INTRODUCTION

The molecular interactions of the solvent with non-ionic and ionic solute play an important role in governing the physico-chemical behavior of interactions present in solution. The role of viscosity has gained the attention of several workers in characterizing the molecular interactions in aqueous and non-aqueous solution during the past decade [1-10]. There are several reports on the properties of perchloric acid which includes spectroscopic, analytical and physical methods [11-15]. The dependence of viscosity of aqueous perchloric acid on concentration has been reported [16]. The effect of acid on catalyzed reactions has also been reported [17]. In water for alkali perchlorates revealed that the ionic association increased with increasing the cationic size of any anion due to the effect of solvation on ion pairing [18].

The effect of solute on the structure of water has been discussed [19]. The role of water in chemical process is closely related to the hydration of reacting species, molecules or free radicals. The information regarding the structure of hydration shell of ions has been studied with the help of diffraction measurements and molecular dynamic computation. Different workers concerned the structure and dynamics of hydrated ions [20-22]. Solute induced modification in the water structure have been studied by many workers [23-25].

For an ionic solute, two types of characters has been defined namely structure maker or structure breaker on the basis of their ability to increase or decrease water structure. From conductance measurements of perchlorates in methanol solution, the structural modification of water has been investigated [26]. In order to observe the structural modification of water on adding perchloric acid, the present study was undertaken.

EXPERIMENTAL

The perchloric acid used was of ExcelaR grade. Doubly distilled water was used to prepare solutions of the acid. The strength of each solution was checked by titrating it against a standard solution of sodium hydroxide (98%) using phenolphthalein as an indicator. The viscosity measurements were taken in a calibrated suspended-level viscometer (Infusil India Pvt. Ltd.) having number BG43500 size 2 and BG43499 size 1. The viscometer was placed in a thermostated water bath (Tanco) having accuracy ± 0.1 K for constant temperature. The solution of perchloric acid of known concentration was taken in the viscometer and the flow time of solution was measured. The densities of solutions were measured using a 15 mL double arm pyknometer having accuracy ± 0.00001 g/mL.

RESULTS AND DISCUSSION

The viscosity (η) of a solution is a function of concentration and temperature. To visualize the actual relationship between the concentrations of perchloric acid 1.0 to 9.0 mol dm$^{-3}$ and the viscosity at 283.65 K. The plot between concentration and viscosity has approximately linear nature (Fig.1) ($R^2 = 0.84$) but there is a deviation in the curve in the concentration region 4.0 to 6.0 mol dm$^{-3}$ with major deviation at concentration 1.0 and 9.0 mol dm$^{-3}$. Such variation was also observed in reported values of viscosities [27,28].

To determine the interaction parameters in perchloric acid-water system, Jones-Dole equation was used which is expressed in eqn. 1:

$$\frac{\eta}{\eta_0} - 1 = A + B c^{0.5}$$

(1)
where $\eta/\eta_0$ is relative viscosity, $\eta$ is viscosity of solution, $\eta_0$ is viscosity of solvent, $A$ is a constant (A-coefficient) which is the measure of solute-solute interaction; $B$ is a constant (B-coefficient) which is the measure of solute-solvent interaction [29,30] and $c$ is the concentration of HClO$_4$ (Table-1). Jones-Dole equation and $dB/dT$ values. The results thus obtained for the study satisfies the validity of Jones-Dole equation in the field of solution chemistry.

The effect of temperatures on the viscosity of solution is well known, the viscosity decreases as temperature increases. The viscosities at 297.65 K for aqueous perchloric acid 1.0 to 9.0 mol dm$^{-3}$ has been considered in the study. The effect of temperatures on viscosity of solution is well known, the viscosity decreases as temperature increases. The viscosities at 297.65 K for aqueous perchloric acid 1.0 to 9.0 mol dm$^{-3}$ has been reported [28]. It has been emphasized by number of workers that $dB/dT$ is a better criteria for determining the structure-making and breaking tendency of any electrolyte rather than simply the B-coefficient [30-33]. The negative sign of $dB/dT$ represent a structure making effect on water structure while the positive sign represent a structure breaking effect on water structure [34,35]. The viscosity B-coefficients of aqueous perchloric acid obtained at 283.65 K were compared with the reported data [28]. It is clear from Table-2 that the viscosity B-coefficient decreases with increase in temperature. This indicates that $dB/dT$ possesses negative sign thereby perchloric acid has a structure making effect on water structure. The structure making character is in agreement with the positive values of B-coefficient as obtained from Jones-Dole equation.

### TABLE-1

<table>
<thead>
<tr>
<th>Concentration (mol dm$^{-3}$)</th>
<th>$\eta$ (cP)</th>
<th>$c^{1/2}$ (mol$^{1/2}$ dm$^{-3/2}$)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\eta/\eta_0$</th>
<th>$(\eta/\eta_0 - 1)c^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.284</td>
<td>1.000</td>
<td>1.041</td>
<td>0.985</td>
<td>-0.014</td>
</tr>
<tr>
<td>2.0</td>
<td>1.311</td>
<td>1.141</td>
<td>1.101</td>
<td>1.005</td>
<td>0.003</td>
</tr>
<tr>
<td>3.0</td>
<td>1.427</td>
<td>1.732</td>
<td>1.173</td>
<td>1.094</td>
<td>0.055</td>
</tr>
<tr>
<td>4.0</td>
<td>1.475</td>
<td>2.000</td>
<td>1.225</td>
<td>1.131</td>
<td>0.065</td>
</tr>
<tr>
<td>5.0</td>
<td>1.724</td>
<td>2.236</td>
<td>1.303</td>
<td>1.322</td>
<td>0.144</td>
</tr>
<tr>
<td>6.0</td>
<td>1.910</td>
<td>2.345</td>
<td>1.328</td>
<td>1.465</td>
<td>0.199</td>
</tr>
<tr>
<td>7.0</td>
<td>2.183</td>
<td>2.449</td>
<td>1.369</td>
<td>1.674</td>
<td>0.276</td>
</tr>
<tr>
<td>8.0</td>
<td>2.621</td>
<td>2.645</td>
<td>1.423</td>
<td>2.010</td>
<td>0.382</td>
</tr>
<tr>
<td>9.0</td>
<td>3.232</td>
<td>2.828</td>
<td>1.464</td>
<td>2.479</td>
<td>0.524</td>
</tr>
<tr>
<td>1.0 to 4.0 mol dm$^{-3}$ (B = 0.106 dm$^{-3/2}$ mol$^{-1}$, A = -0.141); 4.0 to 6.0 mol dm$^{-3}$ (B = 0.461 dm$^{-3/2}$ mol$^{-1}$, A = -0.867); 6.0 to 9.0 mol dm$^{-3}$ (B = 0.804 dm$^{-3/2}$ mol$^{-1}$, A = -1.714)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE-2

<table>
<thead>
<tr>
<th>Concentration range (mol dm$^{-3}$)</th>
<th>B-coefficient (dm$^{-3/2}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283.65 K</td>
<td>297.65 K</td>
</tr>
<tr>
<td>1.0 to 4.0</td>
<td>0.106</td>
</tr>
<tr>
<td>4.0 to 6.0</td>
<td>0.461</td>
</tr>
<tr>
<td>6.0 to 9.0</td>
<td>0.804</td>
</tr>
</tbody>
</table>

### Conclusion

The structure making effect of aqueous concentrated perchloric acid has been proposed which is in agreement with Jones-Dole equation and $dB/dT$ values. The results thus obtained in the study satisfies the validity of Jones-Dole equation in three different concentration regions. These results show that the study can be used as a model for other solvent systems in the field of solution chemistry.

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REFERENCES


