CATALAYTIC AND VISCOMETRIC BEHAVIOR OF CONCENTRATED HYDROCHLORIC ACID IN HYDROLYSIS OF ESTER

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ABSTRACT

In the present study, we have investigated the interactions of hydrochloric acid in concentrated aqueous solution in the concentration range 1.0 to 8.0 moldm^{-3} at 297.65 K viscometrically. The viscosity parameters have been calculated from Jones-Dole equation, modified Jones-Dole equation, Grunberg-Nissan equation and Hind equation. The trends of variations in B-coefficient have been explained in three concentration regions in hydrochloric acid-water system. The existence of all the three regions have been confirmed from kinetic results for the catalyzed hydrolysis of the ester in aqueous solution by the acid. The study is useful for the advancement of solution chemistry.

Key words: Ester hydrolysis, Hydrochloric acid, Viscosity equations, Interaction parameters.

INTRODUCTION

Acidity/basicity of any substance can be influenced by its molecules due to specific solute-solvent interactions like hydrogen bond donor-acceptor or electron pair donor-acceptor interactions in water and other polar solvents. The ion pair formed in solution influenced by dipolar and electrostatic interaction between the solute and solvent molecule. Such types of interactions are more influential in aqueous solutions of acids specifically at higher concentration regions. Hence, we proposed to investigate the interaction behavior of hydrochloric acid in order to understand the actual behavior of acid in concentration range 1.0 to 8.0 moldm^{-3}. H$_2$O-HCl system has been utilized by different workers in order to investigate the associative or dissociative nature of solute in solution[1-5]. Acid dissociation is one of the simplest and most important solvation reaction. Hydrochloric acid in aqueous

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dilute solution readily dissociates to form hydrated chloride and hydronium ion[6-8]. However, the behavior of concentrated aqueous solution of hydrochloric acid is still a subject of investigation as its solubility in water saturates at around 40% wt.[6] The structure of concentrated hydrochloric acid solution has been investigated by X-ray diffraction by many workers in detail. A pentagonal ring is suggested as the basic structural unit of HCl $(H_2O)_6$ and $(HCl)_2(H_2O)_6$ in solution along with hydrated crystals. For concentrated solutions, the possibilities of crystals of hydrated HCl, both H_3O^+ and $H_5O_2^+$ were identified with confirmation[9,10]. The other hydrated species has been proposed with different structures monohydrate $H_3O^+Cl^-$[11], dihydrate $H_5O_2^+Cl^-$[12], trihydrate $H_5O_2^+Cl^-.H_2O$[13] and hexahydrate $H_9O_4^+Cl^-.2H_2O$[14]. The behavior of HCl in polar solvents with varying permittivity has been reported recently[15]. In this study, the behavior of hydrochloric acid in solvents having dielectric constants approximately 10 to 80 has been analyzed and discussed.

In the present study, the viscometric studies of aqueous concentrated hydrochloric acid have been undertaken in order to obtain viscosity parameters and to investigate their influence on rate of hydrolysis of methyl acetate catalyzed by the acid.

EXPERIMENTAL

The hydrochloric acid was purchased from E. Merck and used without further purification. Doubly distilled water was used to prepare all concentrations of the acid. The strength of the each solution checked by titrating against a standard solution of sodium hydroxide using phenolphthalein as an indicator.

Viscosity measurements

The viscosity measurements were taken in a calibrated suspended-level viscometer placed in a thermostated water bath for constant temperature of accuracy ± 0.1 K. The solution of hydrochloric acid of known concentration was taken in viscometer and the flow time of the solution was measured. Each measurement was repeated thrice and average time of flow was used to calculate the viscosity. The viscometer used in the study was purchased from Infusil India Pvt. Ltd. having number BG43500 size 2 and BG43499 size 1. The densities of solutions were measured with calibrated pyknometer and single pan electronic balance citizen make.

Kinetic measurements

The hydrolysis of ester was performed in a glass stoppered conical flask. The solution of acid used as catalyst and ester was thermostated for constant temperature in

different conical flask. The reactions were initiated by mixing thermally pre-equilibrated solutions of acid and ester. The required volume of ester was added in the solution of acid having known strength and simultaneously stop watch was started. 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. In the transfer and withdrawal of the reaction mixture the time corresponding to the moment of half discharge of pipette in the titration flask was recorded. The titer values were used for calculating the rate constant. The titrations were carried out twice or thrice for a single set of reaction mixture in order to accertain the reproducibility of the results. The reproducibility in the results during the study was ± 3%. The ester (methyl acetate) on hydrolysis gives methyl alcohol and acetic acid.

$$CH_3COOCH_3 + H_2O \xrightarrow{\ H^+\ } CH_3COOH + CH_3OH \qquad \text{…(1)}$$

The reaction is catalyzed by hydrogen ions and the concentration of water being in excess can be taken as constant. Hence, the rate of reaction depends only on the concentration of ester and rate expression can be given by the following equation.

$$\frac{dx}{dt} = k\,[CH_3COOCH_3] \qquad \text{…(2)}$$

If 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). The specific rate constant can be given by following reaction.

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t} \qquad \text{…(3)}$$

RESULTS AND DISCUSSION

The viscosity data has been analyzed in terms of Jones-Dole equation: $(\eta/\eta_o - 1)c^{-0.5} = A + Bc^{0.5}$, where A and B are constants, characteristics of ion-ion and ion-solvent interaction, η and η_o are viscosities of the solution and solvent and molar concentration, *c*. The values of A and B were obtained from the intercept and slope of linear plot of $(\eta/\eta_0 - 1)/c^{0.5}$ versus $c^{0.5}$. The plot is given in Fig. 1 and the slope and intercept values are given at the bottom of Table 1. 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 $(n_s/n_w)^{0.5}$ with the help of modified

Jones-Dole equation: $(\eta/\eta_0 - 1)/(n_s/n_w)^{0.5} = A_x + B_x (n_s/n_w)^{0.5}$, where n_s is mole fraction of solute, n_w is mole fraction of solvent and A_x and B_x are interaction parameters. With the help of computer using regression analysis, the three concentration regions have been obtained from the graph. The values of linearity obtained are also given at the bottom of the Fig.1.
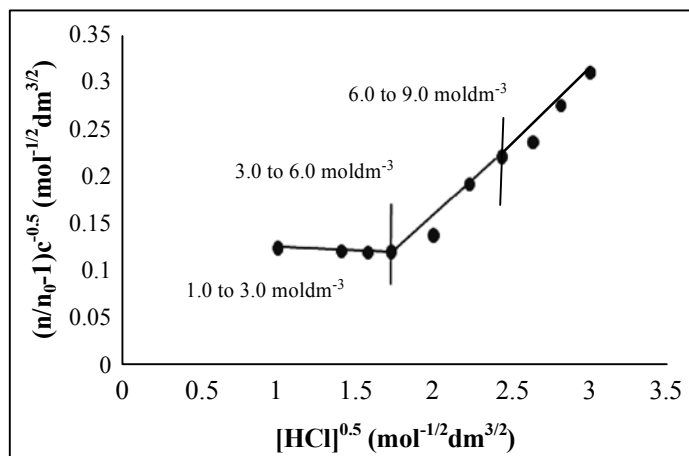
1.0 to 3.0 moldm^{-3}: $y = -0.006x + 0.130$, $R^2 = 0.87$; 3.0 to 6.0 moldm^{-3}: $y = 0.149x - 0.146$, $R^2 = 0.95$; 6.0 to 9.0 moldm^{-3}: $y = 0.163x - 0.184$, $R^2 = 0.96$

Fig. 1: Jones-Dole plot of aqueous hydrochloric acid for different concentration at 297.65 K

Table 1 shows that the value of B is negative in lower concentration range with a small magnitude, which indicates the nearly negligible interaction between ion and ion. In higher concentration region B becomes large and positive. This shows the presence of strong solute-solvent interactions in concentrated solution. On the other hand, the values of A indicates that solute-solute interactions are weak at all concentrations of hydrochloric acid. As reported in literature[16,17] large value of B is responsible for structure making character, hence the large positive values of B-coefficient in case of HCl indicates structure making character of HCl in aqueous solution.

The applicability of Jones-Dole equation was further verified for intermolecular interactions at each concentration of acid with the models Grunberg-Nissan equation: $\ln \eta = x_1 \ln\eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12}$ and Hind equation: $\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12}$, where x_1 and x_2 are the mole fractions of the components having viscosities η_1 and η_2 in pure state whereas η is the viscosity of the mixed solution of two components. d_{12} and H_{12} are interaction parameter, which indicate the nature of interactions between two components.

Table 1: Variation of viscosity (η) and density (ρ) of aqueous hydrochloric acid with increasing concentration at 297.65 K

[HCl](c) (moldm^{-3})	Viscosity of solution η (cP)	[HCl]$^{0.5}$ (mol$^{1/2}$. dm$^{-3/2}$)	ρ (g.cm^{-3})	η/η$_o$	(η/η$_o$-1)c$^{-0.5}$ (mol$^{-1/2}$ dm$^{3/2}$)	(n$_s$/n$_w$)$^{0.5}$	(η/η$_o$-1)/ (n$_s$/n$_w$)$^{0.5}$
1.0	1.1137	1.00	1.0040	1.1250	0.1250	0.1360	0.9191
2.0	1.1600	1.41	1.0129	1.1718	0.1214	0.1954	0.8792
2.5	1.1787	1.58	1.0208	1.1905	0.1206	0.2407	0.7914
3.0	1.1975	1.73	1.0307	1.2096	0.1210	0.2419	0.8664
4.0	1.2641	2.00	1.0408	1.2769	0.1384	0.2835	0.9767
5.0	1.4164	2.23	1.0645	1.4308	0.1932	0.3192	0.9561
6.0	1.5277	2.44	1.0866	1.5432	0.2217	0.3526	1.5405
7.0	1.6116	2.64	1.1112	1.6279	0.2373	0.3836	1.6368
8.0	1.7610	2.82	1.1177	1.7788	0.2762	0.4174	1.8658
9.0	1.9132	3.00	1.1329	1.9326	0.3108	0.4485	2.0793

1.0 to 3.0 moldm^{-3} (B = −0.006 dm$^{-3/2}$mol^{-1}; B$_x$ = −0.862; A$_x$ = 1.039); 3.0 to 6.0 moldm^{-3} (B = 0.149 dm$^{-3/2}$mol^{-1}; B$_x$ = 5.304; A$_x$ = −0.502); 6.0 to 9.0 moldm^{-3} (B = 0.163 dm$^{-3/2}$mol^{-1}, B$_x$ = 5.746; A$_x$ = −0.521)

In Fig. 2, d$_{12}$ values confirm the presence of three concentration region in Grunberg-Nissan plot[18]. Fig. 2 also indicates the relation between concentration and H$_{12}$ parameter of Hind equation[19]. The interaction parameters calculated d$_{12}$, H$_{12}$ for each concentration are listed in Table 2.

Table 2: Values of x$_1$, x$_2$, d$_{12}$, H$_{12}$, E* and k$_{obs}$ for different concentration of hydrochloric acid (1) + water (2) system at 297.65 K

[HCl] (moldm^{-3})	x$_1$	x$_2$	d$_{12}$	H$_{12}$ (cP)	E* (kJ)	k$_{obs}$× 10^4 (s^{-1})
1.0	0.0182	0.9817	5.8370	4.4565	0.25	3.9
2.0	0.0368	0.9631	3.6892	3.3757	0.37	6.4
2.5	0.0548	0.9451	2.5667	2.7826	0.40	7.9
3.0	0.0553	0.9446	2.8429	2.9482	0.45	9.2
4.0	0.0744	0.9255	2.7340	2.9382	0.58	9.0

[HCl] (moldm^{-3})	x_1	x_2	d_{12}	H_{12} (cP)	E^* (kJ)	$k_{obs} \times 10^4$ (s^{-1})
5.0	0.0925	0.9074	3.4362	3.4761	0.86	8.5
6.0	0.1006	0.8893	3.5615	3.6553	1.05	7.5
7.0	0.1283	0.8716	3.4901	3.6891	1.18	6.5
8.0	0.1484	0.8515	3.6706	3.9445	1.27	5.9
9.0	0.1675	0.8324	3.8163	4.1901	1.61	8.4

These results confirm the presence of three concentration regions 1.0 to 3.0 moldm^{-3}, 3.0 to 6.0 moldm^{-3} and 6.0 to 9.0 moldm^{-3} in the concentrated aqueous hydrochloric acid. The system hydrochloric acid and water consists the hydrogen bonded species Cl H········Cl in the water and the protonation of solvent molecule in the form of H_3O^+ ions. It is also possible that HCl may be present in undissociated form in concentrated solution. The possibilities of mono-, di-, tri-hydrates have been investigated. $H_5O_2^+$········Cl$^-$ interactions have been concluded.
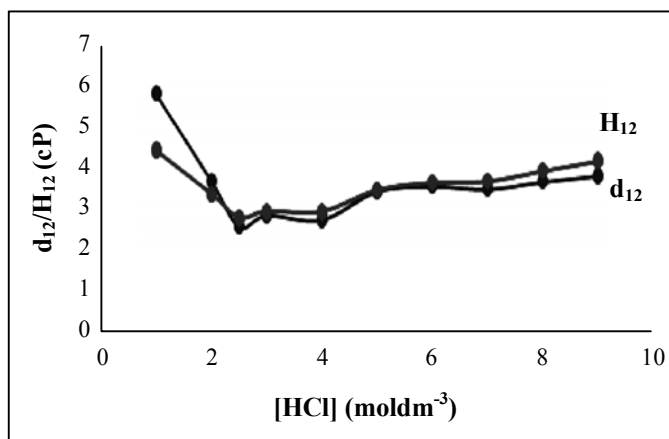
Fig. 2: Grunberg–Nissan and Hind plot for hydrochloric acid (1) + water (2) system at 297.65 K

The free energy of activation of viscous flow has been calculated using Erying viscosity equation[20].

$$\eta = Ae^{E^*/RT} \qquad \qquad ...(4)$$

where E* is energy of activation of molecule taking part in the flow of liquid. The flow depends upon the viscosity and temperature. The values of E* are given in Table 2 for

each concentration. The E* value increases with concentration of acid, which indicates the strong interaction between water and HCl molecule.

In an acid-catalyzed reaction, it has been mentioned that the rate of hydrolysis of ester increases with sulfuric acid concentration from lower concentration 50-55 wt. % and attains the maximum value. Further increase upto 85 wt.% acid concentration, accompanied by decrease in effective rate constant which further increases with increase in acid concentration upto100%[21]. This report not only support the conclusion drawn in the study but also instigate to study the catalytic effect on rate of hydrolysis of methyl acetate in all three proposed concentration region of hydrochloric acid. The dependence of rate of hydrolysis on initial concentration of hydrochloric acid has been given in Table 2. A plot between concentration and rate has been given in Fig. 3. The nature of the plot also indicate the presence of three concentration regions with different interactions present in solution as investigated in the study.

It is clear from the curve that rate of hydrolysis increases with increase of concentration continuously upto 3.0 moldm^{-3} due to the presence of H$^+$ formed by complete ionization of the molecule. The decrease in the rate after 3.0 moldm^{-3} can be explained on the basis of ion-solvent interactions, which are more operative and the activity of water is also influential in higher concentration. Similar results were reported in the hydrolysis of diethyl dithiophosphte catalyzed by hydrochloric acid[22].
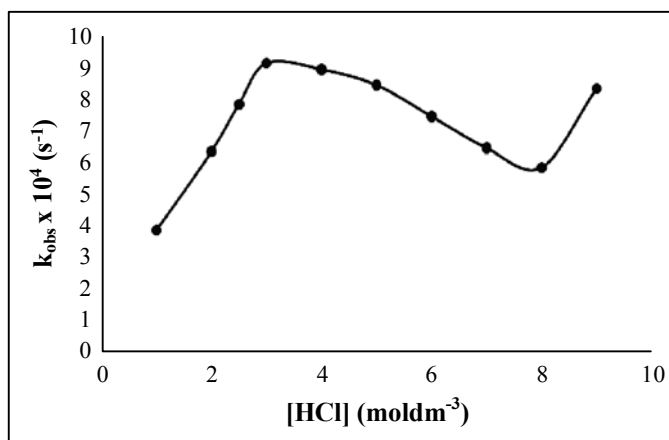
Fig. 3: Plot between rate constant and [HCl] at 297.65 K

The plot between rate of reaction and concentration clearly indicates the three concentration regions as obtained in Jones-Dole plot. If we consider both the plot, concentration versus rate constant and Jones-Dole plot in order to find out the relation

between k_{obs} and B-coefficient, the following relations have been derived in three concentration regions.

$$\text{(i) } k_{obs} = 443.6B \text{ [HCl]} + 1.19 \qquad \qquad …(5)$$

$$\text{(ii) } k_{obs} = -3.73B \text{ [HCl]} + 11.07 \qquad \qquad …(6)$$

$$\text{(iii) } k_{obs} = -4.9B \text{ [HCl]} + 12.23 \qquad \qquad …(7)$$

In rate expression negative sign of B-coefficient indicates the decrease in reaction rate with concentration of acid. These relations also indicate that there is an interaction factor which influence the rate of reaction and depends upon the molecular interactions present in the media. If we consider the interaction factor as the ratio of the slope of plot between rate constant and Jones-Dole plot in a particular concentration range. The general relation can be given as: $K_{obs} = I_f \text{ [HX]} + C$, where [HX] is the concentration of the acid and 'C' is the constant which depends upon the chemical species present in reaction medium.

CONCLUSION

The viscometric data has been utilized to analyze the interaction parameters in concentrated aqueous hydrochloric acid and the relevant relationship between rate of hydrolysis catalyzed by hydrochloric acid in different concentration region have been utilized to correlate the influence of interaction parameters on reaction rate. Highly satisfactorily values for different viscosity equation Jones-Dole, modified Jones-Dole, Grunberg-Nissan and Hind were reported in the study. The study is an illustrative model in the advancement of solution chemistry.

ACKNOWLEDGEMENT

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