Micellar Effect on The Reaction of Acetophenone with Phenylhydrazine

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The kinetics of acetophenone-phenylhydrazine reaction has been studied spectrophotometrically in the presence of anionic surfactant, sodium lauryl sulphate (NaLS), cationic surfactant, cetyl trimethyl ammonium bromide (CTAB) and non-ionic surfactants, polyethylene glycols of different molecular weights (PEG 4000, PEG 6000 and PEG 20000) at 30 ºC. All the above surfactants accelerated the reaction at low concentration, reaching a rate maximum and inhibiting the reaction at post-micellar concentrations. On the basis of kinetic results, it can be inferred that at low concentrations, NaLS and CTAB act as simple electrolytes changing polarity of the medium and in the case of polyethylene glycols, the polarity of N–H bond changes when phenylhydrazine is embedded on to the polyethylene glycol matrix. A plausible mechanism is drawn based on these observations.

Key Words: Surfactants, Kinetics, Acetophenone, Phenylhydrazine, Critical micelle concentration.

INTRODUCTION

During the last decade, there has been growing interest in the influence of surfactants on chemical reaction because of their wide applications in biological, medical and dye industries[1-3]. Organic reactions[4] in aqueous surfactants undergo either rate enhancement or inhibition and this phenomenon has been attributed to the electrostatic and hydrophobic interactions between the surfactant and substrate aggregates. The effect of sodium lauryl sulphate (NaLS) and cetyl trimethyl ammonium bromide (CTAB) on the formation of glucosazone at room temperature has been reported[5]. The kinetic study on the effect of NaLS and CTAB on the reaction between glucose and phenylhydrazine inferred that the reaction is catalyzed by both the anionic and cationic surfactants at lower concentrations but inhibited at higher concentrations[6]. The present investigation reports the effect of NaLS, CTAB and polyethylene glycols on the acetophenone-phenylhydrazine (AP-PH) reaction.

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EXPERIMENTAL

Acetophenone (AP) and phenylhydrazine (PH), of AR grade (Merck) were used for all the reactions. The purity of the chemicals have been checked from their boiling points (phenylhydrazine 242 ºC and acetophenone 201 ºC). Phenylhydrazine solutions were prepared freshly just prior to use. The surfactants were obtained from Ranbaxy. The reactions were carried out in aqueous acetic acid solvent media. Acetic acid of AR grade (Qualigen) was used in all the reactions whose purity has been checked from its boiling point (118 ºC). Double distilled water was used and the products formed have been characterized with the acetophenone-phenylhydrazone prepared by the traditional method. Kinetics of the reaction was carried out spectro-photometrically at 30 ºC with the aid of UV-visible spectrophotometer (Chemito 2600). The specific rate constants were calculated from the integrated rate equation.

$$k = \frac{2.303}{t} \log \frac{A_\infty - A_o}{A_\infty - A_t}$$

where A_o is the absorbance of the product initially, A_t is the absorbance of the product at time t and A_∞ is the absorbance of the product at infinity. The initial concentration of acetophenone was kept at 2×10^{-4} M and in all cases a sufficient excess of nucleophilic reagent (phenylhydrazine) was employed so that pseudo first order rate behaviour was observed.

RESULTS AND DISCUSSION

The rate of the reactions were monitored in the presence of anionic and cationic surfactants by varying the [NaLS] or [CTAB] at fixed [AP] and [PH]. The observed results are presented in Tables 1-2 (Fig. 1).

TABLE-1
EFFECT OF [NALS] ON PHENYLHYDRAZINE-ACETOPHENONE REACTION
[PH] = 2×10^{-2} M, Solvent = 80 %, HOAc-20 % H_2O,
[AP] = 2×10^{-4} M, Temperature = 30 ^{0}C

[NaLS] (M)	$10^4\ k_1 s^{-1}$
Nil	0.870
1×10^{-5}	1.060
5×10^{-5}	4.830
1×10^{-4}	9.660
2×10^{-4}	10.89
5×10^{-4}	12.66
8×10^{-4}	10.58
1×10^{-3}	7.660
2×10^{-3}	6.830
5×10^{-3}	5.590
1×10^{-2}	2.090

TABLE-2
EFFECT OF [CTAB] ON PHENYLHYDRAZINE-ACETOPHENONE REACTION
[PH] = 2×10^{-2} M, Solvent = 80 %, HOAc-20 % H_2O,
[AP] = 2×10^{-4} M, Temperature = 30 $^\circ$C

[CTAB] (M)	$10^4 k_1 s^{-1}$
Nil	0.810
1×10^{-6}	1.290
5×10^{-6}	6.030
8×10^{-6}	10.15
1×10^{-5}	13.51
5×10^{-5}	11.03
1×10^{-4}	8.610
5×10^{-4}	6.680
1×10^{-3}	3.120
5×10^{-3}	1.860
1×10^{-2}	1.090
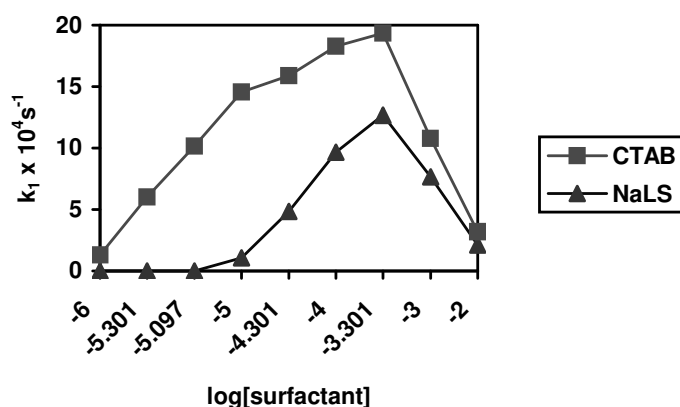
Fig.1. Effect of NaLS and CTAB on AP-PH reaction in 80 % HOAc

It was observed that the rate of the reaction increased at lower concentrations of both NaLS and CTAB, attained a maximum and then decreased at higher concentrations of surfactants.

Similarly the rate of the reactions were monitored in the presence of PEG 4000, PEG 6000 and PEG 20000 at fixed [AP] and [PH]. The observed results are presented in Table-3 (Fig. 2-4).

On increasing the concentration of polyethylene glycols (PEGs), the rate increased reached a maximum at the optimum concentration of polyethylene glycols, then decreased at higher concentrations. It was interesting to note that PEG 4000 catalyses the reaction at millimolar concentrations, PEG 6000 at micromolar concentrations and PEG 20000 exercises its catalytic power even at nanomolar levels. The mechanism behind this reaction is based on the fact that at premicellar concentrations, the surfactants are known to exist as individual molecules and above critical micelle

concentrations (CMC), they form micellar aggregates. Hence at low concentrations, NaLS and CTAB may act as simple electrolytes changing the ionic strength and/or polarity of the medium. However in case if PEGs, the observed rate increase may be ascribed to a change in the polarity of the N–H bond, when phenylhydrazine is embedded on to the PEG matrix as shown below:
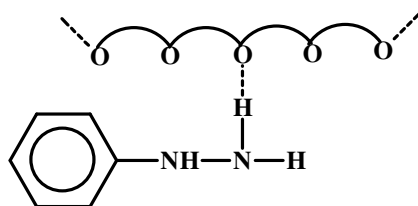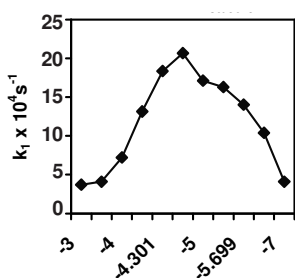
TABLE-3

EFFECT OF [PEGs] ON PHENYLHYDRAZINE-ACETOPHENONE REACTION

[PH] = 2×10^{-2} M, Solvent = 100 % HOAc,

[AP] = 2×10^{-4} M, Temperature = 30 °C

[PEG 4000]	$10^4 k_1 s^{-1}$	[PEG 6000]	$10^4 k_1 s^{-1}$	[PEG 20000]	$10^4 k_1 s^{-1}$
Nil	3.380	Nil	3.380	Nil	3.380
1×10^{-3}	3.710	1×10^{-3}	3.880	1×10^{-5}	5.020
5×10^{-4}	4.090	1×10^{-4}	7.160	1×10^{-6}	7.120
1×10^{-4}	7.210	1×10^{-5}	11.09	1×10^{-7}	12.30
8×10^{-5}	13.15	1×10^{-6}	18.15	1×10^{-8}	16.14
5×10^{-5}	18.35	1×10^{-7}	21.35	5×10^{-9}	20.08
2×10^{-5}	20.67	8×10^{-8}	17.12	2×10^{-9}	25.14
1×10^{-5}	17.12	5×10^{-8}	15.03	1×10^{-9}	23.01
8×10^{-6}	16.29	2×10^{-8}	10.91	8×10^{-10}	19.25
2×10^{-6}	14.02	1×10^{-8}	8.25	5×10^{-10}	12.31
1×10^{-6}	10.39	–	–	1×10^{-10}	7.860
1×10^{-7}	4.100	–	–	5×10^{-11}	5.130

Fig. 2. Effect of [PEG 4000] on the rate of AP-PH reaction
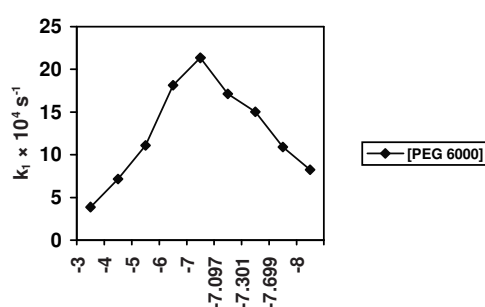
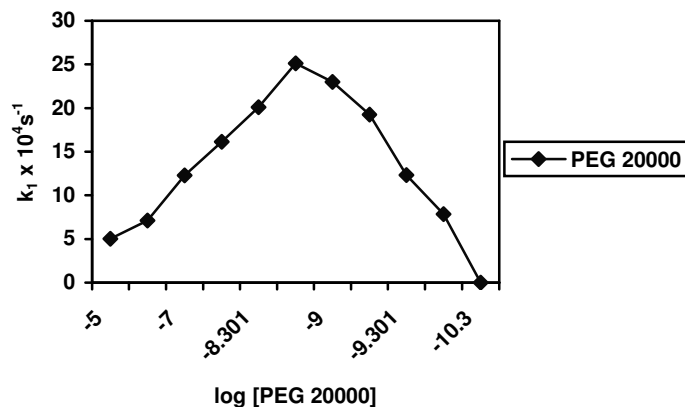Fig. 3. Effect of [PEG 6000] on the rate of AP-PH reaction

Fig. 4. Effect of [PEG 20000] on AP-PH reaction

This interaction would loosen the N–H bond and thus increase the nucleophilicity of phenylhydrazine. At post-micellar concentrations, a decrease in rate with all the three kinds of surfactants was explained assuming that the micelles interact with reactant molecules rendering them inactive.

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