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DETERMINATION OF SOLUTE-SOLUTE AND SOLUTE-SOLVENT INTERACTIONS OF 2, 4 DIOXO PYRIMIDINE CARBONITRILE AND 4-OXO-2-THIOXO PYRIMIDINE CARBONITRILE IN 60% AQUEOUS DMSO AT 303.15 K

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Abstract

Solute-solute and solute-solvent interactions of 4-oxo-2-thioxo pyrimidine carbonitriles have been analysed by densitometric and viscometric study in 60% aqueous dimethyl sulphoxide (DMSO) at 303.15 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.

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

Introduction: Compounds possessing heteroatoms such as oxygen, nitrogen and sulphur are coined as heterocyclic compounds which may be aliphatic or aromatic in nature. Pyrimidine ring are such an important heterocyclic compounds in nature due to many biological significant compounds including nucleosides, nucleotides and biological activity[1-13] such as antiviral, antibacterial, anticancer, antifungal, antioxidant, antimalerial, anti HIV, sedatives, anticonvulsant, antihistamic agent, antihypertensive, anti-inflammatory, anticancer and calcium channel blockers. 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 analyzed in terms of solute-solvent and solute-solute molecular interactions in these systems.

Dimethyl sulphoxide (DMSO) is highly aprotic, high miscibility in water and possess strongly associated S=O group. Owing to highly miscibility property it is used for dissolving many organic as well as inorganic compounds. The study of DMSO is important because of its application in medicine.[14] as it easily penetrates the biological membrane, facilitates chemical transport into biological tissues and is well known to have protective effects in biological systems.[15] It is also used as an inflammatory agent and for cancer treatment. Therefore the unique property of DMSO gives rise to wide use as solvent.

Also the drug water molecule interactions and its temperature dependence is applicable for understanding drug action.

Material: 4-oxo-2-thioxo pyrimidine carbonitriles were synthesized and purified by recrystallization technique in laboratory[16-25]. Triple distilled deionized 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 S D 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 303.15 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[26-29]

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

where M_2, C, , ρ_0 and ρ are the molar mass of 4-oxo-2-thioxo pyrimidine carbonitriles 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[30]

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

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 4-oxo-2-thioxo pyrimidine carbonitriles were plotted in accordance with John Dole equation[31]

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

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 4-oxo-2-thioxo pyrimidine carbonitriles in 60 % aqueous DMSO solution at 303.15 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
	0.002	1.08769	-2702.6402	3.11534	1.04153
	0.004	1.08934	-1618.3474	3.12118	1.04348
A-1	**0.006**	1.08978	-1070.4212	3.12845	1.04591
	0.008	1.09089	-873.90762	3.13354	1.04761
	0.010	1.09112	-674.6197	3.13925	1.04952
	0.002	1.08684	-2019.9361	3.08699	1.03205
	0.004	1.08912	-971.3985	3.09328	1.03415
A-2	**0.006**	1.08942	-632.6639	3.09945	1.03622
	0.008	1.09068	-503.7138	3.105	1.03807
	0.010	1.09072	-371.8382	3.11095	1.04006

Table 2: $(\eta_r\text{-}1)/C^{1/2}$ and $C^{1/2}$ values of 4-oxo-2-thioxo pyrimidine carbonitriles in 60 % aqueous DMSO solution at 303.15 K temperature.

Compound	$C^{1/2}$ mol L^{-1}	$(\eta_r\text{-}1)/C^{1/2}$
	0.04472	0.92865
	0.06325	0.68749
A-1	**0.07746**	0.59274
	0.08944	0.53234
	0.10000	0.49522
	0.04472	0.71672
	0.06325	0.54002
A-2	**0.07746**	0.46757
	0.08944	0.42566
	0.10000	0.40061

Table 3: Masson's and Jones-Dole parameters of 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 303.15 K temperature.

Compound	Φ^{o}_{V}	S_v	A ($dm^{3/2}mole^{-1/2}$)	B ($dm^{3}mole^{-1}$)
A-1	-4100.8	36184	1.2246	-7.6998
A-2	-3050.1	28679	0.9323	-5.6314

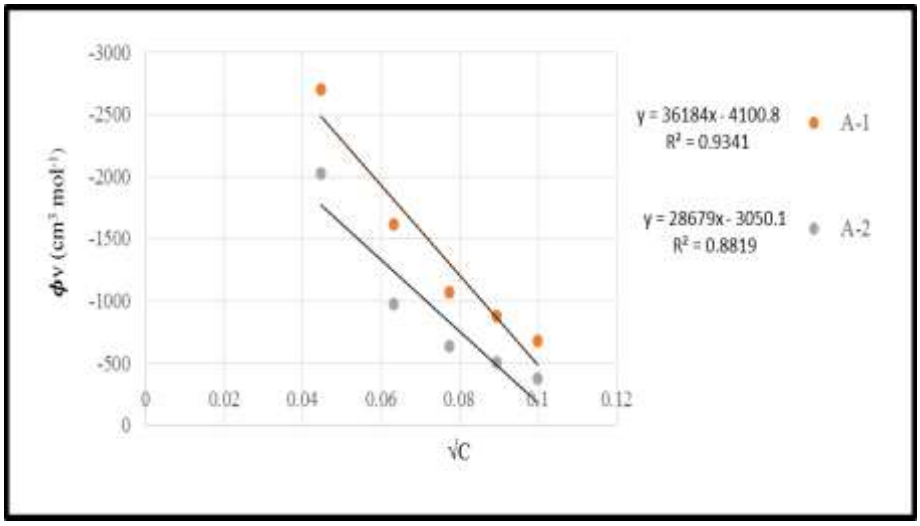


Figure 1: Plot of ϕ_v versus C½ of 4-oxo-2-thioxo pyrimidine carbonitriles in 60 % aqueous DMSO solution at 303.15 K temperature.

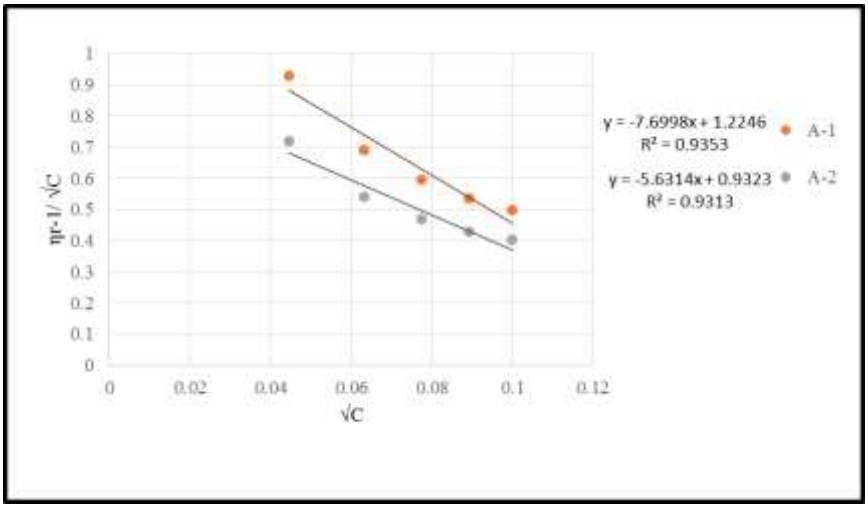
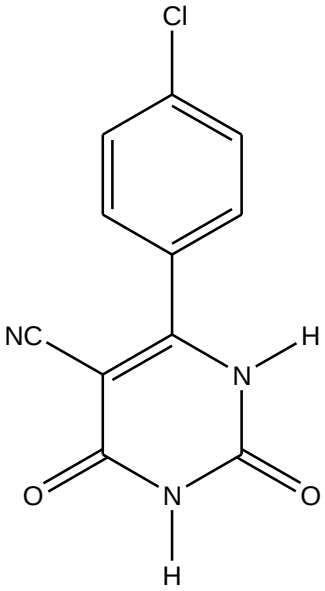
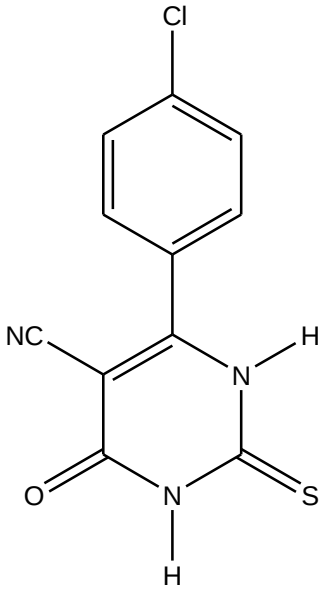


Figure 2: Plot of $(\eta_r-1)/C^{½}$ versus $C^{½}$ of 4-oxo-2-thioxo pyrimidine carbonitriles in 60 % aqueous DMSO solution at 303.15 K temperature.

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 303.15 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 303.15 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 in magnitude. 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 303.15 K. is shown in Table 2. Figure 2 shows variation of $(\eta_r\text{-}1)/C^{1/2}$ against $C^{1/}2$ at 303.15 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 solute-solute and solute-solvent interactions by densitometric and viscometric study of 2,4 dioxopyrimidine carbonitrile and 4-oxo-2-thioxo pyrimidine carbonitrile in 60 % aqueous DMSO solution at 303.15 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 highly negative 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 303.15 K temperature.

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