Volumetric and Viscometric Studies of Nucleosides, Nucleotides and Furanose Sugar in Aqueous Medium from 288.15 to 298.15K

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ABSTRACT: Density ($\rho$/g cm$^{-3}$) and viscosity ($\eta$/$10^{-2}$gcm$^{-1}$s$^{-1}$=1centipoise,CP) of guanosine monophosphate (GMP) and adenosine triphosphate (ATP) referred to as nucleotide, and 2-deoxy adenosine (DOA) and thymidine (TMD) as nucleoside along with their integral furanose sugar, 2-deoxy ribose (DOR) from 0.0004 to 0.0014mol kg$^{-1}$ solution have been measured at 288.15, 293.15 and 298.15K at atmospheric pressure. The $\rho$ was fitted into the Masson and $\eta$ in Jones-Dole equations for apparent molal volume ($V_\phi$/cm$^3$mol$^{-1}$) and viscosity coefficient (($\eta_r$-1)/$m$=B/kg mol$^{-1}$=10$^3$gmol$^{-1}$) data. The $V_\phi$ and $\eta$ were also regressed for $V_\phi^0$ and $\eta^0$ values known as the limiting constants and illustrate solute-solvent and solute-solute interactions of systems. The apparent molal volume of their various integral units like adenine, guanine and thymine of nucleotides and nucleosides are estimated by $V_\phi^0$. The $V_\phi^0$, $\eta^0$ and B values have been used to elucidate the hydrophilic and hydrophobic interactions. The $V_\phi^0$ values are negative over the whole range of the compositions which infer greater intermolecular forces and the biomolecules as water structure breakers.

KEY WORDS: Viscosity, Apparent molal volume, Nucleos(t)ides, Hydrophilic and hydrophobic, Water structure.

INTRODUCTION
Molecular modeling of biomolecules and biopolymers with theoretical and experimental data is becoming thrust area of research [1-3]. The volumetric and viscometric studies of various amino acids and proteins [4-5] in aqueous media along with the role of solvent [6-8] have been used to explain their respective solute-solvent interactions. Notably the enthalpies, heat capacities and apparent molal volume of biomolecules in 1-butanol [2,9,10] and the compressibility of some amino acids by Yayanos et al [11] and Chalikian [12] have been reported. The solute-solvent interactions and the free energy of solvation [13] of proteins in water including the folding and unfolding transitions [14-16] and electrostatic forces based on DLVO (Derjaguin-Landau-Verwey-Overbeek) theory [17] have been found useful. This brief review on biomolecules reveals that despite their known biological properties and functions [18] the thermodynamic and transport properties of DNA and RNA components

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1021-9986/06/1/53 14/$/3.40
namely DOA, DOR, GMP, ATP and TMD have not yet been investigated. Thereby it seems to be an urgent need to design some physico-chemical characterization of their aqueous solutions at variable temperatures. Such studies may give an insight into the folding and unfolding, stabilization, the mechanism of linkages, genetic transformations and energy production in the cell [13-14] and may be an asset in designing proper systems in biotechnology and biosciences. Reportedly Tanford [19], Kauzman [15], Franks [20], Brandts [21], Leach [22], Kierzek [23] and Ladbury [17] have not focused on physico-chemical studies of nucleosides and nucleotides systems. Thereby current studies are assumed to highlight the phenomenon like hydration shell [24,27,28], Van der Waal's forces [19,25,26], denaturation [13,20,29], hydrophobic effects [40,41], electrostriction of solvent [19,25,26] and conformational changes [30,31]. Such conceptual studies are targeted to assess the contribution of the structural aspects [33] of biomolecules. According to Frank and Franks model [33], the functional groups disrupt hydrogen bonding of water structure [34]. Basically the nucleos(t)ide systems are deemed to be of current interests [35,36] for understanding the stability of biomacromolecules [2,37], which could advance the understanding of biopolymer science [33] and medical sciences [38-40]. Such studies of ATP may reveal the role in biological phosphorylation and furnish valuable information [41-45]. The \( \rho \), \( V_\phi \) and \( \eta \) reliably assist the interpretation of the interactions of biomolecules [46-50] with water and other solvents in in-vivo processes [51,52]. The \( V_\phi \) values illustrate intra-and intra-molecular interactions of [37,53-57] biomolecules. The nucleos(t)ides were chosen as model compounds to assess the nonionic backbone contribution to fully hydrated DNA and RNA. This could demonstrate an effect of hydrophilic as well as hydrophobic interactions of side groups [58] like -CH\(_3\) and -CH\(_2\)OH and structure making or breaking effects on water as has been postulated by Franks and Evans [59].

MATERIALS AND PROCEDURE

The 2-deoxyadinosine (Calbiochem, p. no. 2560), 2-deoxyribose (Serva Feinbiochemica, Heidelberg, 18590), and adenosine triphosphate (A-2383) guanosine monophosphate (G-8377) and thymidine (T-9250) were procured from Sigma St Louis, MO, USA. The purity was assured by high-pressure liquid chromatography. The samples were dried in vacuo for 48 hours in a P\(_2\)O\(_5\) filled desiccator. The water used was distilled with KMnO\(_4\) and KOH, degassed by boiling and deionised by passing through Barnstead mixed bed ion-exchanger for solution preparation w/w. The conductivity of water was found to be 1x10\(^{-5}\)\(\Omega\)\(^{-1}\). The density was measured with double-armed pycnometer. The capillaries were vertically fused to the bulb 12mm apart with open ends at the top. The top ends had cone and socketed arrangement with standard glass joint of 5B to avoid the vaporization of the solutions. The weights of empty, solution and solvent filled pycnometer were measured with electronic balance, 0.01mg Dhona, model 100DS for densities. The pycnometer was taken and wiped out to absolute dryness with a tissue paper for weighing.

Viscosity was measured with low shear Ubbelohde viscometer [61]. The flow time noted in thermostat at \( \pm 0.01K \) control noted with electronic racer of 1x10\(^{-2}\) second for viscosity. A Hewlett-Packard quartz thermometer calibrated with a gallium temperature standard measured the bath temperature. The thermostat was kept on the heavy wooden table to avoid the jerks and vibrations and solutions were thermostated for 15-20 min.

The pycnometer was calibrated with aqueous NaCl [60] and viscometer with water at 298.15K. And an accuracy of the concentration of the solutions was better than 1x 10\(^{-5}\) molkg\(^{-1}\). The values 0.99910, 0.99821 and 0.99705gcm\(^{-3}\) for the density of water at 288.15, 293.15 and 298.15K respectively were used. The calibration with NaCl system was repeated immediately before and after each measurement and the reproducibility in the measurements was better than 1x10\(^{-5}\) gcm\(^{-3}\).

RESULTS

The densities (\( \rho \)) and \( \rho_0 \) were calculated from:

\[
\rho = \frac{(W-W_0)/(W_\rho-W_\phi)}{m} = \rho_0 + 0.00121 \left(1-(W-W_\rho)/(W_\rho-W_\phi)\right)
\]

Where \( \rho \) is the solution density, \( \rho_0=\text{density of the solvent and} \ 0.00121(1-(W-W_\rho)/(W_\rho-W_\phi)) \) is the buoyancy correction for air, \( m \) (mol kg\(^{-1}\)) molality, the \( W_\rho \) and \( W \) are weights of empty, solvent and solution filled pycnometer respectively. The error in \( \rho \) values is calculated from weights with reproducibility to 1 part to 1x10\(^{-3}\)g and combination of errors based on the
Table1: Densities (ρ ± 1x10⁻⁵, gcm⁻³) and apparent molal volume (Vφ, cm³mol⁻¹) of aqueous sodium chloride systems.

<table>
<thead>
<tr>
<th>m, mol kg⁻¹</th>
<th>ρ, gcm⁻³</th>
<th>Vφ, cm³mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp.</td>
<td>Lit.</td>
</tr>
<tr>
<td>0.05</td>
<td>0.99968</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>1.00163</td>
<td>1.00116</td>
</tr>
<tr>
<td>0.25</td>
<td>1.00748</td>
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</tr>
<tr>
<td>0.50</td>
<td>1.01723</td>
<td>1.01711</td>
</tr>
<tr>
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<td>1.02698</td>
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<td>1.00</td>
<td>1.03673</td>
<td>1.03630</td>
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<tr>
<td>1.25</td>
<td>1.04648</td>
<td></td>
</tr>
</tbody>
</table>

Lit-Reference: 60

‘propagation of precision indices’ principle. It needs uncertainty in the numerator and denominator of equation.1, which is, calculated with equations (2) and (3).

\[
(W - W_e)/1x10^{-5} + (W_e/1x10^{-5})^2 \approx \pm S_n
\]

\[
(W_0 - W_e)/1x10^{-5} + (W_e/1x10^{-5})^2 \approx \pm S_v
\]

The (± S_n) and (±S_v) are the uncertainties in the weights of solution and solvent and hence an error [61] in ρ is computed from the equation.

\[
\rho(\pm \Delta \rho) = \frac{(W - W_e)(\pm S_n)}{(W_0 - W_e)(\pm S_v)}
\]

Apparent molal volume (Vφ) is calculated from ρ values using the Masson’s[37] equation.

\[
Vφ = 1/\rho [(M - (1000/m).(\rho - \rho_0)/\rho_0)]
\]

Where M is molar mass of solute and the error in Vφ is calculated from equation.

Error in Vφ = ± Δρ1000/m

The data for ρ and Vφ were fitted to polynomial relation with m (molality) as equations (7) and (8).

\[
\rho = \rho^0 + S_d m + S_d' m^2
\]

\[
Vφ = Vφ^0 + S_v m + S_v' m^2
\]

Where \(\rho^0\) and \(Vφ^0\) are the limiting values at m→0 and, \(S_d\) and \(S_v\) are slope constants. The \(\rho\), \(Vφ\) and \(\eta\) are extensive functions and do not explain the solute-solvent interactions, therefore they are least square fitted against molality, m. Likewise \(Vφ^0\) is the limiting value of \(Vφ\) and \(S_v\) slope constants. The \(Vφ^0\) denotes solute-solvent and \(S_v\) solute-solute interactions depending on their nature.

The B (g mol⁻¹) viscosity coefficient and D (g mol⁻¹)² is the slope constant which like \(Vφ^0\), measure the said interactions. The values are given in tables 1 to 6.

The \(Vφ\) values were fitted as :

\[
Vφ = Vφ^0 + S_v m
\]

Where \(Vφ^0\) limit m→0 and \(S_v\) is the slope constant. \(Vφ^0\) is negative and \(S_v\) is positive.

Viscosity \(\eta\) is obtained from \(\rho\) and flow time t with equation.

\[
\eta = (\rho_{sol} \times t_{sol}) \eta_0/(\rho_{solv} \times t_{solv})
\]

(η⁻¹)/m = B + Dm

The relative viscosity (\(\eta_r = \eta/\eta_0\)) values were fitted to Jones- Dole [62] equation.

DISCUSSION

Densities, reproducible to within ±0.05cm³mol⁻¹, of the aqueous NaCl from 0.050 to 1.25mol kg⁻¹ were found in close agreement with the literature [60] (table1), which verifies authenticity of our procedure. Averaged densities found here are found to be higher than those of water by 0.00046, 0.00148 and 0.00097g cm⁻³ at 288.15, 293.15 and 298.15K respectively (table2). Slight decrease in ρ values with temperature for 293.15K reflect reorientation
Table 2: Density ($\rho$), apparent molal volume ($V_\phi$) and viscosity ($\eta$) data of nucleosides, nucleotides and 2-deoxy ribose sugar in water as a function of their composition at three $T/K$. The values written after $\pm$ represent error in the respective functions.

<table>
<thead>
<tr>
<th>Concentration, m, mol kg$^{-1}$</th>
<th>2-deoxy adenosine at 288.15K</th>
<th>293.15K</th>
<th>293.15K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho \pm 10^{-5}$, g cm$^{-3}$</td>
<td>$V_\phi \text{cm}^3\text{mol}^{-1}$</td>
<td>$\eta \pm 10^{-4}$, g cm$^{-1}$ s$^{-1}$</td>
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<tr>
<td>0.0004</td>
<td>0.99977±2.43274</td>
<td>-1398.57±60.82</td>
<td>1.1079±1.41437</td>
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<tr>
<td>0.0014</td>
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<td>-900.50±17.38</td>
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<tr>
<td></td>
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<tr>
<td>2-deoxy ribose at 288.15K</td>
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<td></td>
<td></td>
</tr>
<tr>
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<tr>
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<td>0.99932±2.43199</td>
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<tr>
<td>293.15K</td>
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<tr>
<td>0.0004</td>
<td>0.99825±2.43113</td>
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<td>2-deoxy ribose at 288.15K</td>
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</tr>
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<td>-513.46±17.38</td>
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</tr>
</tbody>
</table>
### Table 2: Continued

#### 293.15K

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Henry's Law Coefficient</th>
<th>Log K</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
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#### 298.15K

<table>
<thead>
<tr>
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#### Guanosine monophosphate at 288.15K

<table>
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<th>Henry's Law Coefficient</th>
<th>Log K</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
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#### 293.15K

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Henry's Law Coefficient</th>
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<th>Temperature (K)</th>
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#### 298.15K

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<tr>
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<th>Temperature (K)</th>
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<tbody>
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</tbody>
</table>
Table 2: Continued

| 0.0008 | 0.99812±2.43113 | -932.96±30.39 | 0.9777±1.41438 |
| 0.0010 | 0.99817±2.43113 | -718.89±24.31 | 0.9799±1.41438 |
| 0.0012 | 0.99821±2.43113 | -562.39±20.26 | 0.9512±1.41438 |
| 0.0014 | 0.99823±2.43113 | -439.74±17.37 | 0.9786±1.41438 |

Adenosine Triphosphate at 288.15K

| 0.0004 | 0.99997±2.43273 | -1630.09±60.82 | 1.1087±1.41437 |
| 0.0006 | 0.99997±2.43273 | -907.48±40.55 | 1.1038±1.41437 |
| 0.0008 | 1.00003±2.43272 | -618.58±30.41 | 1.1040±1.41437 |
| 0.0010 | 1.00010±2.43272 | -450.60±24.33 | 1.1029±1.41437 |
| 0.0012 | 1.00018±2.43272 | -350.82±20.27 | 1.1173±1.41437 |
| 0.0014 | 1.00036±2.43271 | -345.77±17.38 | 1.1082±1.41437 |

293.15K

| 0.0004 | 0.99903±2.43200 | -1507.2±60.80 | 1.0003±1.41405 |
| 0.0006 | 0.99915±2.43200 | -1017.38±40.53 | 0.9994±1.41405 |
| 0.0008 | 0.99928±2.43199 | -793.62±30.40 | 0.9991±1.41405 |
| 0.0010 | 0.99934±2.43199 | -576.80±24.33 | 0.9981±1.41405 |
| 0.0012 | 0.99934±2.43199 | -391.36±20.27 | 0.9973±1.41405 |
| 0.0014 | 0.99942±2.43198 | -317.24±17.37 | 0.9748±1.41405 |

298.15K

| 0.0004 | 0.99825±2.43113 | -2462.80±60.78 | 0.9067±1.41438 |
| 0.0006 | 0.99825±2.43113 | -1463.81±40.52 | 0.8899±1.41438 |
| 0.0008 | 0.99829±2.43113 | -1001.76±30.39 | 0.8990±1.41438 |
| 0.0010 | 0.99830±2.43112 | -707.99±24.31 | 0.8904±1.41438 |
| 0.0012 | 0.99831±2.43112 | -503.20±20.26 | 0.8903±1.41438 |
| 0.0014 | 0.99838±2.43112 | -402.60±17.37 | 0.8892±1.41438 |

Thymidine at 288.15K

| 0.0004 | 0.99986±2.43273 | -1670.57±60.82 | 1.1159±1.41437 |
| 0.0006 | 0.99987±2.43273 | -1044.11±40.55 | 1.1149±1.41437 |
| 0.0008 | 0.99993±2.43273 | -793.26±30.41 | 1.1017±1.41437 |
| 0.0010 | 0.99991±2.43273 | -572.80±24.33 | 1.1145±1.41437 |
of molecular forces that strengthen molecular interactions. The densities of DOA, DOR, GMP, ATP and TMD are higher than that of water by 0.00023, 0.00152, 0.00067, 0.00067 and 0.00069 g cm\(^{-3}\) respectively at around 288.15K and remain constant at other temperatures. It proves that their intermolecular interactions are almost of same strength and DOR causes slightly higher forces. Variation of densities with composition for these systems infers that higher concentrations promote stronger hydrogen bonding between them, resulting in larger intermolecular forces with greater internal pressures on biomolecules. The higher density of DOA with composition in comparison to that of other systems attributed to adenine with free -NH\(_2\) and four N atoms with free deoxyribose. Thus solute-solute interaction with composition of DOR favor stronger hydrogen bond formations. The lower \(\rho\) values of DOR, GMP and ATP than that of TMD prove that their interaction with water can not withstand as of water-water, and infer that thermal changes also contribute to interactions supporting structure-breaking effect of biomolecules by reorientation of molecular forces. An increase in \(\rho\) for TMD system from water by 0.00023 g cm\(^{-3}\) indicates stronger water-TMD interactions than other systems. The DOR density difference at 298.15K is noted higher than of lower temperature by 0.00045 g cm\(^{-3}\) with higher values of TMD. It reveals that biomolecules are more active at this temperature concluding an optimum activity for their smooth functioning at body temperature. Probably it deconfigurizes stronger binding forces of the compounds for DNA and RNA strands with enhancing effect of temperature on intermolecular forces. Similarly a decrease in density of water at around 288.15 and 293.15K is found to be 0.00089 and for DOA 0.00016 g cm\(^{-3}\), it proves temperature causes a more efficient effect on water structure breaking than of DOA system. This effect consistent with DOA, DOR, GMP, ATP and TMD inferring stronger intermolecular forces between water and them than of water molecules themselves. It is possible, the polar centers of the biomolecules generate stronger dipolar forces that resist the thermal forces more than water. Additionally such

### Table 2: Continued

<table>
<thead>
<tr>
<th>(\rho)</th>
<th>(\gamma^{(0)})</th>
<th>(\eta)</th>
<th>(\Delta H_{\text{vap}})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.1020±1.41437</td>
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<tr>
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</table>

293.15K

<table>
<thead>
<tr>
<th>(\rho)</th>
<th>(\gamma^{(0)})</th>
<th>(\eta)</th>
<th>(\Delta H_{\text{vap}})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.0071±1.41405</td>
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<tr>
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<td>0.9736±1.41405</td>
</tr>
<tr>
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<td>1.0047±1.41405</td>
</tr>
<tr>
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<td>1.0197±1.41405</td>
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298.15K

<table>
<thead>
<tr>
<th>(\rho)</th>
<th>(\gamma^{(0)})</th>
<th>(\eta)</th>
<th>(\Delta H_{\text{vap}})</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-1839.94±60.78</td>
<td>0.8926±1.41438</td>
</tr>
<tr>
<td>0.0006</td>
<td>0.99787±2.43115</td>
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<td>0.8936±1.41438</td>
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<td>0.99792±2.43114</td>
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<td>0.8952±1.41438</td>
</tr>
</tbody>
</table>
interactions can also be credited to the geometry of nucleosides and nucleotides where water dipoles get interacted with their polar centers; while DOR causes negligible effect on hydrogen bonds of water (Fig. 1). Probably two oxygen atoms of pyrimidine ring attached to ribose sugar of TMD cause stronger hydrophilic interactions with water. And $\text{PO}_4^{-3}$ group of GMP and ATP reduces intermolecular forces, decreasing $V_\phi$ by -1800 for DOA, 500 for DOR, 300 cm$^3$ mol$^{-1}$ for TMD at each temperature. Hence $\text{PO}_4^{-3}$ induces slightly stronger intermolecular forces in solutions, contrary to this, three $\text{PO}_4^{-3}$ groups along with sugar pucker and purine ring have been noticed to generate slightly higher density values. Thus larger are the numbers of $\text{PO}_4^{-3}$ groups, stronger are the intermolecular forces, although DOR produces higher values than DOA by about 0.00003 g cm$^{-3}$. It predicts that at 288.15K, the $\text{PO}_4^{-3}$ decreases densities proportional to number of $\text{PO}_4^{-3}$ group. The trend of densities of the systems at 293.15K denotes that sugar unit causes stronger intermolecular forces due to O atoms and OH$^-$ groups with stronger hydrophilic interactions. Similarly $V_\phi^0$ is found as DOA > TMD > DOR > ATP > GMP at 288.15K inferring slightly weaker interactions of DOA than other temperatures with stronger intermolecular forces for GMP (table 4). Negative $V_\phi^0$ values proclaim exceptionally very stronger interactions between solute–solvent systems, mathematically $(1000/m)(\rho-\rho_0)/(\rho_0)$ term determines the magnitude of $V_\phi$. If 1000/m term remains constant for an individual composition even though $(\rho-\rho_0)/\rho_0$ term should be fixed. If solute-solvent interactions are stronger than of system, it would produce higher $\rho$ than $\rho_0$ and $(1000/m)$ $(\rho-\rho_0)/(\rho_0)$ term gives positive values (see equation (7)). Molecular weights of our compounds are between 269.1 to 551.1 g mol$^{-1}$ which on dividing by $\rho$, gives lower numerical values than of the number obtained on evaluating $(1000/m)(\rho-\rho_0)/(\rho_0)$ term. So negative $V_\phi$ values describe intermolecular forces operating on the interactions thus an actual shrinkage [63] in $V_\phi$ depends upon attraction for water molecules resulting a stronger compaction i.e. greater than their own values of volume. An existence of negative $V_\phi$ tends to emphasize that excess molal volume is coefficient of the systems. The $V_\phi$ and intrinsic viscosity coefficient ($B$) data (tables 4 and 5) support the interactions of water with DOA, so $V_\phi^0$ and $B$ are static and transport properties respectively. These values predict that behavior of $\text{PO}_4^{-3}$ is exceptional vis-a-vis ATP and GMP with temperature. It highlights effect of thermal energy that plays a crucial role by influencing $\text{PO}_4^{-3}$–water interactions; the $\text{PO}_4^{-3}$ may introduce an element of asymmetry that perhaps pushes the molecules to attain a stable optimization. Flickering model of water facilitates to surround and adhere to $\text{PO}_4^{-3}$ for stable conformation, thus $V_\phi^0$ and $B$ values are complementary to each other supporting their trends with temperatures. The DOA and DOR molecules without $\text{PO}_4^{-3}$ fairly match the trends of $V_\phi^0$ and $B$ values, and their hydrophilic interactions might be prominent, as DOR contains only sugar part and DOA has purine base + sugar unit. Likewise, TMD contains pyrimidine ring with electron deficient methyl (-CH$_3$) group that tends to cause some deviations in intermolecular interactions due to hydrophobic in nature. Viscosity values for biomolecules are found lower than water at 288.15 by 0.0012CP but higher than water by 0.0039CP at 293.15 and 298.15K. The $\eta^0$ values are found as TMD > DOR > GMP > DOA> ATP; GMP > DOR > ATP > DOA > TMD and GMP > DOR > ATP > TMD > DOA at 288.15, 293.15 and 298.15K respectively. These order of values proliferate the state of Newtonian force with temperature.

The $\eta^0$ values at 288.15K have been found lower than water by 0.0229 to 0.0376CP, with rise in temperature by 5$,^\circ$C, the $\eta^0$ is found higher than water by 0.0052 to 0.0211$\eta$CP (tables 4 and 5) which are close to the values of 298.15K. It illustrates their structure breaking capacity, which increases with temperature. The $\eta^0$ values are in order of TMD > DOR by 0.005, DOR > GMP by 0.0014, GMP > DOA by 0.0021 and DOA > ATP by 0.0062CP at 288.15K. At 293.15K, the $\eta^0$ values of the systems were found to be GMP > DOR by 0.0378CP, DOR > ATP by 0.0042, ATP > DOA by 0.0091 and DOA > TMD by 0.0172CP. At 298.15K, GMP > DOR by 0.0064, DOR > ATP by 0.0698, ATP > TMD by 0.0156 and TMD > DOA by 0.0002CP. These values support the water structure breaking capacity of these systems,with an order of $B$ values in sequence of TMD > DOR > GMP > DOA > ATP, GMP > DOR > ATP > DOA > TMD and GMP > DOR > ATP > TMD > DOA at 288.15, 293.15 and at 298.15K respectively. This highlight that broken water resists free flow causing torsional forces of high degree with uniform forces applied on viscous flow. It predicts...
Fig. 1: The structures of the nucleoside and nucleotide and their subunits for evaluation of limiting apparent molal volumes.
Fig. 1: Continued
Table 3: Limiting density ($\rho_0$) and apparent molal volumes ($V_0^\ddagger$) along with their slope constants $S_\rho$ and $S_v$ and $S_v'$, respectively obtained on regression of the data as a function of temperature $T/K$.

The values written after ± represent error in the respective functions.

<table>
<thead>
<tr>
<th>Temperature (T/K)</th>
<th>$\rho_0$±10^{-3} g cm^{-3}</th>
<th>$S_\rho$±10^{-2} g cm^{-3} mol^{-1}</th>
<th>$V_0^\ddagger$</th>
<th>$S_v$±10^{-2}, (10^3 g cm^{-1} mol^{-1})$</th>
<th>$S_v'$±10^{-2}, (10^3 g cm^{-1} mol^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>0.99933</td>
<td>1.0152±5</td>
<td>-1839.18±103.24</td>
<td>15.24±129954</td>
<td>-6.28±5</td>
</tr>
<tr>
<td>293.15</td>
<td>0.99917</td>
<td>0.1630±80</td>
<td>-3935.18±103.21</td>
<td>50.15±129913</td>
<td>-18.94±5</td>
</tr>
<tr>
<td>298.15</td>
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<td>0.1848±90</td>
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<tr>
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<tr>
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<td>-15.17±5</td>
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<td>293.15</td>
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<td>43.13±129868</td>
<td>-16.36±5</td>
</tr>
</tbody>
</table>

Table 4: Limiting viscosity ($\eta_0$) and slope constant ($S_v$) obtained by least square fit of $\eta$ data against molality. Intrinsic viscosity ($B = (\eta_0-1)/m$ vs $m, m\to0$) and slope constants $D$ and $D'$. The $\eta\text{ kg m}^{-1}\text{s}^{-1}=10^3\text{ g x 10}^3\text{ cm}^2\text{s}^{-1}$ 10g cm$^{-1}$s$^{-1}$. The values written after ± represent error in the respective functions.

<table>
<thead>
<tr>
<th>Temperature (T/K)</th>
<th>$\eta_0$±10^{-3} 10^-3 cm^2 s^-1</th>
<th>$S_v$±10^{-2} 10^-3 cm^2 s^-1 mol^-1</th>
<th>$B$, 10^3 g mol^-1</th>
<th>$D$, 10^3 g mol^-1</th>
<th>$D'$(10^3 g mol^-1)x10^3</th>
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</table>
Table 5: The \( \rho_0(T) \), \( V_0^\varphi(T) \), \( \eta_0(T) \) and \( B(T) \) functions when \( T \to 0 \) of the aqueous solution systems.

<table>
<thead>
<tr>
<th>Systems</th>
<th>( \rho_0 ), g cm(^{-3} )</th>
<th>( V_0^\varphi(T) ), cm(^3) mol(^{-1} ), (10^6)</th>
<th>( \eta_0 ), 10 g cm(^{-1}) s(^{-1} )</th>
<th>( B ), 10(^3) g mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-deoxy adenosine</td>
<td>1.03290</td>
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<td>-204110</td>
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<tr>
<td>2-deoxy ribose</td>
<td>1.04696</td>
<td>10.00</td>
<td>5.0307</td>
<td>281488</td>
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<tr>
<td>Guanosine monophosphate</td>
<td>1.05133</td>
<td>3.00</td>
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<tr>
<td>Adenosine triphosphate</td>
<td>1.05388</td>
<td>-5.00</td>
<td>6.7646</td>
<td>54655</td>
</tr>
<tr>
<td>Thymidine</td>
<td>1.05515</td>
<td>1.00</td>
<td>7.6438</td>
<td>-322711</td>
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</tbody>
</table>

Table 6: The molar volume contribution of adenine, guanine, thymine, Guanosine, phosphate and comparative estimation of \(-\text{CH}_3\) and imidazole ring for nucleoside and nucleotide molecules.

<table>
<thead>
<tr>
<th>Simulations of ( V^\varphi_0 ) of molecules</th>
<th>T/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V^\varphi_0 ) Adenine = ( V^\varphi_0 ) (2-deoxy adenosine - 2-deoxy ribose)</td>
<td>288.15K, 293.15K, 298.15K</td>
</tr>
<tr>
<td>( V^\varphi_0 ) 3P = ( V^\varphi_0 ) (Adenosine triphosphate - 2-deoxy adenosine)</td>
<td>-1285.69, 1442.59, 166.19</td>
</tr>
<tr>
<td>( V^\varphi_0 ) 1P = ( V^\varphi_0 ) (3Phosphate/3)</td>
<td>-428.56, 480.86, 55.39</td>
</tr>
<tr>
<td>( V^\varphi_0 ) Guanine = ( V^\varphi_0 ) (Guanosine monophosphate – (ribose +1phosphat))</td>
<td>-189.17, 2690.19, 492.99</td>
</tr>
<tr>
<td>( V^\varphi_0 ) Ribose = ( V^\varphi_0 ) (Adenosine triphosphate-(adenine+3 phosphate))</td>
<td>-2666.85, -5954.83, -4411.37</td>
</tr>
<tr>
<td>( V^\varphi_0 ) Thymine = ( V^\varphi_0 ) (Thymidine-Ribose)</td>
<td>-266.71, 2524.37, 1163.96</td>
</tr>
<tr>
<td>( V^\varphi_0 ) Guanosine= ( V^\varphi_0 ) (Guanosine monophosphate-1 phosphate)</td>
<td>-2856.02, -3264.64, -8163.56</td>
</tr>
</tbody>
</table>

that the well-structured water behaves like a laminar or Newtonian flow in the microcapillary and all molecules seem to move along with each other as per cage model of water. The viscosity results prove that later behave as water structure breaker but with the nucleotides and nucleosides due to lower values of viscosity seem to exhibit water structure breaking character.

An apparent contradiction in trends of \( V_0^\varphi \), \( B \) and \( \rho \) values is resolved due to Newtonian flow taken into account for water with its less density than the solution. It shows that the centripetal forces of water are functional in causing compactness with reduction in volume. It is rationalized to dipole-dipole interactions breaking down the water structure generating stronger water-nucleos(t)ides molecular interactions. Thus viscous flow of solutions maintains long range arrangement in heteromolecular forces, like water structure with less decrease in \( B \) value with temperature. The \( B \) values are listed as \( \text{TMD} > \text{ATP} > \text{DOA} > \text{GMP} > \text{DOR} \) and \( \text{DOR} > \text{GMP} > \text{ATP} > \text{TMD} > \text{DOA} \) at 288.15, 293.15 and 298.15K (tables 4 and 5). Thus temperature supports structure-breaking action enhancing intermolecular forces with negligible effect on hydrogen bonds formed between nucleosides-water, nucleotides-water. It seems that the torsional forces in water are higher than systems and \( B \) values reveals that the flow time of water is more than of aqueous biomolecules due to weakening of hydrogen bonds. Thus bulk water breaks into monomer so flow time increase and negative coefficient \( B \) infers weaker intermolecular forces while for positive values the stronger. Like cyclodextrins where an inner cavity is reported to be hydrophobic \[64\] and \( \text{DOR} \) seems to be similar in behavior having hydrophilic outer surface and hydrophobic inner cavity. So the key-lock interactions are partly occur and determined by the hydrophilic interactions due to oxygen atom in \( \text{DOR} \) seem to create some hydrophilic environment as outer. It is
expected from the data that the hydrophilic interactions with approximately same magnitude would dominate in comparison to the hydrophobic. Thus interactions that are important for all nucleos(t)ides have hydrogen bonding between them and charge repulsion at the negatively charged phosphoribose backbone. The calculated \( V_0 \) of their integral units like Adenine, Ribose, Guanine and Thymine and PO\(_4\)-3 groups exerted an internal pressure towards the molecules have been computed as given in table 6. Logically calculation of \( V_0 \) values of integral units from the structures illustrated in Fig. 1 and contribution of common structural units for \( V_0 \) which is nullified by deducting the values of respective units. The \( V_0 \) values of single PO\(_4\)-3 group are calculated from the values of three PO\(_4\)-3 to assess their contribution. The \( V_0 \) values of three Phosphate units of ATP is found greater when they are attached with ribose sugar than in GMP. It proves that larger are the PO\(_4\)-3 units higher are the forces with the nucleotides to bind the PO\(_4\)-3 units. The \( V_0 \) values listed as TMD > ATP > GMP, reveal that GMP has stronger intermolecular forces due to Guanosine unit. Thus for GMP, it gives slightly larger shrinkage in the volume and proves that the PO\(_4\)-3 and the units attached with the purine unit cause comparatively stronger intermolecular interaction at 293.15K.

**Conclusion**

The density, volume and viscosity data of that occur biomolecules seem to be useful tools for elucidating the structural modifications in solutions. The water structure breaking is notable in weakening bulk water resistance along their shear on flow. The trends of the \( V_0 \) values with temperature signify the role of thermal energy in reorienting the interaction forces. Especially at 293.15K, the ATP develops the weakest forces while thymidine does stronger but at 288.15K, the thymidine forces become weaker. Here ribose unit seems to be sandwiched at the center of hydrophilic interactions.

**Acknowledgement**

The authors are thankful to the Department of Science and Technology, Government of India, for financial support.

Received: 13th June 2006; Accepted: 24th September 2005

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