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SHORT COMMUNICATION

Kinetics of the acidic hydrolysis of fenuron in the aqueous and micellar media

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Abstract The kinetics of the hydrolysis of fenuron by hydrochloric acid in aqueous methanol solution was studied spectrophotometrically. The influence of cationic micelles of cetyltrimethylammonium bromide and anionic micelles of sodium lauryl sulfate on the rate of hydrolysis of fenuron have also been studied. The anionic micelles increased the rate of reaction, while the cationic micelles decreased the rate of hydrolysis. The reaction followed first-order kinetics in [fenuron]. The rate of reaction was increased with increase in [HCl] in lower range, but become constant at higher concentration in aqueous and micellar pseudophases. The reaction starts with the protonation of amino group of fenuron followed by rate-determining attack of water. The results in micellar media are accounted for on the basis of distribution of substrate into micellar and aqueous pseudophases.

Keywords Fenuron · Hydrolysis · Kinetics · Sodium lauryl sulfate · Cetyltrimethylammonium bromide · Micelles

Introduction

Phenylureas are widely used in agriculture as active ingredient of efficient herbicides [1, 2]. Among the commonly marketed 25 phenylureas, fenuron is used to control the woody plants and deep-rooted perennial weeds. Fenuron is systemic and possesses the inhibiting effect on the photosynthesis processes in plants. It is a persistent pollutant in the environment. Due to the poor solubility in water (~10^{-5} g/l), sometimes, surfactants are used in the formulations of pesticides and herbicides [3, 4]. Surfactant used in pesticide formulations [5, 6] increases the solubility of pesticide in micellar media, stabilizes pesticides by controlling evaporation or decomposition and enhances the effectiveness of pesticides by providing fine spray. The surfactant also acts as wetting, dispersing and emulsifying agent.

Surfactants in water or similarly strong hydrogen-bonded solvents self-aggregate at concentrations above critical micelle concentration (cmc) to form association colloids called micelles [7, 8]. It has been well observed that aqueous micelles can influence chemical rates and equilibrium. Micelles act as a reaction media distinct from bulk solvent and may accelerate bimolecular reactions of counterions and inhibit those of coions [9–14]. The effect of micelles on reaction rates is usually treated in terms of pseudophase model in which micelles and water are regarded as distinct reaction media [15]. The overall reaction rate is given by the sum of rates in water and the micelles and, therefore, depends upon the distribution of reactants in each pseudophase and the appropriate rate constants in the two pseudophases. We have successfully applied the pseudophase ion exchange model [16–18] for the acidic hydrolysis of fenuron and are discussed in this paper. The surfactant aggregates mimic enzymes structurally and functionally, and therefore, the study in SLS and cetyltrimethylammonium bromide (CTAB) micelles will be helpful in understanding the mechanism of action of herbicides in biological processes [19]. The influence of temperature and concentrations of H^+, surfactants and fenuron on the rate of hydrolysis of fenuron has been studied well. The observed data can be utilised to determine and interpret the fate of herbicides after its dispersal in the environment.

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Experimental

Materials

Fenuron, 1,1-dimethyl-3-phenylurea (Bharat Pesticides, Bombay) hydrochloric acid (35% Merck, India), cetyltrimethylammonium bromide (99.9% CDH, India), sodium lauryl sulfate (98% CDH), methanol (99%, Merck) sodium chloride (99% Qualigens, India) potassium nitrate (99% CDH) were used as received. All the other chemicals used were of AR grade. Doubly distilled and deionised water was used throughout the experimental work.

Stock solutions of hydrochloric acid (=2.0 mol/dm^3), sodium lauryl sulfate and cetyltrimethylammonium bromide (=1.0×10^{-1} mol/dm^3) were prepared in double distilled water. The stock solution of fenuron (=1.0×10^{-2} mol/dm^3) was prepared in methanol.

Kinetic measurements

Kinetic experiments were carried out by taking the requisite amounts of methanolic solution of fenuron, surfactant and salts in a three-necked reaction vessel. The reaction vessel was fitted with a double surface condenser to check any evaporation. The reaction vessel was kept in a thermostated water bath at the desired temperature (±0.1 °C). The absorbance was measured at λ_{max} (=239 nm) by means of UV spectroscopy on an Elico-SL-164 UV-Vis spectrophotometer using 1-cm path length quartz cuvette. All the kinetic experiments were run under the first-order reaction condition in which the concentrations of H$^+$ and surfactant were kept large excess over [Fenuron]. The pseudo first-order rate constants were determined from the slope of ln (A−A_α) vs t, where 'A' is the absorbance by fenuron (at λ_{max}=239 nm) corresponding to time t. A_α is the absorbance at infinite time. A non-linear least square technique was used for the treatment of data to obtain the values of binding constant (K_S) of fenuron with sodium lauryl sulfate, (SLS) and CTAB micelles.

Results and discussion

Reaction in the aqueous medium

The acidic hydrolysis of fenuron was studied kinetically in water/methanol (9:1) at 80 °C. The experiments were performed at various initial concentrations of fenuron ranging from 4.0×10^{-5} mol/dm^3 to 1.0×10^{-4} mol/dm^3 at a fixed [HCl] (=0.1 mol/dm^3). The ionic strength was kept constant at 1.0. The values of pseudo first-order rate constant were found to be independent on [fenuron], indicating that the order of reaction in [fenuron] is unified.

To find out the dependence of the rate of hydrolysis on [HCl], a number of kinetic experiments at different concentrations of HCl in the range from 1.0×10^{-2} mol/dm^3 to 1.0 mol/dm^3 were carried out. The concentration of fenuron was kept constant at 5.0×10^{-5} mol/dm^3, and the temperature was fixed at 80 °C. Figure 1 illustrates the dependence of rate of hydrolysis on [HCl]. It is observed that the reaction is directly proportional to [HCl] in its lower range, i.e. ([HCl≤0.1 mol/dm^3), but at higher [HCl] (i.e. [HCl]≥0.2 mol/dm^3), the rate of hydrolysis becomes constant. Kinetic runs were also performed within the temperature range of 40–90 °C at fixed concentrations of HCl (=0.1 mol/dm^3) and fenuron (=5.0×10^{-5} mol/dm^3). The energy of activation was determined from the plot of log k_{obs} vs 1/T and is given in Table 1.

The acidic hydrolysis of phenylurea is initiated by the protonation of amino group. There are two possibilities of N-protonation firstly at the phenyl amino group (i.e. $Ph\overset{+}{N}H_2CON(CH_3)_2$) and secondly at the alkyl amino group (i.e. $PhNHCO\overset{+}{N}H(CH_3)_2$. Olah and White [20] and Martinelli et al. [21] have demonstrated that the protonation of alkyl amino group is more abundant than the protonation of phenyl amino group at lower [HCl]. The concentration of N-protonated urea increases with the increase in acid concentration and reaches to a maximum. Thereafter, the further increase in acid concentration causes a decrease in concentration of N-protonated urea and favours the formation of O-protonated urea [22]. The N-protonated urea is reactive entity, while the O-protonated conjugate acid does not decompose. The N-protonated phenylurea is then attacked by water to give an addition

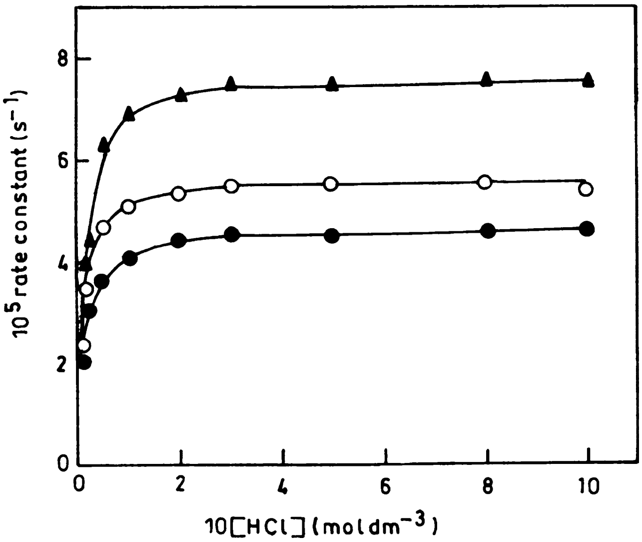


Fig. 1 Effect of variation of [HCl] on the rate constant (k_{obs} for aqueous, k_ψ for CTAB and SLS) in aqueous (*open circle*), CTAB (*filled circle*), SLS (*filled triangle*) media. Reaction conditions: [fenuron] (=5.0×10^{-5} mol/dm^3), [CTAB] (=1.0×10^{-2} mol/dm^3), [SLS] (=1.0×10^{-2} mol/dm^3) at 80 °C

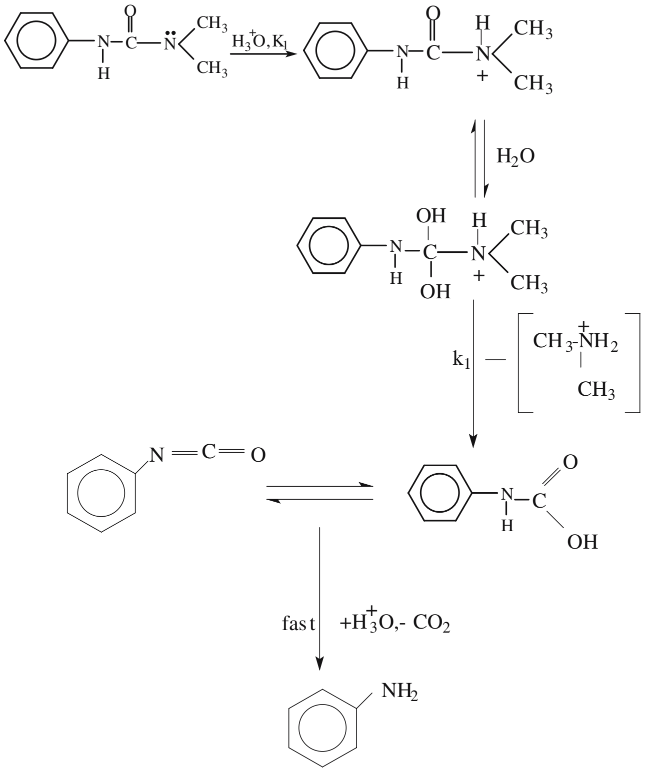
Table 1 Values of activation parameters for the hydrolysis of fenuron by hydrochloric acid in the absence and presence of surfactants

Activation parameters	In the absence of surfactant	In the presence of surfactants	
		SLS	CTAB
Ea (kJ/mol)	36.05±1.24	27.32±1.39	31.28±1.08
$\Delta H^{\#}$ (kJ/mol)	33.58±1.14	24.84±1.05	28.81±0.97
$-\Delta S^{\#}$ (JK^{-1}/mol)	215.87±4.97	242.56±5.79	234.25±6.24

[Fenuron]=5.0×10^{-5} mol/dm^3, [HCl]=0.1 mol/dm^3; [SLS]=1.0×10^{-2} mol/dm^3, [CTAB]=1.0×10^{-2} mol/dm^3

complex, i.e. a tetrahedral intermediate. Water acts as a proton transfer agent in a six-member cyclic transition state and facilitates the intermolecular proton transfer from unprotonated or N-protonated phenylurea (Scheme 1) [23, 24]. The attack by water is a rate-determining step, and the tetrahedral intermediate decomposes to yield phenylisocyanate and dimethylamine.

Phenylisocyanate is unstable in aqueous medium. Moodie et al. [25] reported a half-life period of 20 s for the hydrolysis of phenylisocyanate in aqueous solution at 25 °C. Thus, phenylisocyanate is readily attacked by water and hydrolyses to give carbamic acid, which, in turn, decarboxylates rapidly to give finally aniline.



Scheme 1 Intermolecular proton transfer from unprotonated or N-protonated phenylurea

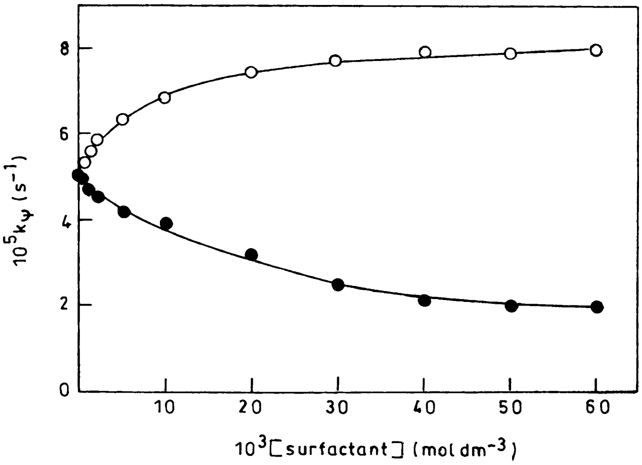


Fig. 2 Effect of variation of [surfactant] [(CTAB, *filled circle*) and (SLS, *open circle*)] on k_ψ. Reaction conditions: [fenuron] (=5.0×10^{-5} mol/dm^3), [HCl] (=0.1 mol/dm^3) at 80 °C

The rate-limiting behaviour of HCl at high concentrations can be explained by considering the existence of equilibrium between the O-protonated and N-protonated fenuron. At lower concentration range of hydrochloric acid, N-protonated phenylurea is favourable, and so, the reaction is linearly dependent on [HCl]. At higher concentrations of acid, the formation of O-protonated phenylurea is more favourable and also reduces the activity of water.

Reaction in the presence of anionic (SLS) micelles

It was observed that the rate of reaction increases with the increase in concentration of SLS micelles. The effect of varying [SLS] (=5.0×10^{-4}–6.0×10^{-2} mol/dm^3) was studied at constant [fenuron] (=5.0×10^{-5} mol/dm^3) and [HCl] (=0.1 mol/dm^3) at 80 °C. The values of the pseudo first-order constant (k_ψ) were determined in the presence of SLS micelles, and the plot of k_ψ vs [SLS] is given in Fig. 2. The kinetic experiments performed at varying initial concentrations of fenuron (=4.0×10^{-5} mol/dm^3–1.0×10^{-4} mol/dm^3) in the presence of fixed concentrations of HCl (=1.0×10^{-1} mol/dm^3) and SLS(=1.0×10^{-2} mol/dm^3) shows that the pseudo first-order rate constants are independent of the initial concentrations of fenuron. The values of rate constants initially increased with the increase in [HCl] (up to 2.0×10^{-1}mol/dm^3), and the further increase in [HCl] kept the rate of reaction constant as illustrated in Fig. 1.

Micelles are assemblies of surfactants, or surface-active agents, i.e. amphiphiles that have ionic or polar head groups and hydrophobic residues. Micelles are assumed to be spherical and regarded as a micro-reactor that influence reaction rates by incorporating or partitioning the reactants. Quantitative treatment of the micellar rate effects can be explained by means of pseudophase kinetic model proposed by Menger and Portnoy [26] and developed by Bunton and

Savelli [27], Romsted [28] and Vera and Rodenas [12]. The aqueous micelles are considered as submicroscopic reaction media, and the reactants are distributed between water and the micelles, which are regarded as distinct reaction regions. The overall reaction rate is given by the sum of rates in the water and in the micelles. Thus, the hydrolysis of fenuron occurring in presence of SLS micelles can be presented by Scheme 2.

In this scheme, S denotes fenuron, D_n is the micellized surfactant (i.e. $[D_n]$ = [total surfactant] − cmc), and K_s is the binding constant of fenuron with SLS micelles. Subscripts w and m denote aqueous and micellar pseudophases, respectively. Corresponding to the Scheme 2, the overall rate constant in terms of the first-order rate constants in aqueous (k'_w) and micellar (k'_m) pseudophases are given by:

$$k_\psi = \frac{k'_w + k'_m K_s[D_n]}{1 + K_s[D_n]} \tag{1}$$

For bimolecular reaction, the rate-[surfactant] profile can be treated quantitatively by taking into account the distribution of both reactants in water and in micelles. Therefore, the first-order rate constants k'_w and k'_m can be expressed in terms of the second-order rate constants by considering the reactant concentrations in each aqueous and micellar pseudophases, and the Eq. 1 can now be written as:

$$k_\psi = \frac{k_w[H_T^+] + (k_m K_s - k_w) m^S_{H^+}[D_n]}{1 + K_s[D_n]} \tag{2}$$

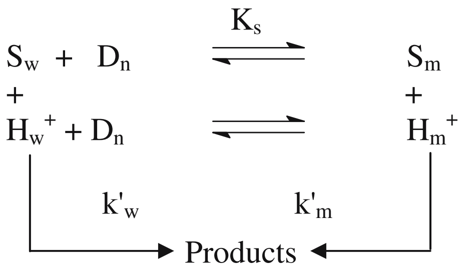
where

$$k'_w = k_w\left[H_w^+\right] \tag{3}$$

and

$$k'_m = \frac{k_m\left[H_m^+\right]}{[D_n]} = k_m m^S_{H^+} \tag{4}$$

where k_m and k_w are second-order rate constants for reaction in micellar and aqueous pseudophases, respectively. $\left[H_m^+\right]$ and $\left[H_w^+\right]$ are the respective concentrations of hydrogen ion in micellar and aqueous pseudophases.



Scheme 2 Hydrolysis of fenuron in the presence of SLS micelles

The ionic and polar reactants mainly exist in interfacial region called Stern layer. The Stern layer is highly aqueous and contains a high concentration of ionic head groups and counterions. Quantitatively, the concentration of reactant counterions (i.e. H^+) in the interfacial region is assumed to be that in the bulk water plus an increment predicted by the pseudophase ion exchange model developed by Romsted [28]. Romsted assumed that ions bind to micelles according to the following equilibrium developed for ion exchange resin:

$$H_w^+ + Na_m^+ \underset{}{\overset{K_{H^+/Na^+}}{\rightleftharpoons}} H_m^+ + Na_w^+ \tag{5}$$

The equilibrium constant for the exchange of H^+ and Na^+ at micellar surface is given by:

$$K_{H^+/Na^+} = \frac{\left[Na_w^+\right]\left[H_m^+\right]}{\left[Na_m^+\right]\left[H_w^+\right]} \tag{6}$$

The distribution of H^+, Na^+ and fenuron are in dynamic equilibrium between micellar and aqueous pseudophases. On applying the mass balance for Na^+, H^+ and surfactant, the following quadratic Eq. 7 results:

$$\left(m^S_{H^+}\right)^2 + \left[\frac{\left[Na_t^+\right] + \left[H_w^+\right]}{[D_n]} - \beta\right] m^S_{H^+} - \frac{\beta\left[H_w^+\right]}{[D_n]} = 0 \tag{7}$$

Where β (=0.75) is the fraction of ionic head groups neutralised by counterions and $m^S_{H^+} = \frac{[H_m^+]}{[D_n]} \cdot \left[H_w^+\right]$ was obtained from the measured pH value of the solution using the relationship $\mathrm{pH} = -\log\left[H_w^+\right]$. The value of $m^S_{H^+}$ was obtained from Eq. 7, and the fitting values of k_m and K_s were evaluated from the computer program by minimising the deviation between the simulation and observed values for the k_ψ–[SLS] profile. The values of these parameters are given in Table 2.

The rate enhancements of bimolecular reactions are ascribed largely to an increase in concentration of reactants in the small volume of the Stern layer of association

Table 2 Parameters used to simulate k_ψ–[surfactant] profile

Parameters	Values	
	SLS	CTAB
K_s (dm^3/mol)	400	28.82
k_m (mol^{-1} dm^3 s^{-1})	$1.41 \pm 0.11 \times 10^{-4}$	–
β	0.75	–
K_{H^+/Na^+}	1.00	–
cmc (mol/dm^{-3})	8.64×10^{-3}	8.52×10^{-4}

[Fenuron]=5.0×10^{-5} mol/dm^3, [HCl]=0.1 mol/dm^3; [SLS]=1.0×10^{-2} mol/dm^3, [CTAB]=1.0×10^{-2} mol/dm^3, temperature=80 °C colloids. Addition of surfactant leads to binding of both the reactants to micelles and results into increased concentrations of reactants in the small volume of Stern layer. Therefore, an overall increase in reaction rate is observed. But the comparison of the second-order rate constant of micellar pseudophase to that in water, the actual value of rate constant in micellar pseudophase, is observed to be smaller than in water.

$$k_2^{\mathrm{m}} = V_{\mathrm{m}} k_{\mathrm{m}} \quad \text{and} \quad k_2^{\mathrm{m}} / k_{\mathrm{w}} = 0.0524$$

Where V_m is the molar volume of Stern layer of SLS micelles, and its value is 0.14 dm^3/mol [29].

The lower value of rate constant in the micellar pseudophase (k_2^m) may be due to the (1) lower polarity of micellar surface in comparison with water; (2) strong binding between hydrophilic H_3^+O and anionic SLS micelles (which reduces the activity of H_3O^+) and (3) the lower activity of water (~0.6) at the surface of SLS micelles [30]. Also, the bulk water is a better hydrogen bond donor than water at the Stern layer. Thus, these factors contribute towards the lowering of value of k_2^m.

Fenuron is protonated in acidic medium and is, therefore, positively charged. The extent of binding constant (K_s) depends upon the charge density and the hydrophobicity of substrate. The ionic binding between the reactant and micelles became more dominant over hydrophobic binding between the organic molecules and micelles. The higher value of K_s (=400) is indicative of the strong association between the anionic SLS micelles and the positively charged hydrophobic fenuron.

Reaction in the presence of cationic (CTAB) micelles

A continuous inhibition in the rate of acidic hydrolysis of fenuron in the presence of cationic CTAB micelles was observed. The variation in [CTAB] was studied at fixed initial concentrations of fenuron (=5.0×10^{-5} mol/dm^3) and hydrochloric acid (=0.1 mol/dm^3) at temperature 80 °C (Fig. 2). The pseudophase ion exchange model explains the micellar inhibition of bimolecular reactions of coions in terms of incorporation of the organic substrate and exclusion of reactive ion. The acidic hydrolysis of fenuron is not completely suppressed by CTAB micelles because of the presence of very small concentrations of H^+ and N-protonated fenuron at the micellar surface as coions.

The concentration gradient of coions between water and the interface region is very large with dilute coions, but it decreases as the total concentration of coions is increased [31]. Thus, under the condition of high concentration of coions, the concentration gradients disappear between the aqueous and the interfacial region. The inhibition reaction is decreased significantly as the total coion concentration is increased. The Coulombic model also predicts that there will be a small but finite concentration of coions at micellar surfaces. The residual hydrolysis of fenuron by HCl at CTAB micellar surface is considered to be very small and negligible as compared to the reaction rate in aqueous

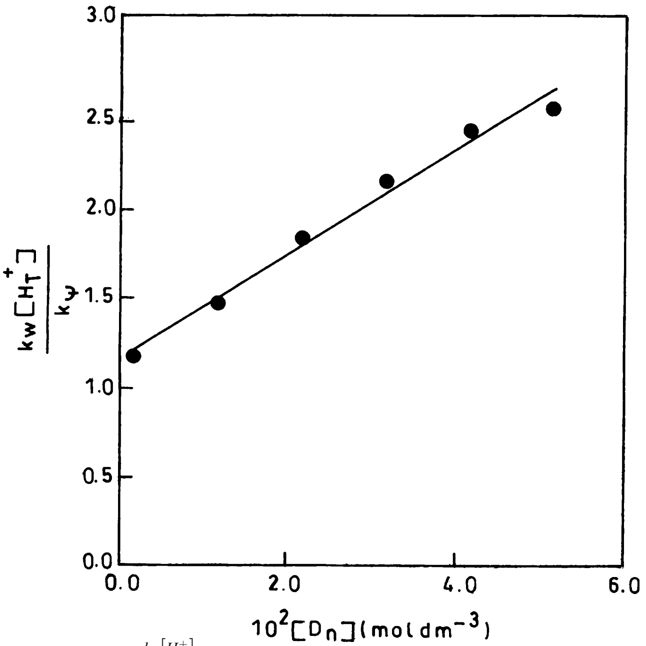


Fig. 3 Plot of $\frac{k_w[H_T^+]}{k_\psi}$ vs [D_n]. Reaction conditions: [fenuron] (=5.0× 10^{-5} mol/dm^3), [HCl] (=0.1 mol/dm^3) at 80 °C

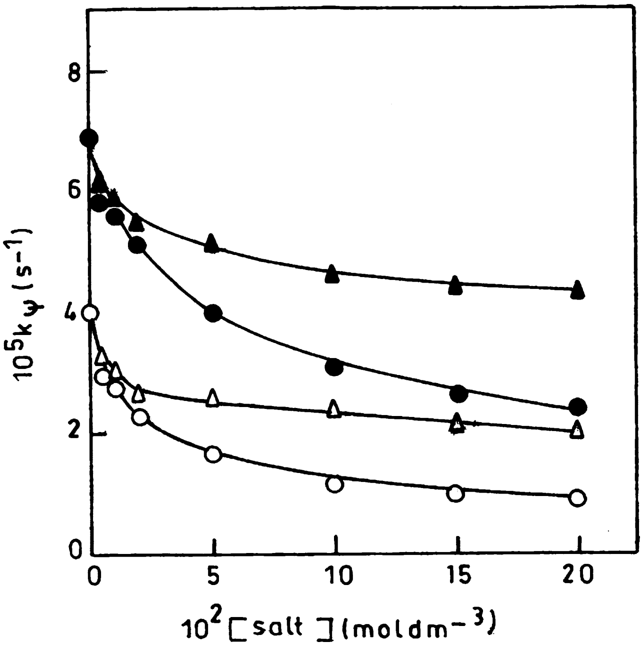


Fig. 4 Effect of variation of [KNO_3] and [NaCl] on the k_ψ (*filled triangle, filled circle*) for KNO_3 and NaCl respectively in [SLS] (=1.0× 10^{-2} mol/dm^3), (*open triangle*, *open circle*) for KNO_3 and NaCl respectively in [CTAB] (=1.0×10^{-2} mol/dm^3). Reaction conditions: [fenuron] (=5.0×10^{-5} mol/dm^3), [HCl] (=0.1 mol/dm^3) at 80 °C

pseudophase. The observed rate of reaction is due to the reaction occurring in aqueous pseudophase. The terms k_m and $m^s_{H^+}$ in Eq. 2 is assumed to be negligible and the rate equation takes the following form:

$$k_\Psi = \frac{k_w[H^+_T]}{1 + K_s[D_n]} \tag{8}$$

or

$$\frac{k_w[H^+_T]}{k_\Psi} = 1 + K_s[D_n] \tag{9}$$

A plot of $\frac{k_w[H^+_T]}{k_\Psi}$ vs $[D_n]$ gave a straight line (Fig. 3) with slope K_s (=28.8). The lower binding constant, K_s between the cationic CTAB micelles and hydrophobic fenuron coions is an indicative of a weak association. The similar behaviour of rate–[fenuron] and rate–[HCl] profiles in aqueous and micellar (SLS and CTAB) media suggests that the acidic hydrolysis of fenuron obeys the same mechanism in both aqueous and micellar media along with all intermediates.

The pseudo first-order rate constants were obtained for the acidic hydrolysis of fenuron at varying temperatures (40–90 °C). A straight-line plot was obtained for log k vs 1/*T* in each case of aqueous, anionic and cationic micellar media. From the slope of these plots the values of energy of activation were determined. The other activation parameters were calculated using Arrhenius and Eyring equation and are given in Table 1.

The added salts (NaCl and KNO_3) decreased the pseudo first-order rate constant in both anionic, SLS and cationic CTAB micelles (Fig. 4). The competition between the inert ions, i.e. (K^+ and Na^+) and reactive H^+ ions takes place for binding to SLS micelles [32, 33]. The low-charge-density ions displace the high-charge-density ions from the micellar surfaces, and therefore, the addition of Na^+ and K^+ cause displacement of H^+ from the micellar surface and decreases reaction rates. Apart from the exclusion of H^+ from the micellar surface, the added electrolyte also causes micelles to grow and change their shape and influence the reactivity.

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