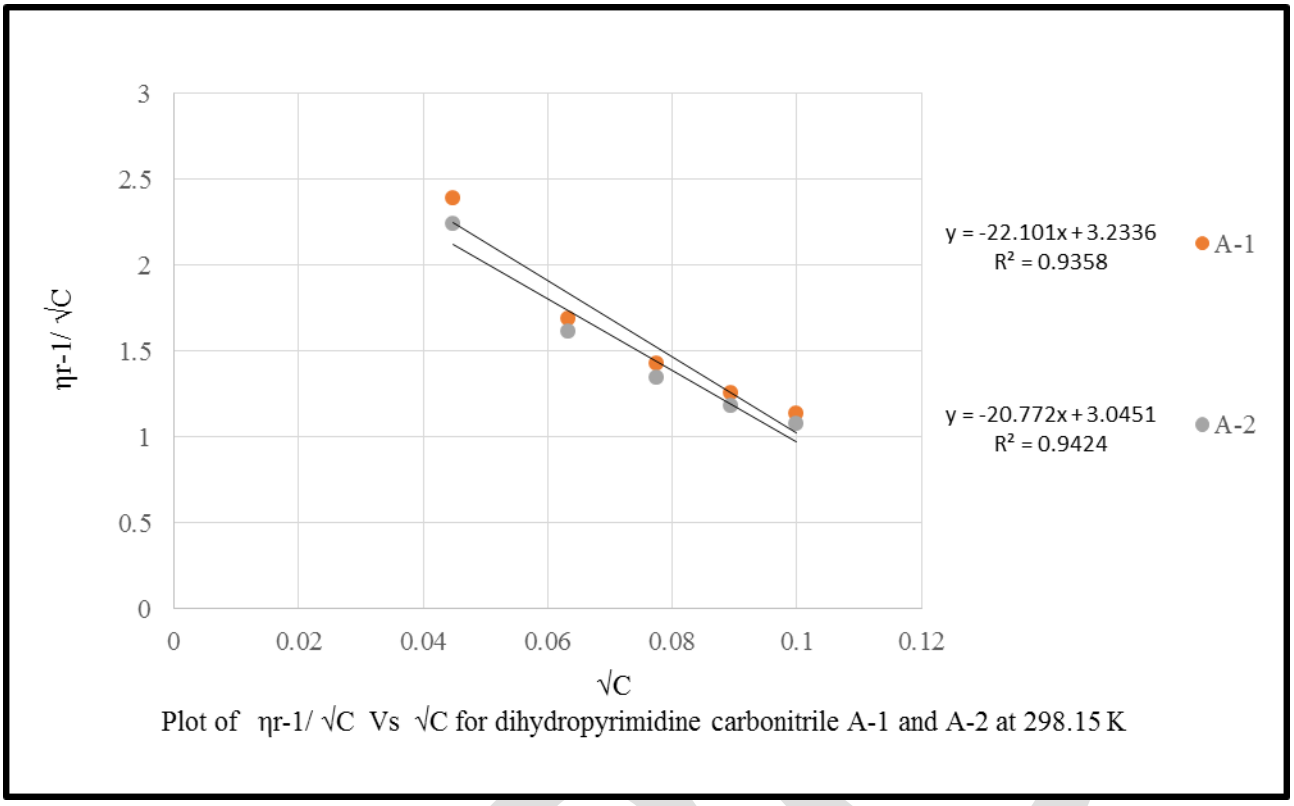


Figure:Plot of √C Vs ϕv for dihydropyrimidine carbonitrile A-1and A-2 at 298.15 K

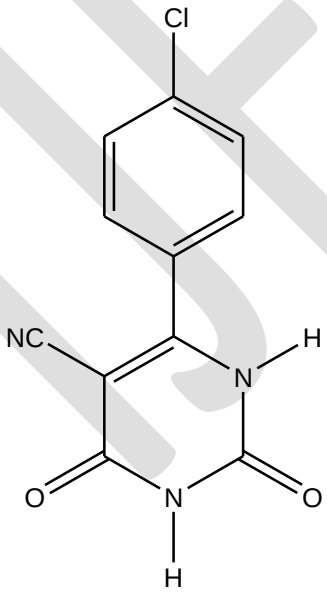
Figure 1: Plot of ϕ_v versus C½ of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 298.15 K temperature.



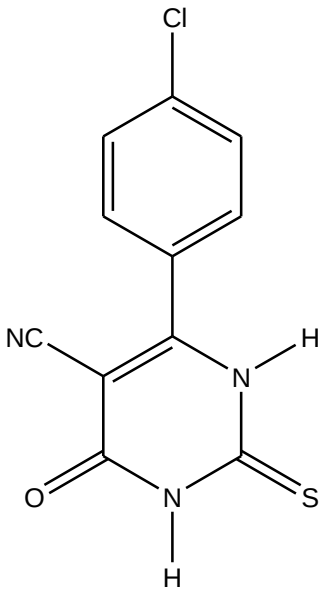
Plot of ηr-1/ √C Vs √C for dihydropyrimidine carbonitrile A-1 and A-2 at 298.15 K

Figure 2: Plot of $(\eta_r-1)/C^{½}$ versus $C^{½}$ of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 298.15 K temperature.

Structure:



A-1



A-2

RESULT AND DISCUSSION: The values of the densities, molar volumes, viscosities and relative viscosities of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 298.15 K

temperature are shown in Table 1. For A-1 and A-2 the densities increases slightly with increase in concentration, Similarly Φv values also increases with increase in concentration. The negative value indicate the electrostrictive salvation of ions. The Φv values are more negative in A-1 as compared to A-2 which suggest that there is strong molecular association in A-2 than A-1 i.e. presence of electrostriction and hydrophilic interaction (solute solvent interactions).

Figure 1 shows linear plots of Φv vs $C^{1/2}$ of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 298.15 K temperature. Masson's parameter Φ^o_V (limiting apparent molar volume) and S_v (experimental slope or semi empirical parameter or associated constant) were obtained from linear plots in Table 3. The values of Φ^o_V are negative shows weak or absence of ion solvent interactions. In other words hydrophobic-hydrophobic group interactions are present. The values of Φ^o_V follow the trend A-1 > A-2. The positive value of S_v indicates the presence of solute-solute interactions. A-1 has high solute-solute interactions than A-2. The viscosities of solution increases with increase in concentration of solution. The value of $(\eta_r-1)/C^{1/2}$ vs $C^{1/2}$ studied at 298.15 K. is shown in Table 2. Figure 2 shows variation of $(\eta_r-1)/C^{1/2}$ against $C^{1/}2$ at 298.15 K. 'A' is constant independent of concentration and represent Falkenhagen coefficient (solute-solute interactions) while 'B' is Jones-Dole coefficient representing measure of order and disorder introduced by solute in solvent (solute-solvent interactions). Positive 'A' coefficient shows strong solute-solute interactions. The Jones-Dole parameters are shown in Table 3. The negative values of 'B' shows weak solute-solvent interactions. The value of 'A' in A-1 are high than A-2 indicates presence of strong solute-solute interactions in A-1 and focuses high electronegativity of oxygen in A-1 which gives rise to strong molecular association as compared to A-2.

CONCLUSIONS: From the present studies we have systematically reported densitometric and viscometric study of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 298.15 K temperature. It has been observed that negative values of (Φv) indicates strong molecular associations. in A-2 as compared to A-1. The values of Φ^o_V are negative which are high in A-1 suggests weak ion-solvent interactions. The value of Jones-Dole coefficient 'B' in A-2 indicates strong interactions between solute and solvent while Falkenhagen coefficient 'A' indicates strong solute-solute interaction in A-1 pointing presence of high electronegativity in oxygen than sulphur. The Jones Dole and Masson's equations are found to be obeyed for study of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution system at 298.15 K temperature.

ACKNOWLEDGEMENT: The authors are thankful to UGC WRO, Pune and BCUD Savitribai Phule Pune University, Maratha Vidya Prasarak Samaj Nashik for providing infrastructure and Principal, K. R. T. Arts B. H. Commerce and A. M. Science College, Gangapur Road, Nashik-422 002, (MS), India for providing the research facilities.

REFERENCES:

1 Clark J., Shahhet M. Korakas D., Varvounis G., 1193. Synthesis of thieno[2,3-D] pyrimidines from 4,6-Dichloropyrimidine-5-carbaldehydes. Heterocyclic Chem., 30, 1065-1072.

2 Ogowva K., Yamawaki I., Matsusita Y., Nomura N., Kador P., Kinoshita J., 1993. Syntheses of substituted 2,4-dioxo-thienopyrimidin-1-acetic acids and their evaluation as aldose reductase inhibitors. Eur. J Med Chem., 28, 769-781.

3 Tozkoparan B., Ertan M., Kelicen P., Demirdar R., 1999. Synthesis and anti-inflammatory

activities of some thiazolo[3,2-a]pyrimidine derivatives. Farmaco, 54, 588-593.

4 Jacob S., Rosenbanm E., Wood D., 1971. Dimethyl Sulphoxide, Marcel Dukker, New York.

5 Lal J., 1995. Exess partial molar enthalpies, entropies, Gibbs energies and volumes in aqueous dimethyl sulphoxide. J. Sol. Chem., 24(1), 89–102.

6 Scaduto R., 1995. Oxidation of DMSO and methanesulfinic acid by hydroxyl radical Free Radical. Biol. Med., 18(2), 271–277.

7 Muhammad J, Chaudhry M., 2009. Thermodynamic study of three pharmacologically significant drugs: density, viscosity and refractive index measurements at different temperatures. J. Chem. Therm., 41, 221-226.

8 Kambe S., Satio K., Kishi H., 1979. A one step synthesis of 4-oxo-2-thioxopyrimidine derivatives by the ternary Condensation of ethyl cyanoacetate, aldehydes and thiourea. Synthesis, 287-289.

9 Patel A., Pasha T., Modi A., 2015. Synthesis and biological evaluation of 4-aryl substituted -2-(5-carboxylicacid-1, 6-dihydro)-2-thiophenylethylene-6-oxo-Pyrimidine as protein tyrosine phosphatase PTP-1B) inhibitors. Inter. J. Phar Tech Res, 8, 136-143.

10 Murthy Y., Saveri L., Parimi A., Naresh S., 2013. $Mg(OMe)_2$ as a versatile catalyst for one po synthesis of 6-aryl-5-cyano-2-(oxo/thio) uracil derivatives and their antimicrobial evaluations. Org Commun., 6(1), 47-54.

11 Das M., Das S. Patnaik A., 2013. Molecular interionic interaction studies of benzimidazolium dichromate and 2 methyl imidazolium dichromate in water and DMSO + Water at different temperatures. J. Phy. Sci., 24(1), 37-50.

12 Sumathi T., Varalakshmi M., 2010. Ultrasonic velocity, density and viscosity measurement of methionine in aqueous Electrolytic solutions at 303k. Rasayan. J. Chem., 3(3), 550-555.

13 Sikarwar S., . Chourey V., Ansari A., 2015. Apparent molar volume and Viscometric study of alcohols in aqueous solution. Inter. J. Chem. Phy. Sci., 4(1), 115-120.

14 Das M., Pradhan S., Das S. Patnaik A., 2015. Density, viscosity and excess parameters of nicotinium dichromate in protic and aprotic solvent media. Der Pharma Chemica., 7(2), 315–322.

15 Chauhan S., Syal V., Chauhan M., Sharma P., 2007. Viscosity studies of some narcotic analgesic drugs in aqueous-alcoholic mixtures at 25°C. J. Mol. Liqs., 136, 161-164

16 Jones G., Dole M., 1929. The viscosity of aqueous solutions of strong electrolytes with special reference to Barium Chloride. J. Am. Chem. Soc., 51, 2950-2964.