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RESEARCH ARTICLE

Catalytic and Viscometric Behavior of $HClO_4$-H_2O System

RENU LOSHALI* and NARAIN D. KANDPAL

Physical Chemistry Laboratory, Department of Chemistry, Kumaun University,
S. S. J. Campus, Almora 263601, Uttarakhand, India
renu.loshali@gmail.com

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Abstract: The interaction parameters A_x and B_x were calculated using modified Jones-Dole equation. The three concentration region in $HClO_4$-H_2O system were obtained which have been confirmed from kinetic data. To show the influence of interaction parameter on reaction rate, the hydrolysis of methyl acetate catalyzed by perchloric acid has been performed. The study is an illustrative model in the advancement of solution chemistry.

Keywords: Intermolecular interactions, Viscosity, Modified Jones-Dole equation, Ester hydrolysis

Introduction

The water-ion interaction represents a central topic in chemistry and biology which is used as universal solvent[1]. The properties of perchloric acid in aqueous solution have been studied by various spectroscopic, analytical and physicochemical methods[2-5]. Chemical shifts of NMR spectrum and viscosity of aqueous solution of $HClO_4$ has been studied and their dependence on acid concentration has been established[6,7]. The distribution of perchloric acid between water and tributylphosphate was investigated as a function of concentration and solvent extracts by measuring the viscosity, density and conductivity[8]. The effect of solvent may be considered as being two-fold: firstly stabilized the pair due to the hydrogen bond chains in the water and secondly solvate anions by hydrogen bond. In case of perchloric acid, the ion-pair formation equilibrium involves both steric and coulombic effects. On the basis of this approach, the structure modification of the water takes place by the addition of an acid. Such an influence has been investigated by conductance measurements for S-acetylthiocholine halides and perchlorates in methanol solution[9]. Many investigations have been carried out in aqueous solution catalyzed by both acid and base[10-12]. Hydrolysis of methyl acetate to methanol and acetic acid is an important reaction.

$$CH_3COOCH_3 + H_2O \xrightleftharpoons{H^+} CH_3OH + CH_3COOH \tag{1}$$

The mechanisms of many acid and base-catalyzed reactions have been established using kinetic data in order to measure the reaction rate in a wide range of acid or base concentrations[13]. In this study, viscometric studies of aqueous concentrated perchloric acid 1.0 moldm^{-3} to 9.0 moldm^{-3} have been undertaken in order to obtain viscosity parameters and to investigate their influence on rate of hydrolysis of methyl acetate catalyzed by perchloric acid.

Experimental

The perchloric acid was purchased from Qualigens and all solutions of acid were prepared using doubly distilled water. A suspended level viscometer or the Ubbelohde viscometer used in the study was obtained from Infusil India Pvt. Ltd. having number BG43500 size 2 and BG43499 size 1. A thermostat (Tanco make) working on 220 volt A.C. mains, an electronic digital single pan balance (cx220 citizen scale. Co. Ltd. U.K.) and stop watch (Racer) having least count 0.01s were employed. In hydrolysis, required volume of ester was added in the solution of perchloric acid having known strength. The titrations were carried out rapidly as possible so that practically no change can occur during the course of titration. The reaction mixture was titrated against standard sodium hydroxide solution using phenolphthalein as an indicator. The rate of reaction depends only on the concentration of ester and the specific rate constant can be given by following relation.

$$k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t} \qquad (2)$$

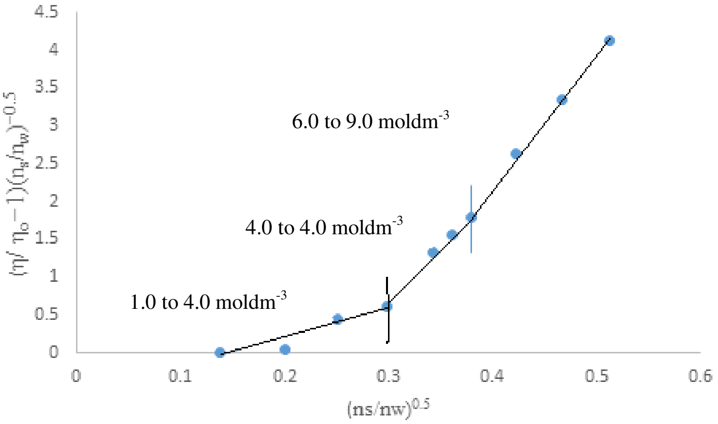
Where V_0, V_t and V_∞ are the titer values at time zero, time t and infinite (after 48 hours when the reaction is completed).

Results and Discussion

The viscosity of a solution depends on the perchloric acid concentration and the temperature of the solution. At each concentration (c) from 1.0 to 9.0 moldm^{-3}, the value of the viscosities, relative viscosities (η/η_o) were measured, where η and η_o are viscosities of the solution and solvent respectively and are listed in Table 1. The viscosity data has been analyzed using modified Jones- Dole equation which is also applicable for concentrated solutions[14].

$$(\eta/\eta_o - 1)(n_s/n_w)^{-0.5} = A_x + B_x\,(n_s/n_w)^{0.5} \qquad (3)$$

Where A_x and B_x are interaction parameter, n_s is mole fraction of solute, n_w is mole fraction of solvent. A_x and B_x are characteristics of solute-solute and solute-solvent interaction respectively. The values of A_x and B_x were evaluated from the intercept and slope of the linear plot of $(\eta/\eta_0-1)/(n_s/n_w)^{0.5}$ *versus* $(n_s/n_w)^{0.5}$ and are given at the bottom of the Figure 1.



1.0 to 4.0 moldm^{-3}*:* $A_x = -0.640$, $B_x = 4.102$; *4.0 to 6.0 moldm*$^{-3}$*:* $A_x = -3.847$; $B_x = 14.95$; *6.0 to 9.0 moldm*$^{-3:}$ $A_x = -4.721$; $B_x = 17.26$

Figure 1. Modified Jones-Dole plot for aqueous perchloric acid at 297.65 K

The three concentration regions have been obtained from the graph using regression analysis. The validity of modified Jones-Dole equation was checked graphically and the plot display three straight line between the concentration region 1.0 moldm^{-3} to 9.0 moldm^{-3}. For all three concentration regions, 1.0 moldm^{-3} to 4.0 moldm^{-3}, 4.0 moldm^{-3} to 6.0 moldm^{-3} and 6.0 moldm^{-3} to 9.0 moldm^{-3}, B_x coefficient calculated with the help of modified Jones-Dole equation are positive which suggests that perchloric acid acts as a structure maker in the given concentration range. The value of B_x coefficient increases with increase in concentration which shows the increase in solute-solvent interaction.

The hydrolysis of methyl acetate has been carried out in the concentration range 1.0 to 9.0 moldm^{-3} of perchloric acid at 297.65 K and the value of pseudo order rate constant has been summarized in Table 1 in order to show the influence of concentration on reaction rate. A graph between concentration and rate constant has been given in Figure 2. It is clear from the graph that there exist three concentration region in $HClO_4$-H_2O system as obtained from the modified Jones-Dole equation. In the first concentration region 1.0 to 4.0 moldm^{-3}, the rate of reaction increases with increasing concentration of perchloric acid which may be due to maximum protonation of $HClO_4$.

Table 1. Values of viscosity (η), density (ρ), rate constant (k_{obs}) of aqueous perchloric acid + water system at 297.65 K

c moldm^{-3}	η c P	ρ g cm^{-3}	η/η_o	$(n_s/n_w)^{0.5}$	$(\eta/\eta_o-1)(n_s/n_w)^{-0.5}$	k_{obs}x10^4, s^{-1}
1.0	0.97	1.030	0.98	0.13	−0.09	4.2
2.0	0.99	1.091	1.00	0.20	0.04	7.6
3.0	1.10	1.156	1.11	0.25	0.44	9.9
4.0	1.17	1.202	1.18	0.29	0.60	14.2
5.0	1.44	1.270	1.45	0.34	1.33	12.9
5.5	1.55	1.310	1.56	0.36	1.56	11.3
6.0	1.66	1.350	1.68	0.38	1.79	10.0
7.0	2.09	1.408	2.11	0.42	2.63	10.5
8.0	2.54	1.461	2.56	0.46	3.35	12.0
9.0	3.09	1.517	3.12	0.51	4.13	12.7

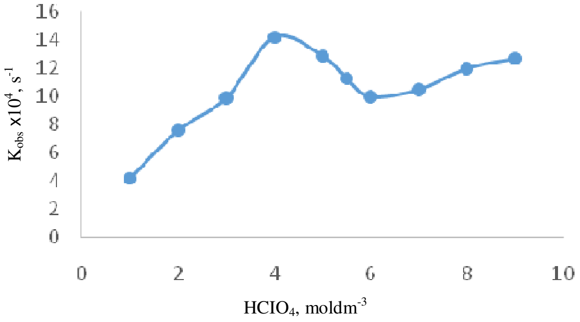


Figure 2. Plot between rate constant and [$HClO_4$] at 297.65K

In the second concentration region 4.0 to 6.0 moldm^{-3}, the rate of reaction decreases due to the variation in the activity of water. Such nature in hydrolysis of toluene phosphate has also reported[15]. In the third concentration region 6.0 to 9.0 moldm^{-3}, the rate of reaction further increases with increase in concentration which may due to higher value of the B_x coefficient.

The relationship between B-coefficient and k_{obs} for all the three regions has been derived as follows:

$$\text{(i)}\ k_{obs} = 0.56B_x\,[HClO_4] + 0.90 \quad (4)$$
$$\text{(ii)}\ k_{obs} = -0.14B_x\,[HClO_4] + 22.8 \quad (5)$$
$$\text{(iii)}\ k_{obs} = 0.055B_x\,[HClO_4] + 2.93 \quad (6)$$

These relations confirm the influence of B_x-coefficient on rate of hydrolysis of ester catalyzed by $HClO_4$. The similar study has been carried out for aqueous solution of concentrated hydrochloric acid[16].

Conclusions

It is concluded that perchloric acid acts as a structure maker in the concentration range1.0 to 9.0 moldm^{-3}. There is an interaction factor which influences the reaction rate and depends upon the molecular interactions present in the media. The interaction parameters obtained from modified Jones-Dole equation confirm the presence of three concentration regions in $HClO_4$-H_2O system which has been verified by the kinetic data. The conclusions drawn are justified by the H_3O^+structure as reported in literature[17]. The study is an illustrative model in the advancement of solution chemistry.

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