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Effect of Temperature and Concentration on the Viscosity of Perchloric Acid

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In the present study, the effect of concentration and temperature on the viscosities of aqueous solution of perchloric acid is discussed. The experiments were done at 283.65 and 297.65 K. The three concentration regions in perchloric acid-water system have been identified from Jones-Dole viscosity equation and the positive value of B-coefficient indicates strong ion-solvent interaction or water structure making character. The effect of temperature on viscosity B-coefficient confirms that perchloric acid have water structure making character.

Keywords: Perchloric acid, Jones-Dole equation, B-coefficient.

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, ions 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:

$$(\eta/\eta_0 - 1)\, c^{-0.5} = A + B\, c^{0.5} \quad (1)$$

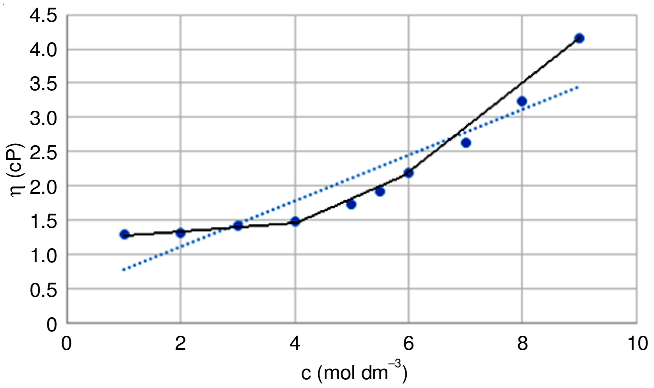

Fig. 1. Variation of viscosity of aqueous perchloric acid with concentration at 283.65 K

where η/η_o is relative viscosity, η is viscosity of solution, η_o 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 plot for aqueous perchloric acid at 283.65 K is given in Fig. 2.

TABLE-1
VARIATION OF VISCOSITY (η) AND DENSITY (ρ) OF AQUEOUS PERCHLORIC ACID WITH INCREASING CONCENTRATION AT 283.65 K

c (mol dm^{-3})	η (cP)	$c^{0.5}$ (mol$^{1/2}$ dm$^{-3/2}$)	ρ (g cm^{-3})	η/η_0	$(\eta/\eta_0\text{-}1)c^{-05}$
1.0	1.284	1.000	1.041	0.985	–0.014
2.0	1.311	1.414	1.101	1.005	0.003
3.0	1.427	1.732	1.173	1.094	0.055
4.0	1.475	2.000	1.225	1.131	0.065
5.0	1.724	2.236	1.303	1.322	0.144
5.5	1.910	2.345	1.328	1.465	0.199
6.0	2.183	2.449	1.369	1.674	0.276
7.0	2.621	2.645	1.423	2.010	0.382
8.0	3.232	2.828	1.464	2.479	0.524
9.0	4.160	3.000	1.569	3.190	0.730

1.0 to 4.0 mol dm^{-3} (B = 0.106d m$^{-3/2}$ 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)

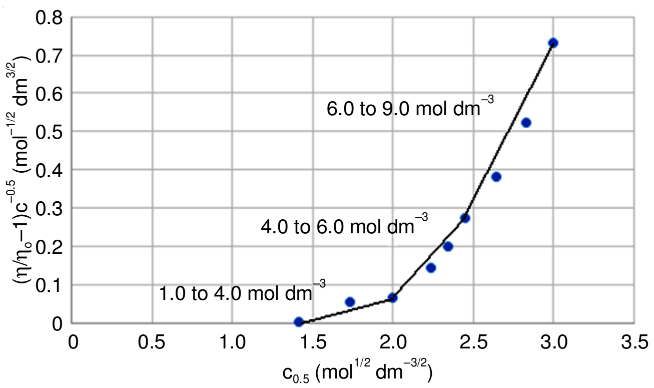

Fig. 2. Jones-Dole plot for 1.0 to 9.0 mol dm^{-3} aqueous perchloric acid at 283.65 K

On comparison of the gradients calculated with the help of computer clearly indicates that there exist three perchloric acid-water systems in the concentration range 1.0 mol dm^{-3} to 9.0 mol dm^{-3} (Fig. 2). It can be assumed that perchloric acid interacts with the water molecule and forms the perchloric acid-water system having different species in three different concentration regions: 1.0 to 4.0 mol dm^{-3}, 4.0 to 6.0 mol dm^{-3} and 6.0 to 9.0 mol dm^{-3}. The values of viscosity A-coefficient and viscosity B-coefficient were obtained from the intercept and the slope of linear plot of $(\eta/\eta_o - 1)c^{-0.5}$ *versus* $c^{0.5}$ as shown in Fig. 2, for all three concentration region are listed in Table-1.

With increase in concentration of perchloric acid, viscosity B-coefficient which is a measure of solute-solvent interaction increases and viscosity A-coefficient which is a measure of solute-solute interaction decreases. The viscosity B-coefficient follows the order: 1.0 to 4.0 mol dm^{-3} < 4.0 to 6.0 mol dm^{-3} < 6.0 to 9.0 mol dm^{-3}. The positive value of viscosity B- coefficient shows that perchloric acid in aqueous solution acts as structure maker [28,29].

In order to confirm the nature of solute in concentrated solution, the effect of temperatures on viscosity B-coefficient at 283.65 and 297.65 K has been considered in the study. The effect of temperatures on the viscosity of solution is well known, the viscosity decreases as temperature increases. The viscosities at 297.65K 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-2
VISCOSITY B-COEFFICIENT OF AQUEOUS PERCHLORIC ACID AT 283.65 K AND 297.65 K

Concentration range (mol dm^{-3})	B-coefficient (dm$^{-3/2}$ mol^{-1})	
	283.65 K	297.65K
1.0 to 4.0	0.106	0.097
4.0 to 6.0	0.461	0.420
6.0 to 9.0	0.804	0.773

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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