CHAPTER 3

RESULTS AND DISCUSSION

3.1 Glycine ester hydrolysis in aqueous micellar medium

Studying hydrolysis of aminoacid ester in micellar medium is somewhat mimicking the biological reactions as micelles provide the microenvironment similar to biological system[1]. Glycine ester hydrolysis in presence of surfactants has not been studied much. Many of the studies have been carried out in the field of ester hydrolysis in presence of surfactants at high or at low pH [2-6], but rarely one finds these studies around pH 7, which is the pH of almost all biological systems. Therefore, although study has been carried out at various pH values, more emphasis is given to study at pH 7 in this section.

Kinetics of hydrolysis of glycine esters (MeGly, EtGly, diMeGly and PhGly) were studied under different pH, temperature and surfactant environment. The pseudo first order rate constants (k) determined under various conditions are presented in the form of graphs and tables.

pH :

The variation of rate constants for the hydrolysis of glycine esters in the pH range 4-11, in presence and absence of surfactants are depicted in figs (1-6) The change in pH has tremendous effect on the rate of hydrolysis of glycine esters The results show that, in the absence of surfactants, the rate constant for glycine ester hydrolysis decreases as the pH is changed from 4 to 5, and then there is a slow but steady increase up to pH 7, thereafter a sharp rise is observed with increase in pH.

The rate constants (k) at pH 6.8 for all the esters studied were low, where as at high and low pH, quite high values of k were obtained When compared, the k values at pH 4 were nearly $3x10^3$ times that at pH 6.8, where as at pH 11, they were ≈ 400 times larger. For example, the observed rate constants (k_0) at 40°C, for MeGly hydrolysis at pH 4, 6.8 and 11 were $7.20x10^{-3}$ S^{-1}, $2.44x10^{-6}$ S^{-1} and $9.7x10^{-4}$ S^{-1} respectively. This observation is simply because of the strong catalytic power of H^+ ions at low pH and OH^- ions at high pH. It is reflected in the fact that, as the pH was changed from 4 to 5, there was a large decrease in the values of rate constants, due to decrease in H^+ ion concentration. From pH 5 to 7, there was a slight increase in the rate, but the rate of hydrolysis in this region was very small due to low concentration of H^+ as well as OH^- ions. Above pH 7, the sharp rise in rate is due to increase in OH^- ion concentration.

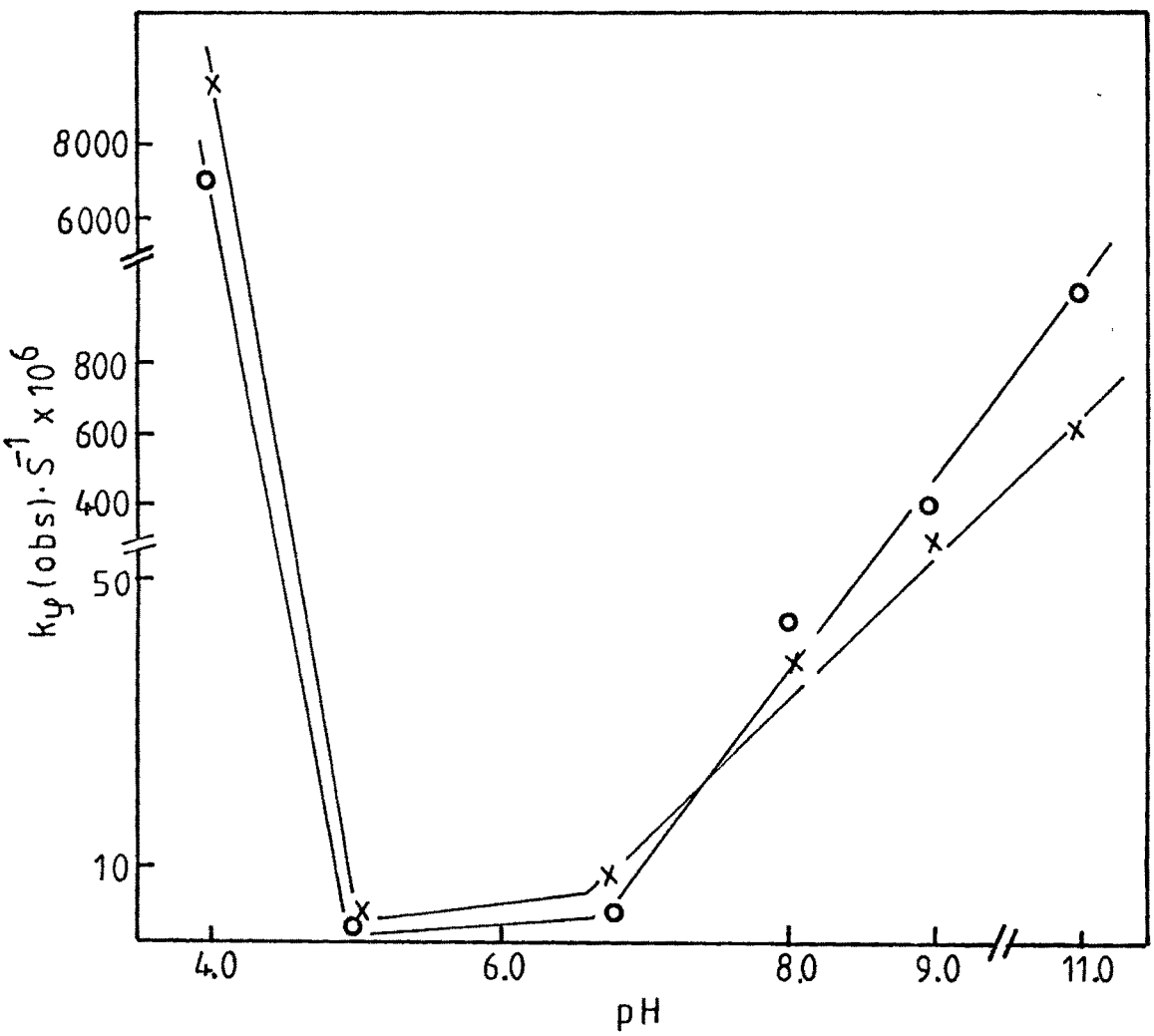


Fig 1 Effect of pH (O - In absence of SDS, X - In presence of SDS) on MeGly hydrolysis at 40°C

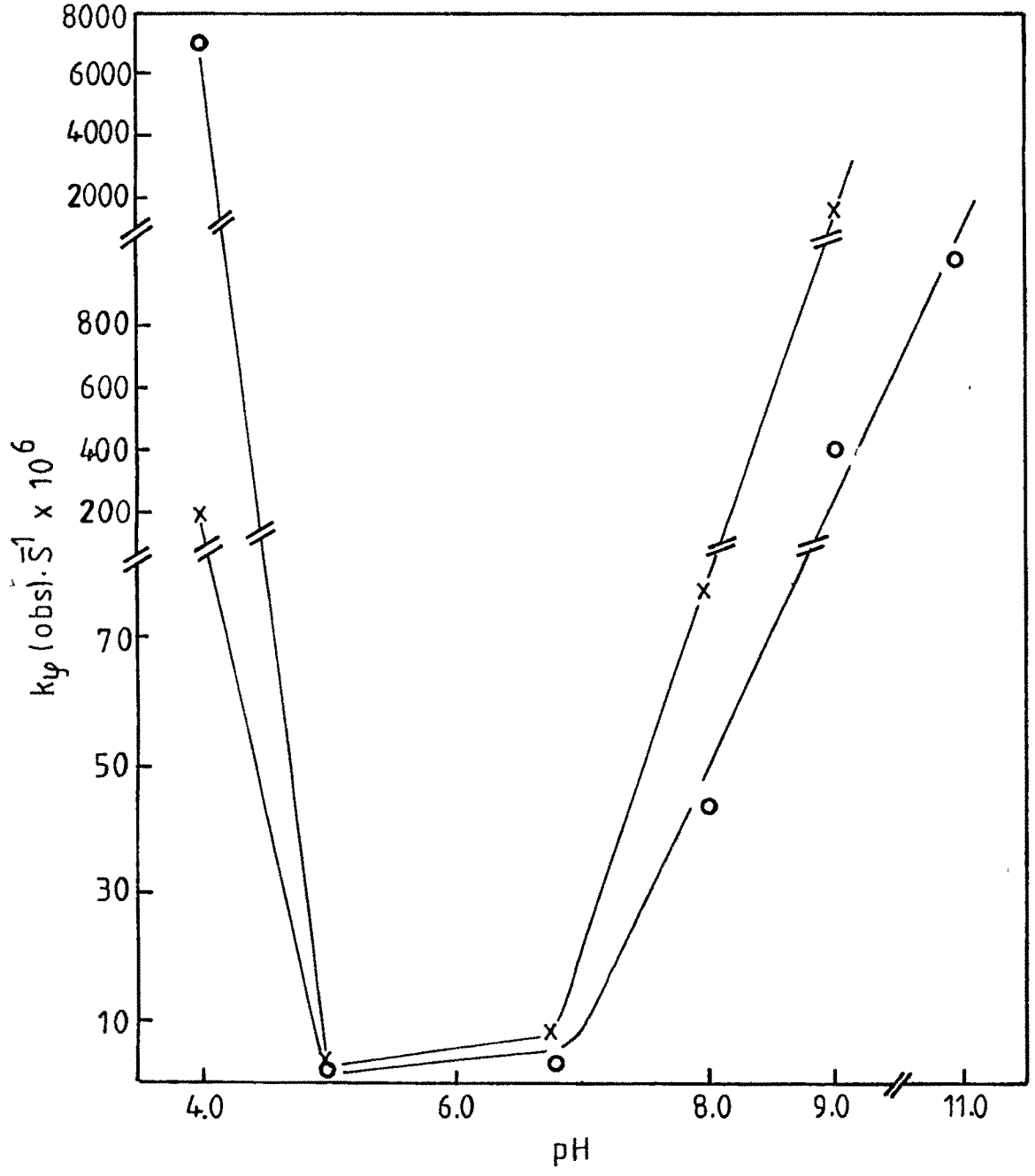


Fig 2 Effect of pH (O - In absence of CTAB, X - In presence of CTAB) on MeGly hydrolysis at 40°C

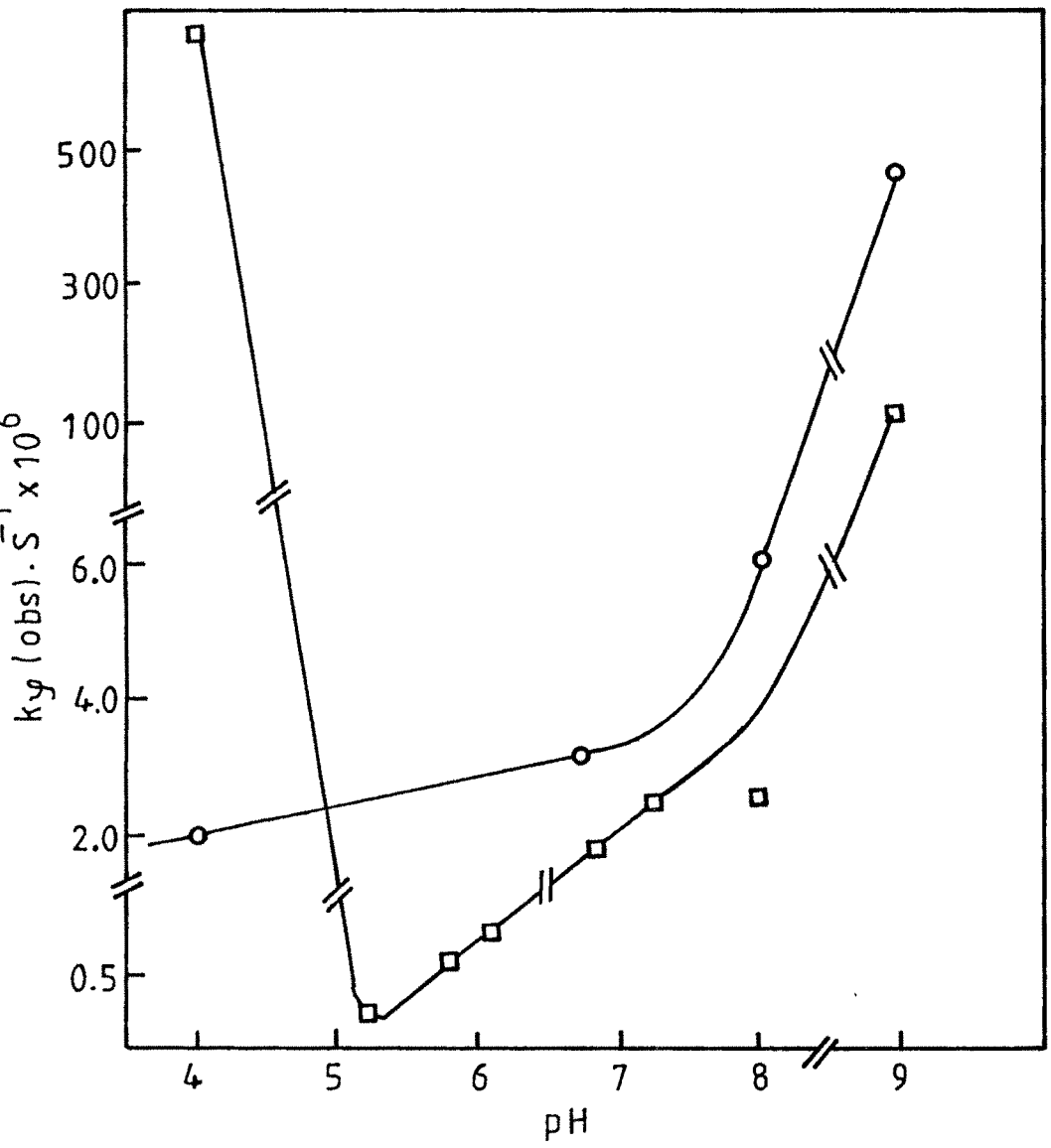


Fig 3 Effect of pH (□- In absence of CTAB, X - In presence of CTAB) on EtGly hydrolysis at 40°C

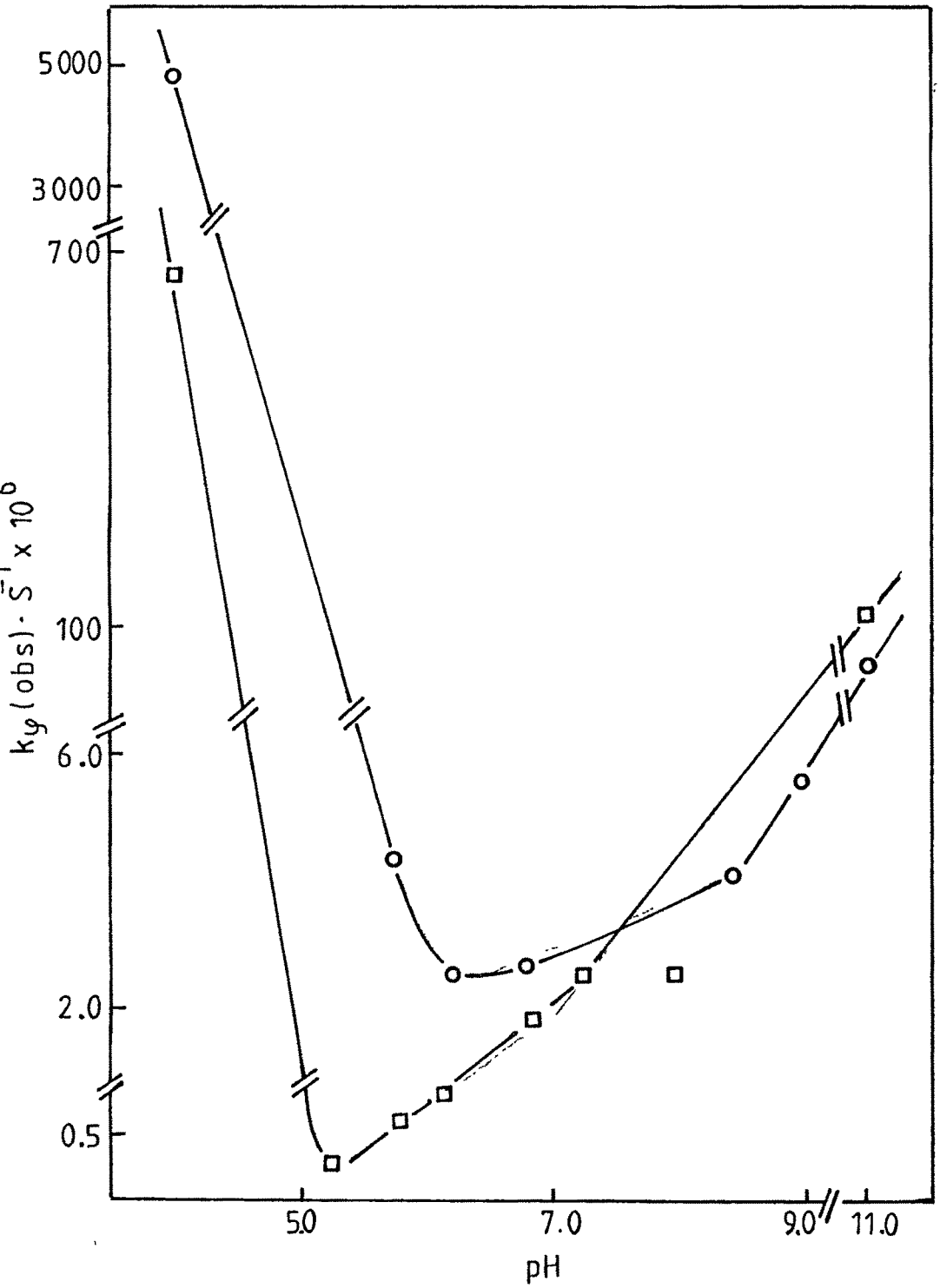


Fig 4 Effect of pH (□ - In absence of SDS, O- In presence of SDS) on EtGly hydrolysis at 40°C

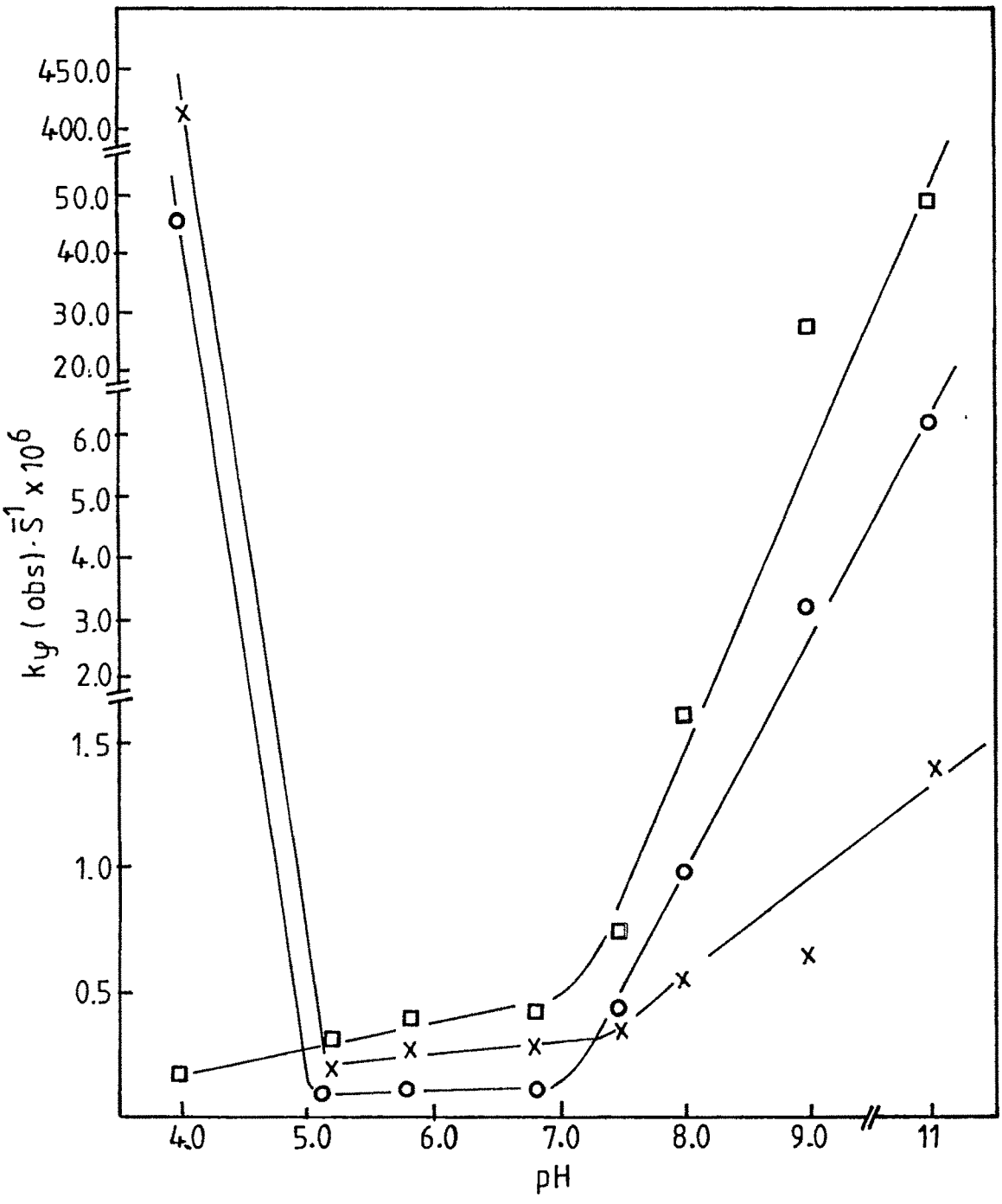


Fig 5 Effect of pH (O - In absence of Surfactant X - In presence of SDS, □- in presence of CTAB) on diMeGly hydrolysis at 40°C

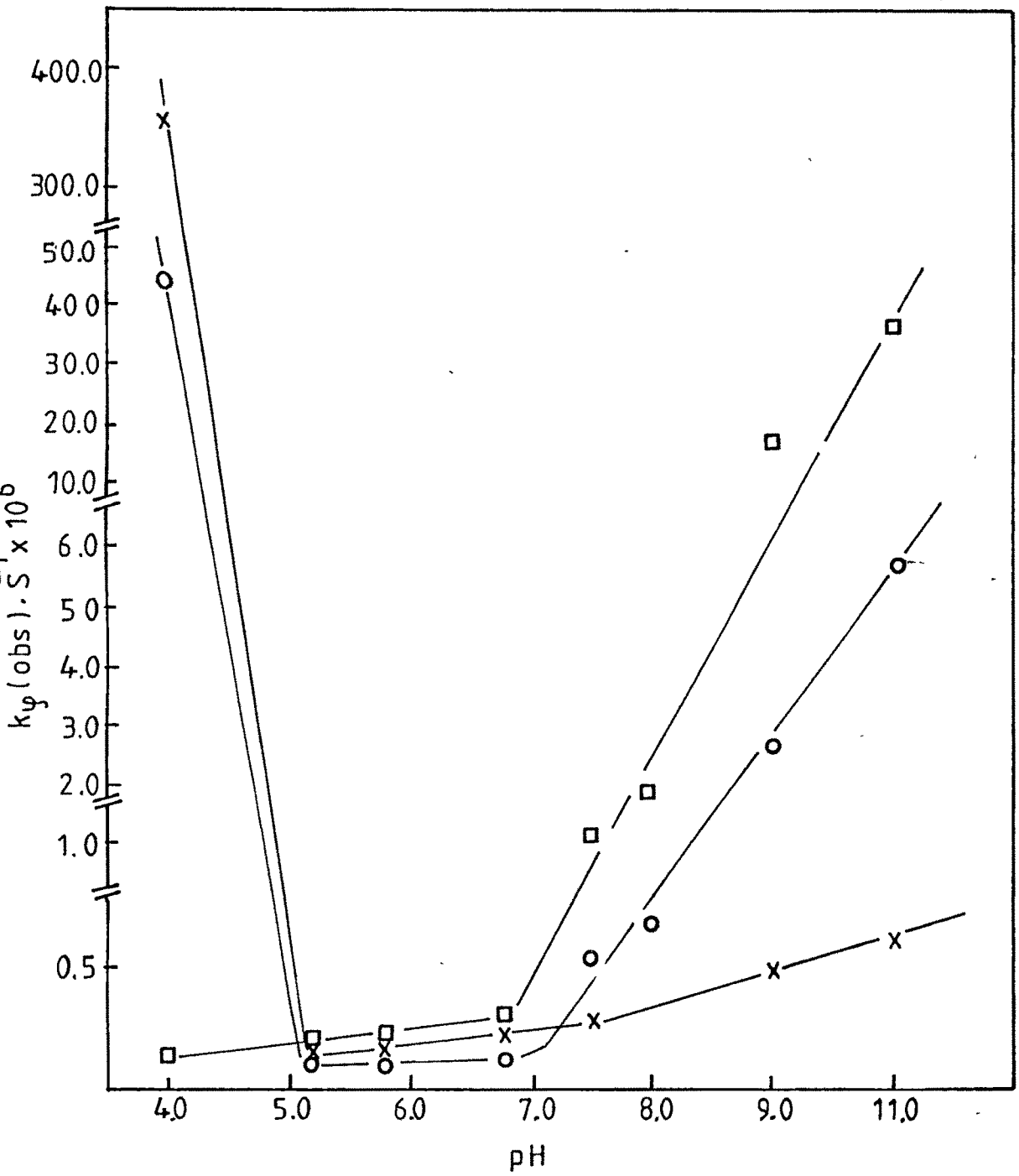


Fig 6 Effect of pH (O - In absence of Surfactant, X - In presence of SDS, □- in presence of CTAB) on PhGly hydrolysis at 40°C

When the hydrolysis was carried out in presence of surfactant, the effect on the value of rate constant depended on the pH value as well as on the type of the surfactant (cationic/anionic/non-ionic) used. In presence of cationic micelle, CTAB, the rate of hydrolysis of aminoacid esters at pH 4 was very much suppressed, where as with anionic micelle, SDS, a significant enhancement in rate was observed. For PhGly hydrolysis at pH 4, the rate was inhibited to an extent of ≈ 350 times in presence of CTAB (0 03 M), but in presence of SDS (0.03 M), there was 8.5 times enhancement in the rate CTAB at pH 11, enhanced the rate significantly, but SDS at this pH showed an opposite effect, i e , an inhibition of the rate was observed For example, the rate enhancement for diMeGly hydrolysis in presence of CTAB at pH 11 was about 7 8 times, but with SDS at the same pH, there was 4.2 times inhibition. Similar observations of enhancement and inhibition by CTAB/SDS were reported by many research workers [7-11]. The micellar medium can affect the rate of a reaction by bringing the reactants in close proximity of each other and thus enhancing the rate or keeping the reactant away from each other, thereby reducing the rate.[12,13]

These rate effects can be attributed to electrostatic and hydrophobic interactions between the substrate and the micelle [14].

The concentration of H^+ ions at pH 4 and OH^- ions at pH 11 are very large Thus at these pH values, electrostatic interaction is predominant CTAB being positively charged, attracts OH- ions at pH 11 and the negatively charged SDS, attracts H+ ions at pH 4. The attracted ions are brought to close proximity of micellar bound ester, thus making the attack of ions easier and faster and hence, the enhancement in the rate. When the attacking ions have the same charge as that of micelle, they are repelled. CTAB repels H^+ ions at pH 4 and SDS repels OH^- ions at pH 11. This results the distancing of attacking ions from the substrate and thus the rate is decreased

The importance of electrostatic interaction was confirmed, when Brij-35 was used as the surfactant It had no effect on the rate at low as well as at high pH. It is non-ionic, and has no charge on its surface, therefore, it can neither attract nor repel any ion, thus it shows neither catalytic nor inhibiting effect on the hydrolysis of ester at pH 4 and pH 11.

Surfactant concentration

The hydrolysis rate is affected by the concentration of surfactant in the medium The effect of concentration of surfactant on the rate of hydrolysis was studied in the range of $1x10^{-4}$ to $1x10^{-1}$ M, and the results are depicted in figs (7-15)

High and low pH

Effect of CTAB ·

With the increase in concentration of CTAB, the rate constant for hydrolysis, at low pH (pH 4) decreased upto certain concentration (0.02-0.03 M) of CTAB, and then it became constant, i.e., beyond this concentration, the rate was not affected by the change in concentration of CTAB. At pH 11, the rate constant increased initially, but became constant after 0 03 M CTAB

As explained earlier, H^+ ions are repelled by CTAB. This repulsion increased with increase in concentration of CTAB, because more and more positive charge were introduced in to the solution due to increase in CTAB concentration. This phenomena of repulsion reached a limit, when almost all H^+ ions catalysing the hydrolysis reaction were kept away from the ester, thus further increase in concentration of CTAB did not cause any more decrease in rate.

At high pH, the effect of CTAB was opposite to that at pH 4, i.e., the OH- ions were attracted to the micellar surface in this case and thus the reactive site of the glycine ester became accessible for these attacking ions. As the concentration of CTAB in the medium increases i e., as the micellar concentration increases, the amount of glycine ester bound to micellar medium also increases, not only that, more and more OH^- will be attracted towards the micelle, thus making its attack on ester more conducive. But a limit of this is reached after 0.03 M CTAB Beyond this concentration of CTAB, the counter ions of the surfactant is high enough to prevent any further increase of OH^- near the micelle. With the increase in micellar concentration the concentration of ester per unit volume of micelle decrease, that means there is a dilution effect which depends on the extent of hydrophobic interaction between glycine ester and micelle The rate should decrease as a result of dilution effect, but at pH 11 this effect is negligible compared to the

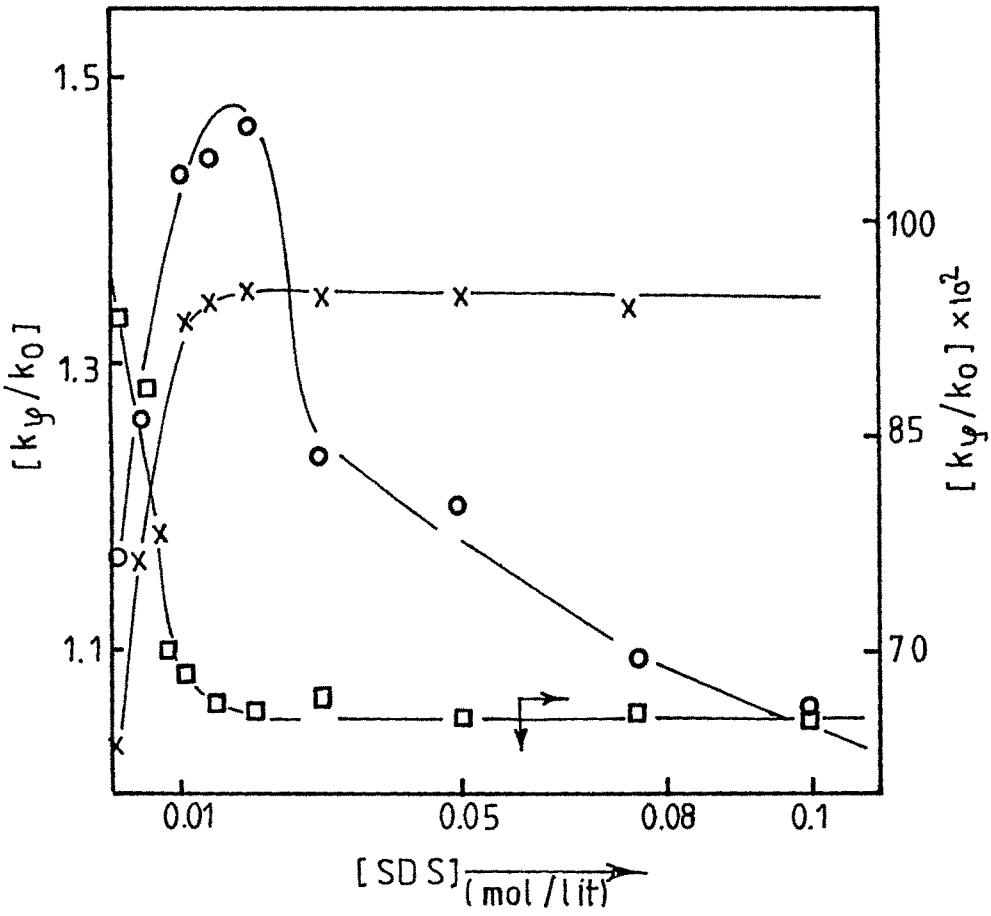


Fig.7 Variation of rate constant of hydrolysis of MeGly with concentration of SDS and pH at 40°C O - pH 6 8, X - pH 4, □ - pH 11

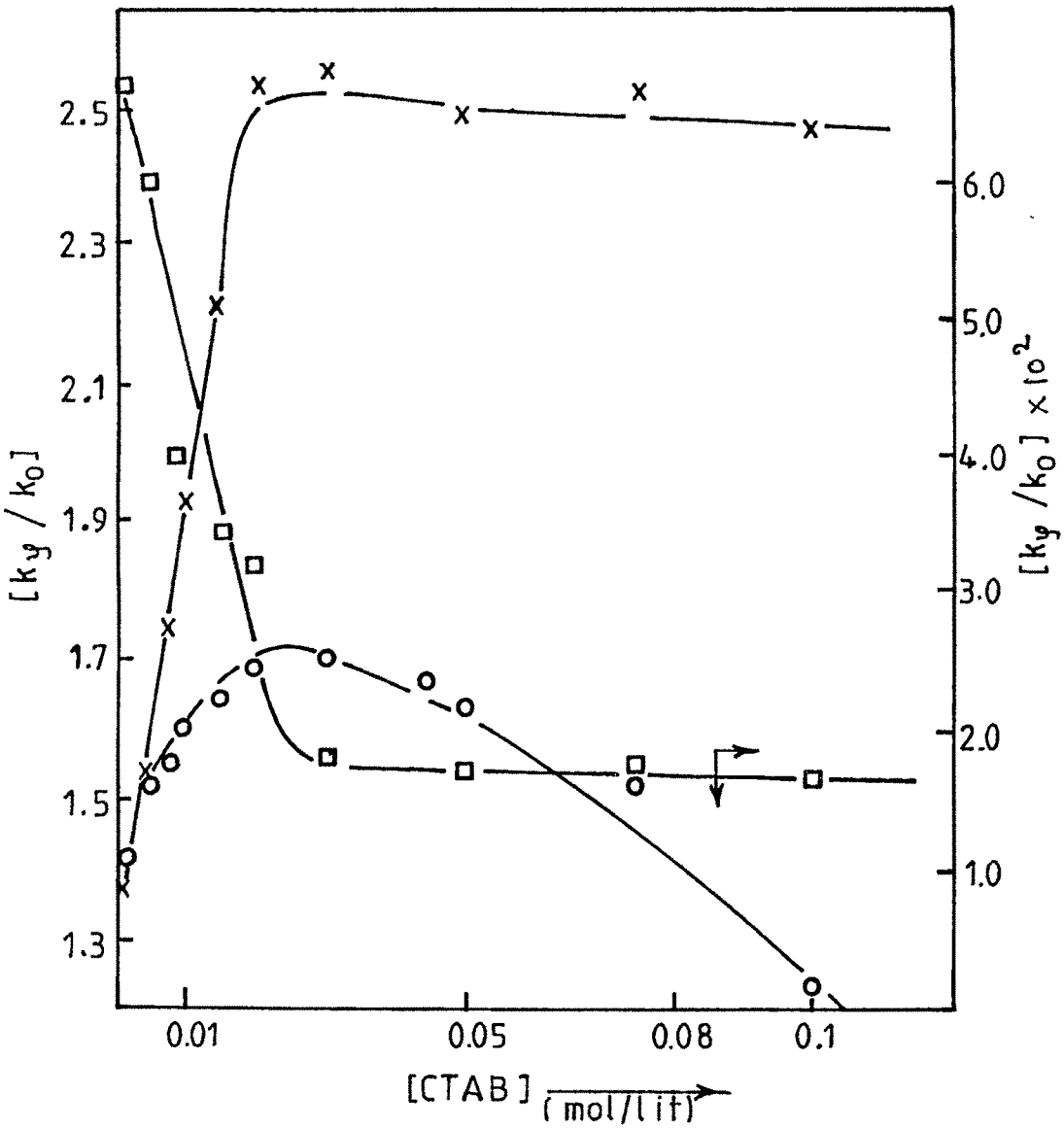


Fig 8 Variation of rate constant of hydrolysis of MeGly with concentration of CTAB and pH at 40°C O - pH 6.8, X - pH 11, □ - pH 4,

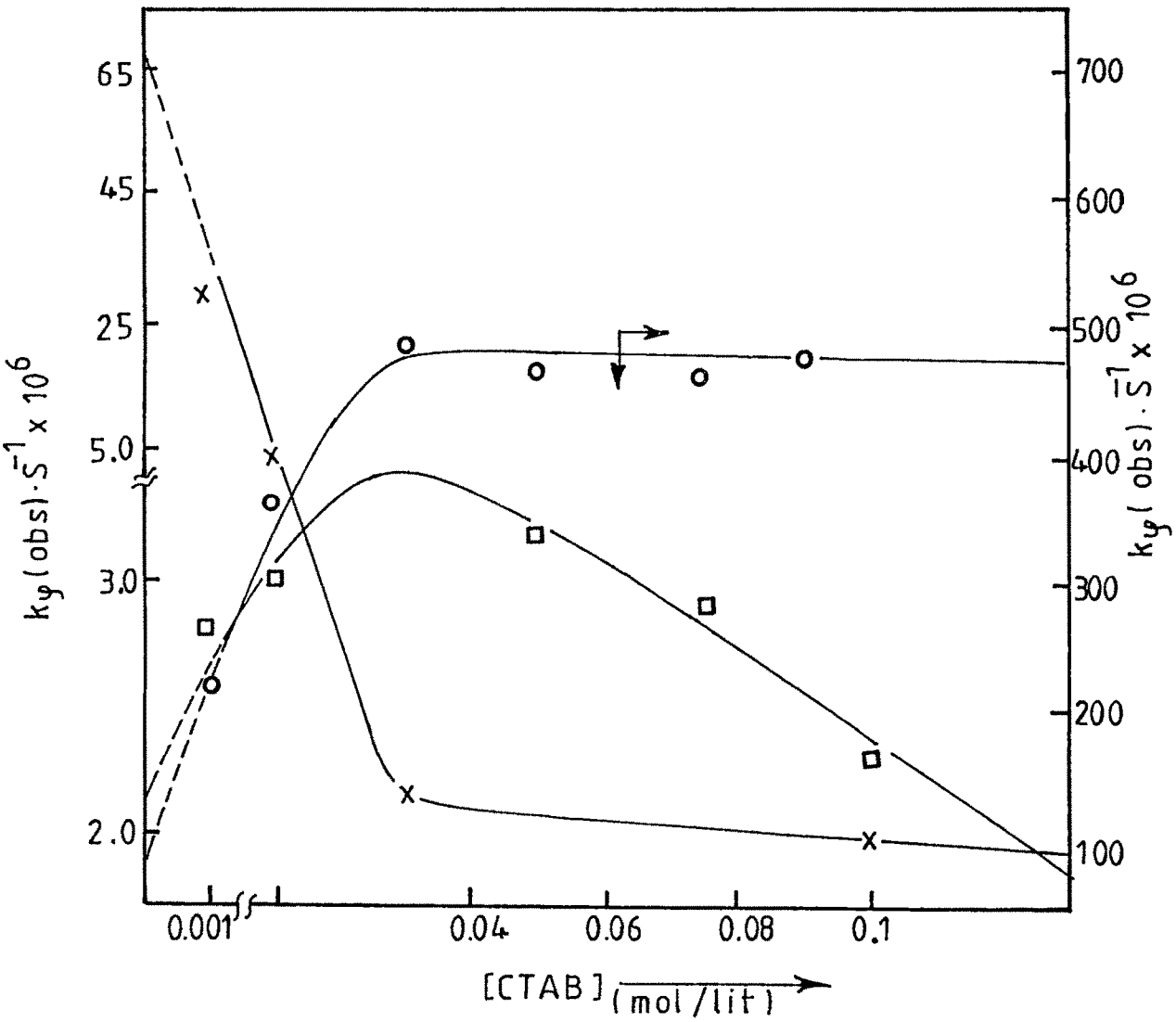


Fig 9 Variation of rate constant of hydrolysis of EtGly with concentration of CTAB and pH at 40°C O - pH 11, □ - pH 6 8, X - pH 4

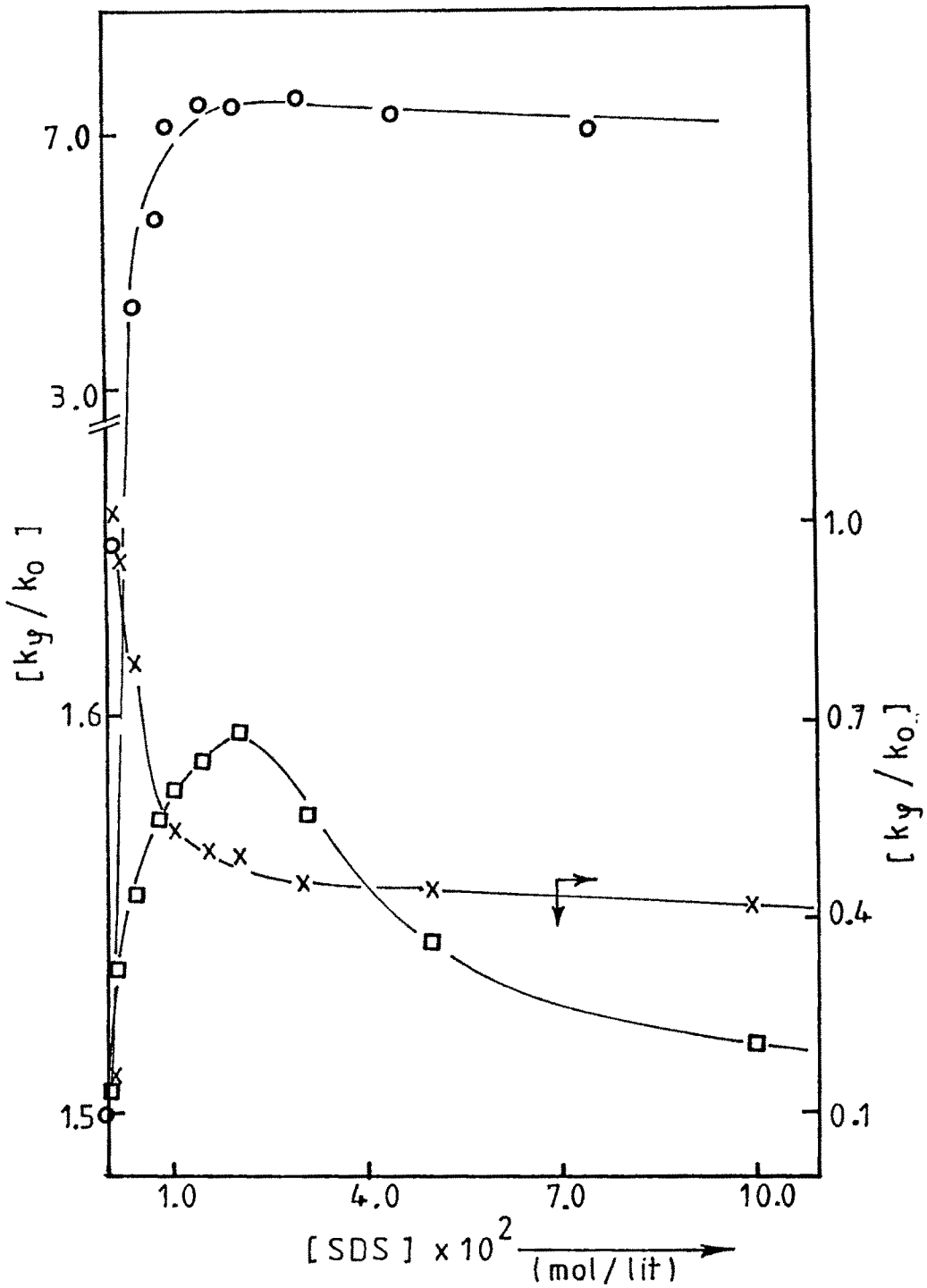


Fig 10 Variation of rate constant of hydrolysis of EtGly with concentration of SDS and pH at 40°C : □ - pH 6.8, X - pH 11, O - pH 4.

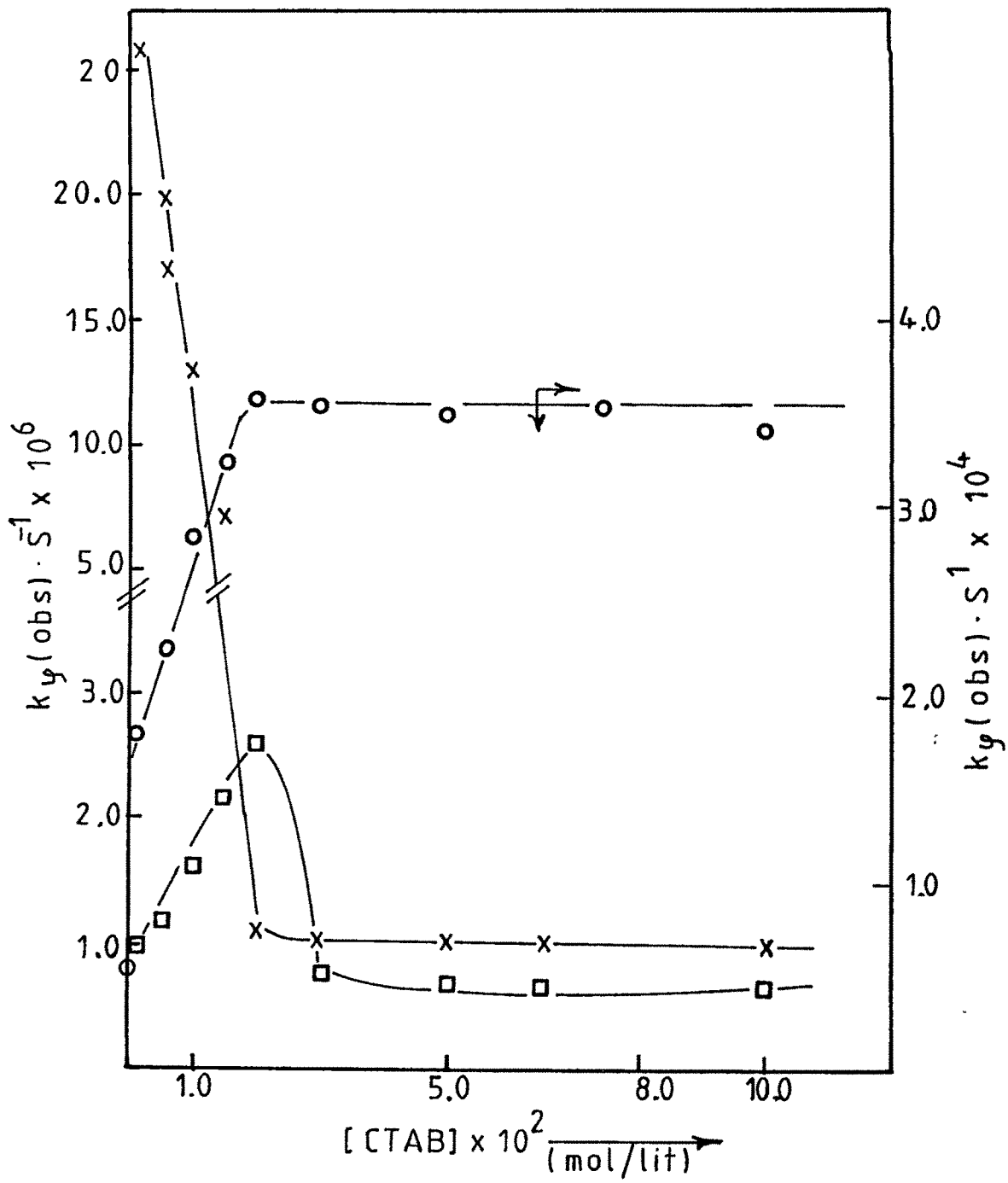


Fig.11 Variation of rate constant of hydrolysis of PhGly with concentration of CTAB and pH at 40°C : □ - pH 6.8, X - pH 4, O - pH 11.

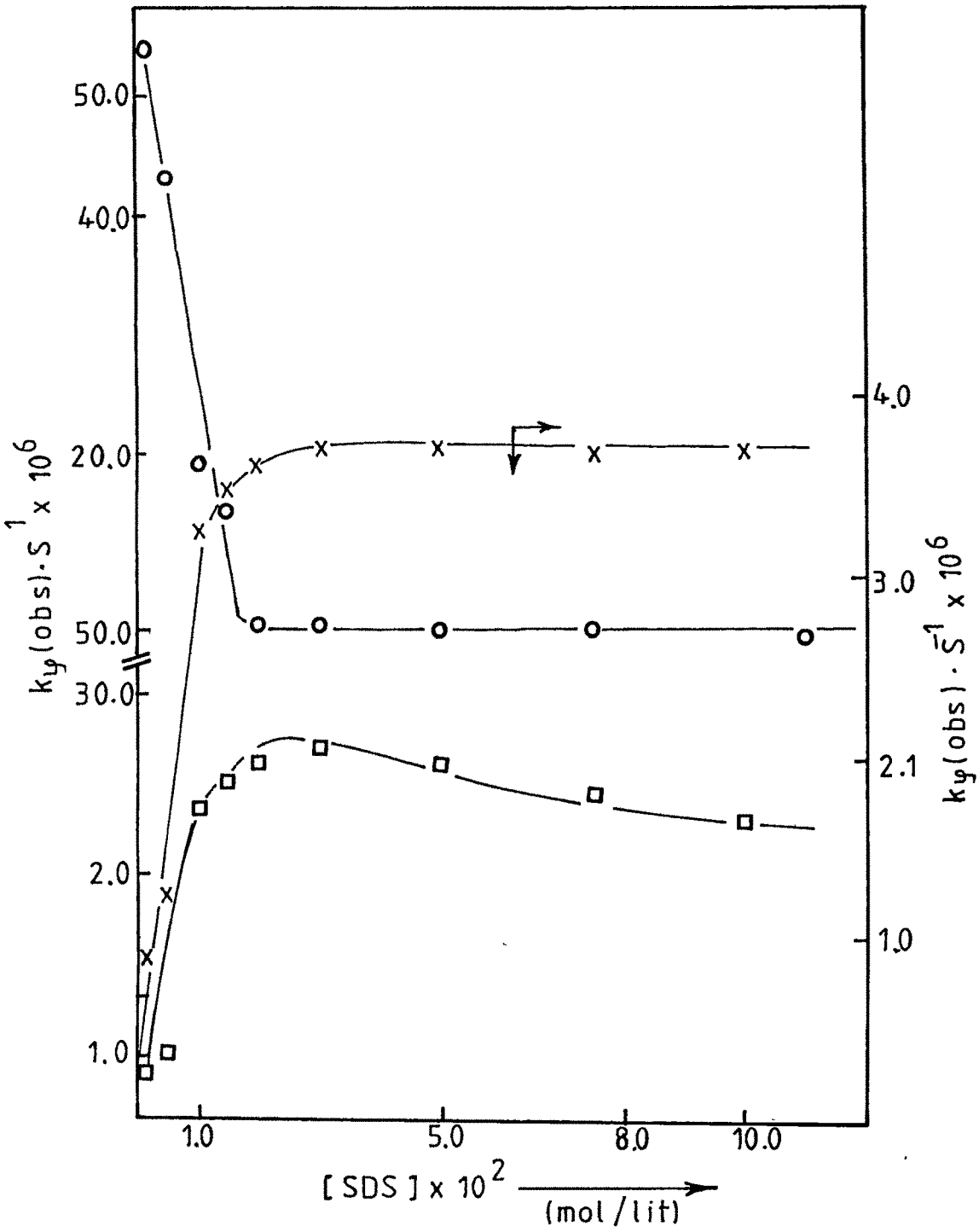


Fig 12 Variation of rate constant of hydrolysis of PhGly with concentration of SDS and pH at 40°C : □ - pH 6 8, X - pH 4, O - pH 11

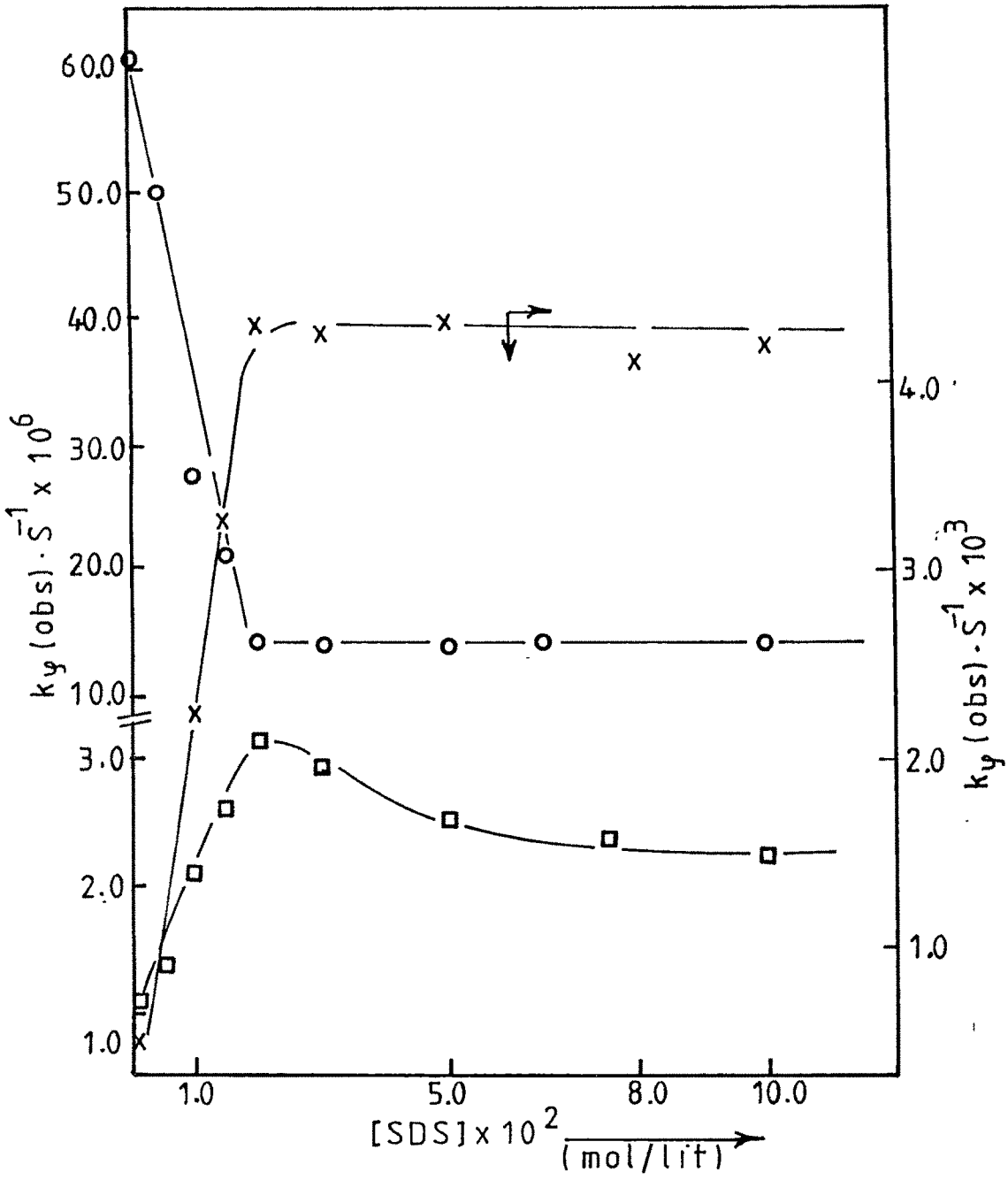


Fig 13 Variation of rate constant of hydrolysis of diMeGly with concentration of SDS and pH at 40°C · □ - pH 6.8, X - pH 4, O - pH 11.

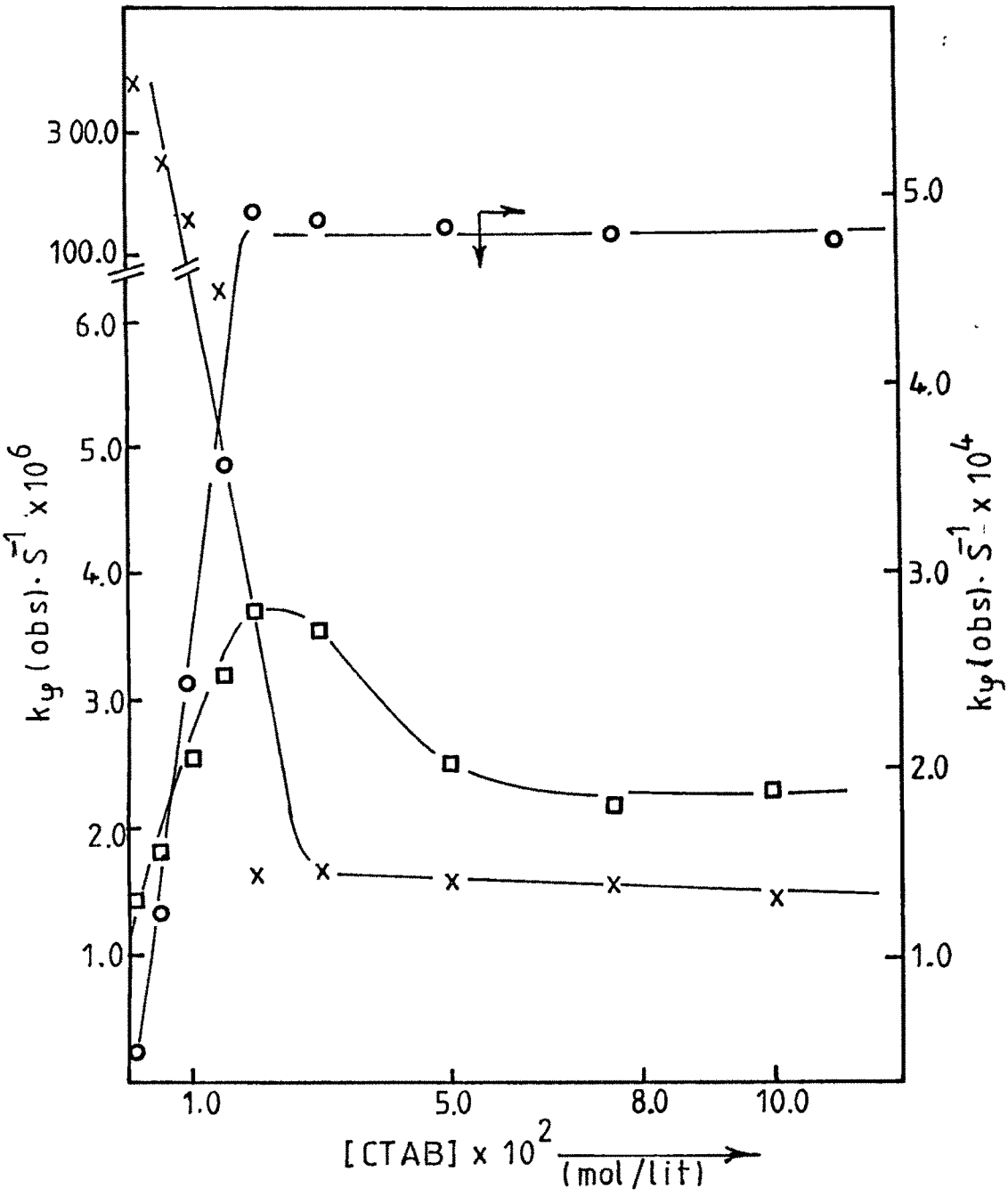


Fig.14 Variation of rate constant of hydrolysis of diMeGly with concentration of CTAB and pH at 40°C · □ - pH 6 8, X - pH 4, O - pH 11.

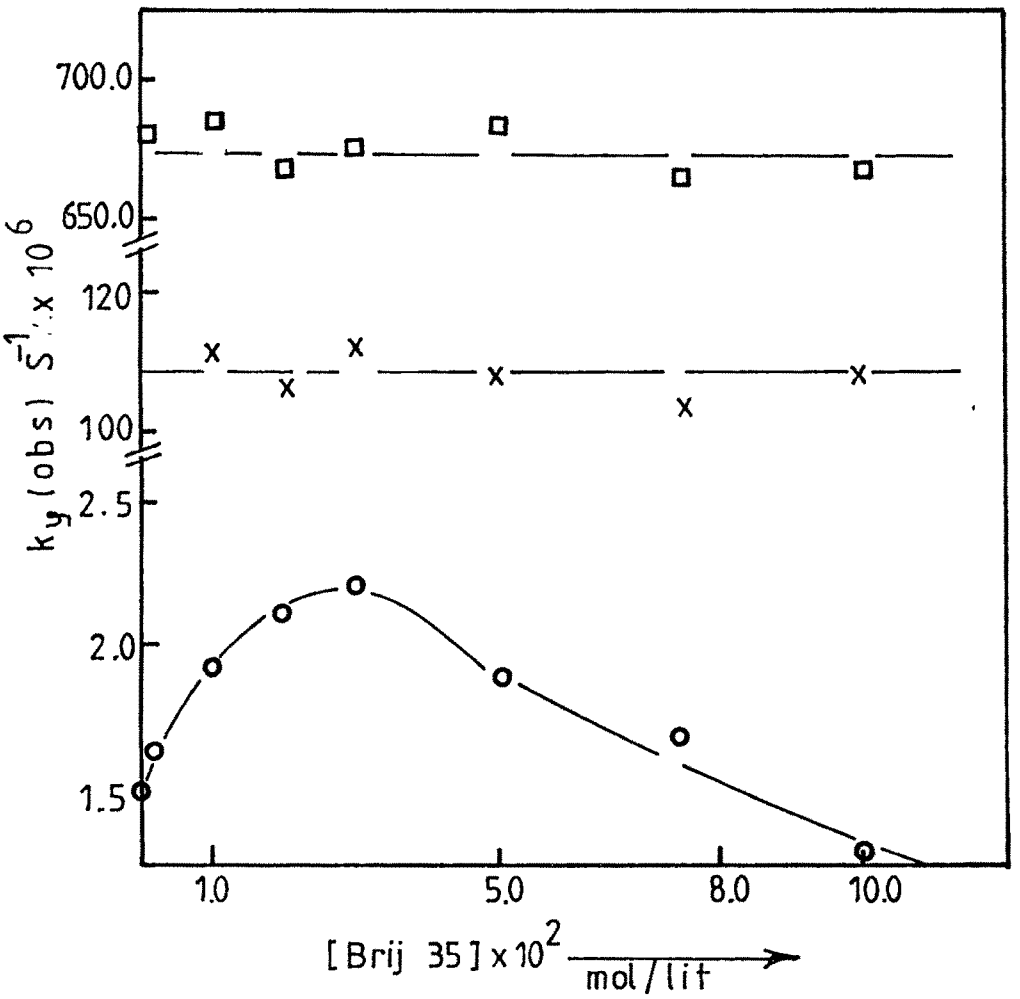


Fig 15 Variation of rate constant of hydrolysis of EtGly with concentration of Brij 35 and pH at 40°C : □ - pH 4, X - pH 11, O - pH 6.8

effect due to high OH^- ion concentration Thus the rate at pH 11 reach a limit and then become independent of the concentration of CTAB.

Effect of SDS :

The concentration effect of SDS on the ester hydrolysis was found to be opposite to that of CTAB at low and high pH. This is due to the electrostatic attraction of H^+ ions and repulsion of OH^- ions by SDS at pH 4 and pH 11 respectively. The enhancement in the rate at pH 4 with increase in concentration of SDS is due to increase in H+ ions as well as substrate concentration within the micellar pseudo phase. But the rate reached a limit at high concentration of surfactant and became constant due to no additional electrostatic interaction between H^+ ions and the negatively charged SDS micelle. The dilution effect of glycine ester at high concentration of SDS might not affect the rate, as explained earlier. At pH 11, the repulsion between OH^- and the SDS micelle, increased with the increase in concentration of micelle resulting into a decrease in rate and reached a limit, when all the OH^- ions were kept away from the ester. Thus the rate became independent of the concentration of surfactant beyond 0 02 M.

Effect of Brij-35 :

It was observed that, at high and at low pH, the non-ionic micelle did not have any effect on the rate of hydrolysis, as it could not affect any electrostatic interaction with the reactive ions (H^+ or OH^-) [3], and thus a change in concentration of Brij 35 in the medium $1.0x10^{-4}$ to $1x10^{-4}$ M has shown no change at all and a straight line graph parallel to concentration axis is obtained when k is plotted against the concentration of Brij 35 (Fig.15).

pH ≈ 7

At pH 6 8, the hydrolysis of all amino acid esters exhibited a similar rate profile with change in concentration of CTAB, SDS or Brij 35 (Fig. 7-15). The rate constant increased (though to a small extent) initially, with increase in concentration of surfactant,

reached a maximum and then decreased with further increase in surfactant concentration The maximum rate was obtained in the range of 0.02 to 0 03 M surfactant concentration.

Around pH 7, the concentration of H^+ and OH^- ions are equal and very low, and thus the rates of hydrolysis of aminoacid esters were also found to be very low ($\approx 10^{-6} S^{-1}$). The micellar medium, although has an effect, it is very small. The rate constant in presence of different surfactants has the following order,

CTAB > SDS > Brij 35

Brij 35 being non-ionic, does not have any electrostatic influence on H^+ or OH^- ions of the medium, still it has an effect on rate of hydrolysis. This could be due to hydrophobic interaction, which brings the substrate into a small volume of micelle thereby increasing the concentration of substrate, k values in presence of CTAB and SDS were little higher as there is electrostatic interaction between oppositely charged micelle and the ions, along with hydrophobic interaction Further, the rate in presence of CTAB is more than that in SDS, this could be due to the fact that, above pH 5, OH^- ion attack is more predominant[15] and hence CTAB may be having more effect At high and low pH, as the effect of electrostatic interaction is very high, the effect due to hydrophobic interaction becomes negligible, if the ester does not have high hydrophobicity.

It was observed that at all pH values studied (Table 1) in the absence of surfactant the rate of hydrolysis for the four glycine esters, have the following order:

MeGly > EtGly > diMeGly ≥ PhGly

As the ester group becomes larger, the hydrophobicity increases, decreasing the interaction with water and therefore, rate of hydrolysis decreases. When both the hydrogen of NH_2 group of glycine ester were substituted by methyl groups, there was an increase in the hydrophobicity of the molecule, causing the hydrolysis to be slower. But the greater the hydrophobicity of the molecule the easier for it to dissolve in micelle and hence there is a higher concentration of ester in micellar pseudo phase and thereby a greater enhancement in the rate as a result of presence of surfactant. The order of enhancement in the rate was

diMeGly > PhGly .> EtGly > MeGly

Thus it is very clear that, hydrophobic interaction in micellar medium plays an important role. The enhancement at pH 6.8 was found to be much less as compared to that at pH 4 or pH 11, showing that at low and high pH, when hydrophobicity of the substrate is high, the

Table 1 : Effect of hydrophobic interaction on glycine ester hydrolysis in micellar medium at different pH and at 40°C

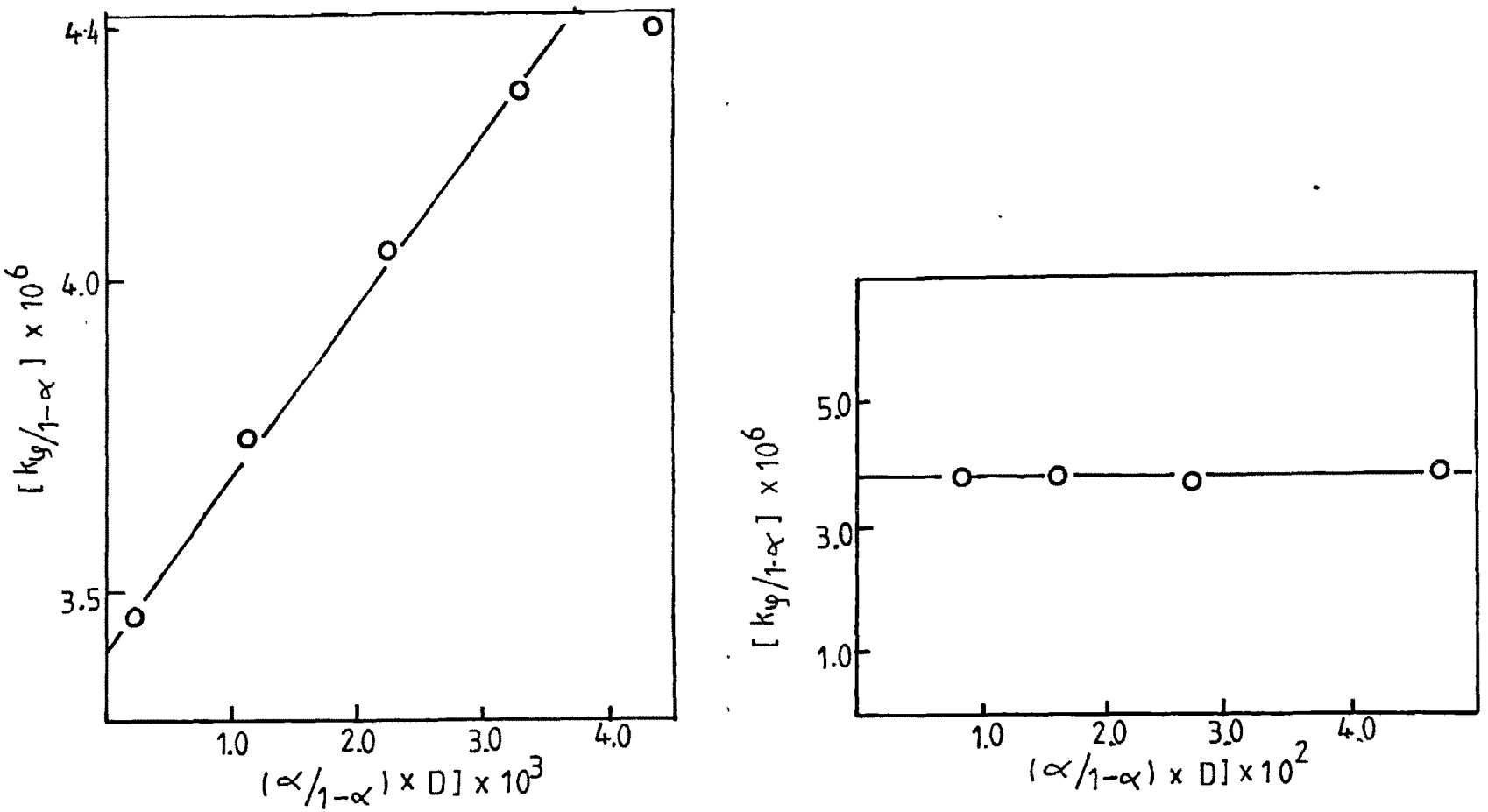
		pH 4	pH 6 8	pH 11	pH 4	pH 6.8	pH 11
Ester	Surfactant	$k_{\varphi(obs)}x10^4$	$k_{\varphi\ (obs)}x10^6$	$k_{\varphi\ (obs)}x10^4$	k_φ/k_0	k_φ/k_0	k_φ/k_0
MeGly	-	72.70	2.44	9 70	-	-	-
	CTAB	1.31	4.15	24.70	0.018	1.70	2.55
	SDS	98 0	3.59	6 47	1.35	1.47	0.667
	Brij35	72 40	2.83	9.74	0.995	1.16	1.0
EtGly	-	6 80	1.82	1.12	-	-	-
	CTAB	0.022	3.41	4.71	0.003	1.87	4.21
	SDS	52.10	2.87	0.49	7.66	1.58	0.44
	Brij35	6 77	2.17	1.14	0.995	1.20	1.01
PhGly	-	4.23	0.88	0.576	-	-	-
	CTAB	0.012	2.73	3.57	0.0027	3.09	6.20
	SDS	36.10	2.62	0.062	8.53	2.97	0.107
diMeGly	-	4.53	0.89	0 62	-	-	-
	CTAB	0 17	3 64	4 82	0.0038	4.10	7.77
	SDS	41.90	3.12	0.14	9.25	3.50	0.237

enhancement in the rate of hydrolysis is a combined effect of hydrophobic and electrostatic interactions.

The rate maxima observed for glycine ester hydrolysis in presence of cationic, anionic as well as non-ionic surfactant around pH 7 (well above the CMC of surfactant) also shows the importance of hydrophobic interaction in micellar medium. The maximum rate could be, at the surfactant concentration reacting at which the maximum amount of substrate might be bound with micelle. The micelle is considered as a seperate phase in the aqueous micellar system[16] with small volume as compared to aqueous phase. Therefore, the concentration of glycine ester within the micellar phase would be much higher than its stochiometric concentration. This concentration effect of glycine ester within micelle could be the major reason for maximum rate. Similar observations were reported in earlier studies also[17-21] But beyond this concentration of surfactant, at which the rate maximum was found, the effective concentration of glycine ester in micellar phase would be decreased, as a result of increase in number of micelles, which in turn was due to the addition of more and more surfactant to the system. Hence, the rate constant decreased from 0 03 M to 0.1 M of surfactant in the medium At 0.1 M surfactant concentration in the medium, the value of rate constant was found to be higher than that without surfactant in the medium It shows that there is no inhibition effect by any of the surfactant used at pH 6 8.

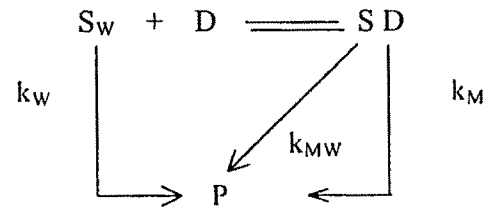
In short, the increase and decrease in rate profile for glycine ester hydrolysis around pH 7 is mainly due to the increase and decrease of concentration of glycine ester in the micellar phase. This shows the importance of hydrophobic interaction in micellar catalysis.

The PPIE model suggested by Bunton et al [22] and modified by Neve's et al [23] is used to explain the observed kinetic behaviour for glycinester – CTAB, as well as glycine ester –SDS systems. The model assumes micelle as a separate phase, uniformly distributed through out the bulk, and the micelle can affect catalysis by increasing the local concentration of reactants within the small volume of micellar pseudophase. The overall rate constant for a reaction in micellar medium is the combination of rate constant due to reaction between, bound substrate and reactive ion within micellar pseudophase, and the rate constant for reaction between micellar bound substrate, and the reactive ion from the aqueous phase The scheme for the reaction is as shown below·



a) [SDS] = 1 x 10^{-3} M to 2 x 10^{-2} M b) [SDS] = > 2 x 10^{-2} M

Fig. 16 Plot of [$k_{\psi(obs)}$ /α1-α] vs [(α/1-α) x D] for methyl glycinate hydrolysis in presence of SDS .



S_W	Substrate in water
D	Micellized surfactant
W and M	Water and Micellar pseudophase
k_M	Rate constant for reaction within micellar pseudophase
k_{MW}	Rate constant due to the reaction between micellar bound substrate and the reactive ion from aqueous phase.

For D>>CMC, the equation for rate constant is given as,

$$k_\varphi = \alpha\, k_{MW}\, [D] + k_M\, (1-\alpha) \qquad .. \ (1)$$

Where [D] is the concentration of the surfactant and α is the degree of micellar dissociation. The value of α is determined by the conductivity method [23], from the ratio of the slope of the plot of conductivity versus surfactant concentration, above and below the critical micelle concentration (CMC) of the surfactant. Using these values, k_M and k_{MW} were determined

Rearranging the equation (1), we have,

$$k_{\varphi(obs)} /(1-\alpha) = [\alpha /1-\alpha]\, [D]\, k_{MW} + k_M \qquad (2)$$

The slope and intercept of the plot of

$[k_{\varphi(obs)} /(1-\alpha)]$ vs $[\alpha/1-\alpha)\ [D]\ ]$, give the values of k_{MW} and k_M respectively. In the range of $1x10^{-3}$ M to $2x10^{-1}$ M surfactant, two linear plots were obtained for all the systems (Fig. 16). The values of α, k_M and k_{MW} are given in Table (2-4).

Many research workers in this field have reported α to be constant [18,22,24-26]. In the present study of hydrolysis of glycine ester in presence of surfactant, it was observed that, at very high and very low pH values, i.e., at pH 11 and pH 4, the α values were constant through out the concentration range of 0.001 M to 0.1 M surfactants,. But at pH 6 8, α values were found to be constant upto Cm. Cm is the concentration of the surfactant at which the rate constant attains either maximum or minimum value and beyond which the

Table 2 : α , k_M and k_{MW} values for Glycine ester hydrolysis in presence of CTAB

		α	$k_M.S^{-1}x10^4$		$k_{MW}\ S^{-1}x10^2$
Esters	[CTAB]→	0 001 to 0 1M	<0 02M	≥0.02M	< 0 02M
MeGly	pH 4	0 22	4.35	1.64	-2.47
	pH 11	0 20	14 50	30 40	33.20
EtGly	pH 4	0 20	0.40	0 026	-0.45
	pH 11	0.21	2 70	5.90	4.16
PhGly	pH 4	0 21	0 316	0.015	-0.566
	pH 11	0 21	2.22	4.54	4.58
diMeGly	pH 4	0 19	4 73	0 020	-13.20
	pH 11	0 19	0 074	5 92	12.80

Table 3 · α,k_M and k_{MW} values for Glycine ester hydrolysis in presence of SDS

		α	$k_M.S^{-1}x10^4$		$k_{MW}\ S^{-1}x10^2$
Esters	[SDS]→	0 001 to 0 1M	<0.02M	≥0.02M	< 0.02M
MeGly	pH 4	0 26	131 0	97 8	0.079
	pH 11	0.26	8 86	8.64	-0.030
EtGly	pH 4	0 19	26.6	62.0	111.0
	pH 11	0 18	0 998	0 58	-0 855
PhGly	pH 4	0 20	35 8	46.0	18.5
	pH 11	0.20	4 14	0 795	-6.50
diMeGly	pH 4	0 17	6.84	51 4	108
	pH 11	0.17	0 497	0 175	-0.778

Table 4: Values of α, k_M and k_{MW} for the Glycine ester hydrolysis in presence of Surfactants at 40°C and 6 8 pH

Ester	[Surfactant]→	α					$k_M x10^4$ S^{-1}		$k_{MW}x\ 10^2$ S^{-1}
		001 to 0 02M	0 03M	0 05M	0 075M	0 1M	<0.02M	>0 02M	<0.02M
MeGly	CTAB	0 22	0 22	0 25	0 30	0 32	0 046	0 053	0 012
	SDS	0 18	0 22	0 24	0 28	0 32	0 034	0 038	0 027
EtGly	CTAB	0 24	0 26	0 28	0 39	0 45	0 037	0 038	0 009
	SDS	0 18	0 25	0 35	0 36	0 26	0 029	0 035	0 015
PhGly	CTAB	0 21	0 22	0 24	0 25	0 26	0 0097	0 0095	0 046
	SDS	0 20	0 21	0.22	0 24	0 26	0 021	0.033	0.026
diMeGly	CTAB	0 19	0 19	0 21	0 22	0 26	0 016	0.045	0 065
	SDS	0 17	0.18	0.29	0 32	0 33	0 012	0 035	0 063

profile of rate constant changes. In all the cases studied Cm was found to be 0.02 M for SDS and 0.03 M, for CTAB. Above Cm, the α value at pH 6.8 slowly increased upto 0.1M of surfactant.

The values of k_M, though constant, were different above and below Cm The k_M values were found to be higher above Cm, where there was catalysis and lower where there was inhibition. k_{MW} values were either (-)ve, where there was inhibition or (+)ve for catalysis upto Cm For EtGly hydrolysis in presence of CTAB at pH 11, where there was catalysis, the values of k_{MW} and k_M upto Cm were 4.16×10^{-2} S^{-1}, and 2.70×10^{-4} S^{-1} respectively, where as above Cm, $k_M = 5.9 \times 10^{-4}$ S^{-1} For EtGly hydrolysis in presence of SDS at pH 11, where the inhibition is observed, the k_{MW} value was found to be -8.55×10^{-3} S^{-1}. Thus, the rate constant $k\varphi$ depended on α, k_{MW}, k_M and D.

CMC for CTAB and SDS in presence of MeGly, EtGly, PhGly and diMeGly were determined by conductivity and surface tension method The values are given in table 5. It is observed that the CMC values decrease with increase in the hydrophobicity of the glycine esters. It indicates that if the substrate is more hydrobhobic, it readily solubilizes within the micellar phase As the solubilization of the hydrocarbon in to the micellar core increase, the micelle become larger and swollen, and it gives more room for surfactant molecule and thus the CMC decreases The decrease in CMC with increase in solubilization of hydrocarbon was observed in earlier studies also[27]

In the case of CTAB, at pH 7 and pH 11, as the micellar concentration icnreases, initially it enhances (though to a very small extent at pH 7), the concentration of OH^- near the micellar surface due to strong electrostatic attraction and thus facilitate the attack of OH^- on the bound amino acid ester. The attack on the ester is not only from the micelle bound OH^- (k_M), but also there is an additional attack of these reactive counter-ions from across the boundary of micelle (k_{MW}) as shown in the scheme. Therefore, according to equation (2), the overall rate constant (k_φ) should increase linearly with increase in surfactant concentration. The rate constant increased upto 0.03 M CTAB. Beyond this concentration, the concentration of counter ions around micelle might be increased to such an extent that, it almost shields the attack of OH^- from the aqueous pseudophase to the micellar bound ester, i e , k_{MW} should be zero and the rate constant should depend only on k_M and α , and therefore equation (2) becomes,

Table 5 Values of CMC, Aggregation number and Binding constant for glycine ester hydrolysis in presence of surfactants at 35°C

Ester	Surfactant	CMC mole/dm^{-3}		Agg. No N	Binding Const K
		S T Method	Cond method		
MeGly	CTAB	8.90×10^{-4}	8.84×10^{-4}	62	1.90×10^{4}
	SDS	9.14×10^{-3}	8.90×10^{-3}	61	5.33×10^{5}
EtGly	CTAB	8.70×10^{-4}	8.50×10^{-4}	61	2.14×10^{4}
	SDS	9.0×10^{-3}	8.70×10^{-3}	61	5.66×10^{5}
diMeGly	CTAB	8.51×10^{-4}	8.40×10^{-4}	62	8.75×10^{4}
	SDS	8.70×10^{-3}	8.71×10^{-3}	60	1.41×10^{5}
PhGly	CTAB	8.47×10^{-4}	8.34×10^{-4}	59	8.97×10^{4}
	SDS	8.70×10^{-3}	8.62×10^{-3}	62	2.12×10^{5}

$$k_{\varphi} = k_M (1 - \alpha) \qquad \ldots (3)$$

Above 0.03 M CTAB (Cm), k_{MW} is zero and it was observed that, at pH 7, the value increased with the increase in concentration of CTAB, where as k_M was constant. Therefore, there should be a decrease in the value of observed rate constant (k_{φ}) with increase in concentration of CTAB. However, at pH 11, the α as well as k_M were constants and consequently the k_{φ} values should remain constant with increase in surfactant concentration above 0.03 M.

Equation (2) and (3), hold good for hydrolysis in presence of CTAB at pH 4 also. In this case, as α and k_M were constants and the k_{MW} value was negative (eqn.2), the k_{φ} value decreased with increase in surfactant concentration The negative sign of k_{MW} implies the inhibition, which is due to electrostatic repulsion between positively charged CTAB micelle and the attacking H+ ions at this pH. This inhibition effect increased with increasing concentration of the surfactant in the system and reached a limit around 0.03M CTAB. Beyond this concentration of the surfactant, the attack of H^+ ion, from aqueous phase, on the ester in the micellar pseudophase was not possible and thus k_{MW} became zero, and the rate constant k_{φ} follows equation (3) The k_{φ} value became independent of concentration of CTAB, as k_M and α remained constant above 0.03M CTAB.

As mentioned earlier, at pH 4, in presence of SDS, the rate increased with increase in surfactant concentration and then attained a limit around 0.02M SDS. But at pH 7, the rate was decreased beyond this concentration, similar to what was observed in the case of CTAB In presence of SDS, the initial enhancement in rate at pH 4 and 7, was due to the close proximity of H^+ ions and ester within the micelle. The strong electrostatic attraction between H^+ ions and SDS micelle, causes the additional attack of H^+ ions from the bulk phase (aqueous pseudophase) on the ester bound with micelle Hence k_M and k_{MW}, both contribute to the overall rate constant k_{φ} and equation (2) should be applicable in this case also As k_M and k_{MW} were having positive values and α was constant, k_{φ} should increase linearly with increase in SDS concentration, and which was found to be so

Beyond 0.02 M SDS, the attack of H+ ion from aqueous phase on the micellar bound ester was effectively stopped by the unreactive counter ions of SDS at pH 4 as well as at pH 7, therefore k_{MW} should be zero k_M and α being constant at pH 4, the k_{φ} becomes

constant. At pH 7, α values increased above 0.02 M SDS and thus k value was decreased At pH 11, SDS inhibits the reaction, because at this pH, k_M is positive but k_{MW} is negative and is constant At pH 4 as well as 11, beyond 0.02 M SDS, k_{MW} =0, and k_M are constants and hence k_φ became constant.

Using the values ofα, k_M and k_{MW}, k_φ was calculated ($k_{\varphi\ (cal)}$) and the results are presented in table (6-13). Kinetic simulation of the observed rate constants for some of the results are shown in figs (17-24). The model applied in this study was found to be satisfactorily agreeing with the experimental data.

The rate also depends on the reactivity of the substrate in the micellar phase and in the bulk phase. The extent of micelle substrate interaction had been estimated by K (binding constant) (Fig. 25) using the equation (4),[28].

$$1/k_0-k_\varphi\ (obs) = 1/k_0-k_M + [1/k_0-k_M]\ N/K(C_D-CMC) \qquad (4)$$

and plotting the graph,

- $[\ 1/\ k_0-k_\varphi(obs)]$ vs $1/(C_D-CMC)$

where K is the binding constant and N the aggregation number determined by fluorescence method [29] and the values of N obtained for CTAB and SDS (Table 5) were found to be close to the literature values [30,31]. C_D is the total surfactant concentration.

The k_M values determined using both the equations (2 and 4) were nearly same for each systems The k_M obtained using equation (4) for EtGly hydrolysis in presence of CTAB at pH 6.8 was 3 $10x10^{-6}$ S^{-1}, which is close to the value ($3.50x10^{-6}$ S^{-1}) obtained by equation (2) The extent of the effect of surfactant on the rate can be obtained from the k_M value. According to this model the extent of catalysis and inhibition can be predicted from ratio of k_M and k_0

If $k_M/k_0 > 0$, catalysis is observed and if $k_0/k_M > 0$, inhibition is observed. For example in case of EtGly hydrolysis in presence of CTAB at pH 6 8, k_M/k_0 = 1 70, showing that an enhancement of nearly 1 70 times should be obtained and the experimentally obtained enhancement was 1.87 times. k_M/k_0 at pH 11 was 4.8 and the experimental enhancement was 4.3 times. At pH 4, k_0/k_M=322.7 and the inhibition observed was 324 times.

Although this model (equation 4) could be used to explain the rate phenomenon up to the concentration of surfactant at which rate maxima is observed, it failed to explain the

Table 6. Experimental and calculated values of rate constants of MeGly hydrolysis in presence of CTAB at 40°C

[CTAB]	pH 4		pH 6 8		pH 11	
M	$k_{\psi obs}$ x 10^{4} S^{-1}	$k_{\psi cal}$ x 10^{4} S^{-1}	$k_{\psi obs}$ S^{-1} x 10^{6}	$k_{\psi cal}$ x 10^{6} S^{-1}	$k_{\psi obs}$ x 10^{3} S^{-1}	$k_{\psi cal}$ x 10^{3} S^{-1}
-	72.70	-	2.44	-	0.97	-
0.001	4.84	3.40	3.65	3.60	1.34	1.23
0.005	4 41	3.12	3 71	3.71	1.47	1.49
0.008	2.94	2.95	3.77	3.79	1.69	1.69
0.01	2.71	2.80	3.89	3.84	1.87	1.82
0.015	2.51	2.57	4.01	3.98	2.14	2 16
0 02	2.34	2.31	4.11	4.12	2.45	2.48
0.03	1.31	1.28	4.15	4.16	2.47	2.43
0.045	-	-	4.10	4.10	-	-
0.05	1.27	1.28	4.02	3.99	2.41	2.43
0.075	1.29	1.28	3.74	3.62	2.44	2.43
0.1	1.21	1.28	3.01	3.41	2.38	2.43

Table 7 Experimental and calculated values of rate constants of MeGly hydrolysis in presence of SDS at 40° C

[SDS]	pH 4		pH 6 8		pH 11	
M	$k_{\varphi obs}$ x 10^{3} S^{-1}	$k_{\varphi cal}$ x 10^{3} S^{-1}	$k_{\varphi obs}$ x 10^{6} S^{-1}	$k_{\varphi cal}$ x 10^{6} S^{-1}	$k_{\varphi obs}$ x 10^{4} S^{-1}	$k_{\varphi cal}$ x 10^{4} S^{-1}
-	7 27	-	2.44	-	9 70	-
0 001	7 47	9 69	2.84	2.85	9 01	6.56
0 005	8 41	9 69	3.08	3.04	8 51	6.56
0 008	8 61	9 69	-	-	6 76	6.56
0 010	9 70	9.69	3.32	3.28	6 66	6 55
0 015	9 76	9 68	3.52	3.51	6.44	6.56
0 020	9 80	9.68	3.59	3.75	6 41	6 57
0.030	9 79	9 68	3.01	2.96	6.47	6.40
0 500	9 77	9.68	2 93	2.89	6.36	6.40
0 075	9 68	9.68	2.68	2.73	6.39	6.40
0 100	8.67	9.68	2.61	2.58	6.42	6.40

Table 8 · Experimental and calculated values of rate constants of EtGly hydrolysis in presence of CTAB at 40°C

[CTAB]	pH 4		pH 6.8		pH 11	
M	$k_{\psi obs}$ x 10^{6} S^{-1}	$k_{\psi cal}$ x 10^{6} S^{-1}	$k_{\psi obs}$ x 10^{6} S^{-1}	$k_{\psi cal}$ x 10^{6} S^{-1}	$k_{\psi obs}$ x 10^{6} S^{-1}	$k_{\psi cal}$ S^{-1} x 10^{6}
0 001	30.40	30 60	2 81	2 82	2.17	2.19
0 005	25.40	26 00	-	-	-	-
0.01	6 06	2.21	3.02	3.01	3.63	3.02
0 02	12 90	12.70	3.20	3 22	3.87	3.93
0.03	2 21	2.08	3.41	3 42	4 81	4.85
0.05	2.10	2.11	3.21	2.81	4 71	4 72
0.075	2 01	2.08	2.70	2.74	4.65	4.66
0 1	2.18	2.11	2.33	2.32	4.77	4.72
0.2	-	-	2.08	2.09	4.72	4 72

Table 9 . Experimental and calculated values of rate constant of Et Gly hydrolysis in presence of SDS at 40oC

[CTAB] M	pH 4		pH 6 8		pH 11	
	$k_{\psi obs}$ x 10^3 S^{-1}	$k_{\psi cal}$ x 10^3 S^{-1}	$k_{\psi obs}$ x 10^6 S^{-1}	$k_{\psi cal}$ x 10^6 S^{-1}	$k_{\psi obs}$ x 10^5 S^{-1}	$k_{\psi cal}$ x 10^5 S^{-1}
-	0 68	-	1.82	-	11 20	-
0 0001	0 689	-	1.95	-	11.60	-
0.001	1 27	-	2.20	-	10.60	-
0 005	3.01	3 21	2 39	2 56	8 72	7 41
0.008	3.87	3 84	2.64	2.60	6 77	6 90
0.010	4.89	4 26	2.71	2.65	6 59	6.64
0.015	5 01	5 30	2.79	2 78	5 67	5.87
0 020	5.10	5 02	2.87	2.79	5 70	4.76
0 030	5.21	5 02	2.63	2.59	4.90	4 76
0 045	-	-	2.34	2.38	-	-
0.050	4 95	5 02	2.27	2.24	4.79	4.76
0.075	-	-	2.19	2.20	-	-
0 100	2.31	5 02	2.02	2.51	4.67	4.76

Table 10 · Experimental and calculated values of rate constants of diMeGly hydrolysis in presence of CTAB at 40°C

[CTAB]	pH 4		pH 6 8		pH 11	
M	$k_{\varphi obs}$ x 10^{5} S^{-1}	$k_{\varphi cal}$ x 10^{5} S^{-1}	$k_{\varphi obs}$ x 10^{6} S^{-1}	$k_{\varphi cal}$ x 10^{6} S^{-1}	$k_{\varphi obs}$ x 10^{4} S^{-1}	$k_{\varphi cal}$ x 10^{4} S^{-1}
0 001	36 7	35 8	1.47	1 42	0 26	0.30
0 005	25 2	25 8	1 84	1 91	1 21	1 28
0.01	13 1	13 2	2 55	2 54	2 37	2.49
0 015	0 65	0.70	3 17	3.16	3.60	3.71
0.02	0 16	0 16	3 64	3 65	4 90	4.92
0 03	0 17	0.16	3.63	3 65	4 82	4 80
0.05	0.15	0.16	3.52	3.56	4.84	4.80
0.075	0.16	0.16	3 46	3 51	4.76	4.80
0.1	0 14	0 16	3 30	3.33	4.67	4.80

Table 11 Experimental and calculated values of rate constants of diMeGly in presence of SDS at 40°C

[SDS]	pH 4		pH 6.8		pH 11	
M	$k_{\varphi obs}$ x 10^{3} S^{-1}	$k_{\varphi cal}$ x 10^{3} S^{-1}	$k_{\varphi obs}$ x 10^{6} S^{-1}	$k_{\varphi cal}$ x 10^{6} S^{-1}	$k_{\varphi obs}$x 10^{5} S^{-1}	$k_{\varphi cal}$ x 10^{5} S^{-1}
0 001	10 46	-	1 17	-	6.07	-
0 005	10 88	1.41	-	-	5 01	-
0 010	2 36	2.40	2.14	2.04	2 77	2.80
0.015	3.25	3 32	2.61	2.58	2 17	2.14
0 020	4 27	4.24	3.12	3.11	1.44	1.48
0 030	4.19	4.27	2 90	2.89	1.47	1.45
0 050	4.23	4 27	2.46	2.50	1.42	1.45
0 075	4 01	4.27	2 41	2.39	1.37	1.45
0 100	4.16	4.27	2.30	2.36	1.39	1.45

Table 12 Experimental and calculated values of rate constants of PhGly hydrolysis in presence of CTAB at 40°C

[CTAB]	pH 4		pH 6 8		pH 11	
M	$k_{\phi obs}$ x 10^6 S^{-1}	$k_{\phi cal}$ x 10^6 S^{-1}	$k_{\phi obs}$ x 10^6 S^{-1}	$k_{\phi cal}$ x 10^6 S^{-1}	$k_{\phi obs}$ x 10^4 S^{-1}	$k_{\phi cal}$ x 10^4 S^{-1}
0.001	20 41	23 88	1.01	0 86	1 75	1 85
0 005	17.34	19 02	1 21	1.25	2.24	2 24
0 010	12.82	13 10	1.60	1.73	2 88	2.72
0.015	7 10	7.14	2.17	2 21	3.24	3.20
0 020	1 17	1 19	2.73	2.70	3 57	3.68
0 030	1.13	1.16	0.76	0 74	3.56	3.58
0.050	1.15	1.16	0.73	0.72	3 51	3.58
0.075	1.17	1.16	0 72	0.71	3 56	3.58
0 100	1.17	1.16	0.68	0 70	3 48	3.58

Table 13· Experimental and calculated values of rate constants of PhGly hydrolysis in presence of SDS at 40°C

[SDS] M	pH 4		pH 6.8		pH 11	
	$k_{\psi obs}$ x 10^3 S^{-1}	$k_{\psi cal}$ x 10^3 S^{-1}	$k_{\psi obs}$ x 10^6 S^{-1}	$k_{\psi cal}$ x 10^6 S^{-1}	$k_{\psi obs}$ x 10^5 S^{-1}	$k_{\psi cal}$ x 10^5 S^{-1}
0 001	0.87	-	0.91	-	5.41	-
0 005	1.21	-	1.09	-	4.27	-
0.010	3.24	3.23	2.38	2.20	1.92	2.01
0 015	3.40	3.42	2.50	2.46	1.56	1.36
0.020	3.61	3.60	2.62	2.72	0.62	0.71
0 030	3.65	3.68	2.65	2.62	0.64	0.64
0.050	3.62	3.68	2.60	2.58	0.63	0.64
0 075	3.63	3.68	2.48	2.50	0.60	0.64
0.100	3.64	3.68	2.40	2.45	0.61	0.64

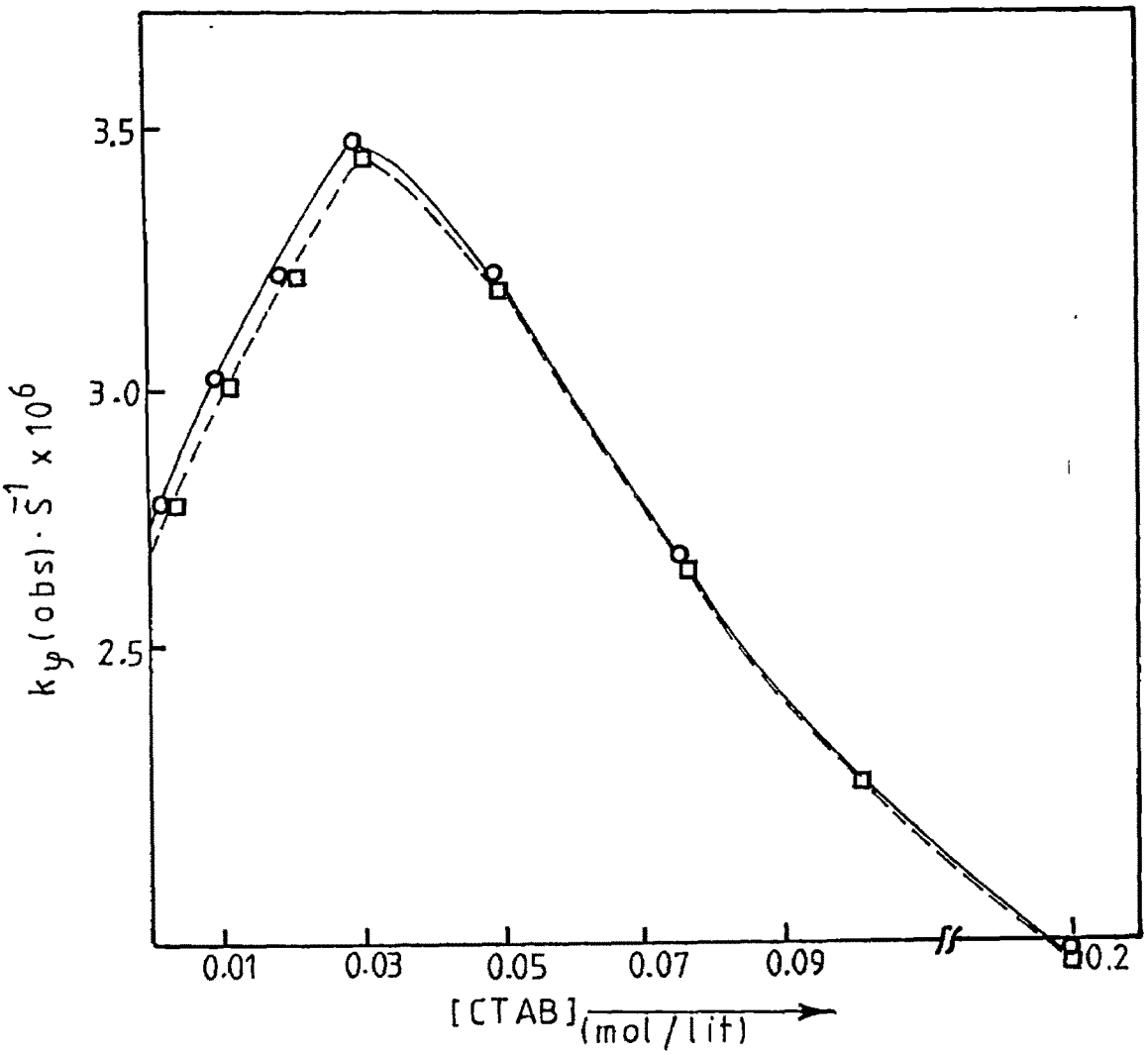


Fig 17 PPIE simulation of kinetic data for EtGly hydrolysis in presence of CTAB at pH 6.8 and at 40°C (O - $k_{\psi\,(observed)}$, □ - $k_{\psi\,(calculated)}$)

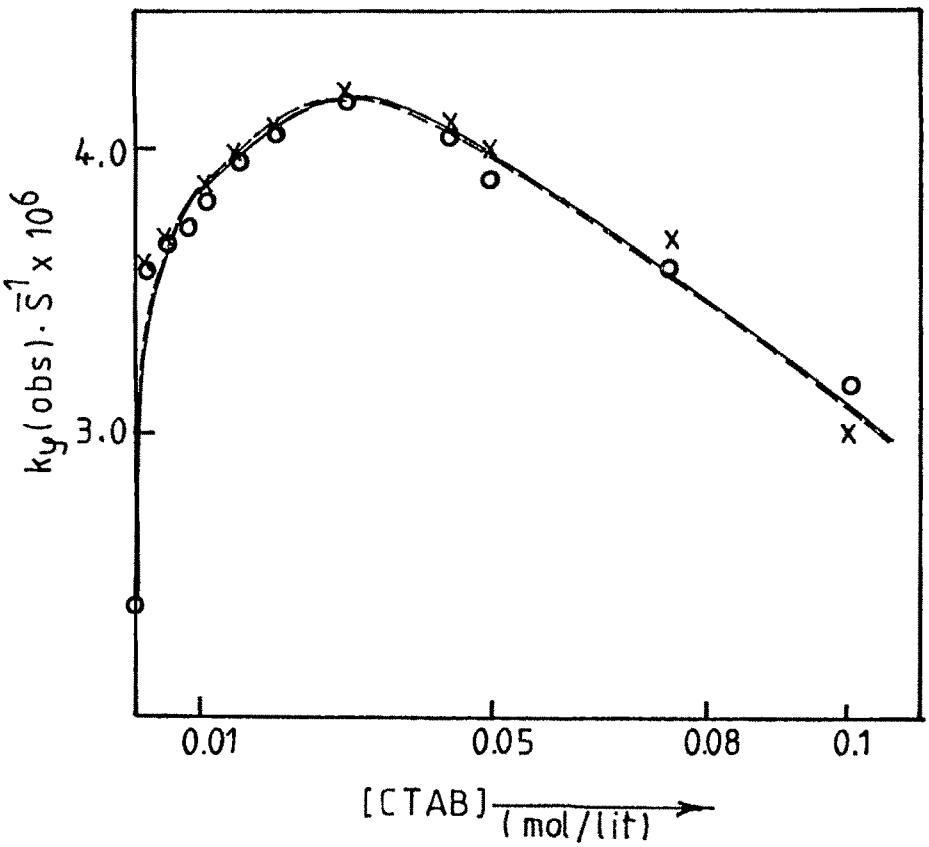


Fig. 18 PPIE simulation of kinetic data for MeGly hydrolysis in presence of CTAB at pH 6 8 and at 40°C (O - $k_{\varphi\,(observed)}$, X - $k_{\varphi\,(calculated)}$)

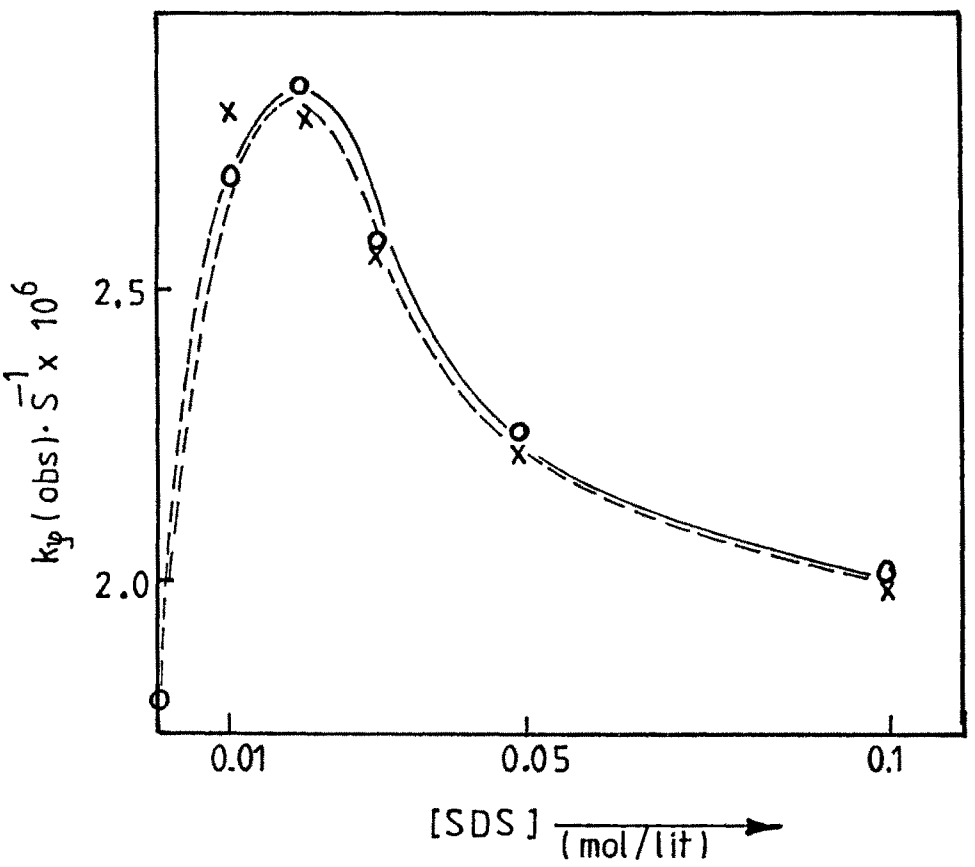


Fig 19 PPIE simulation of kinetic data for EtGly hydrolysis in presence of SDS at pH 6.8 and at 40°C (O - $k_{\varphi\,(observed)}$, X - $k_{\varphi\,(calculated)}$)

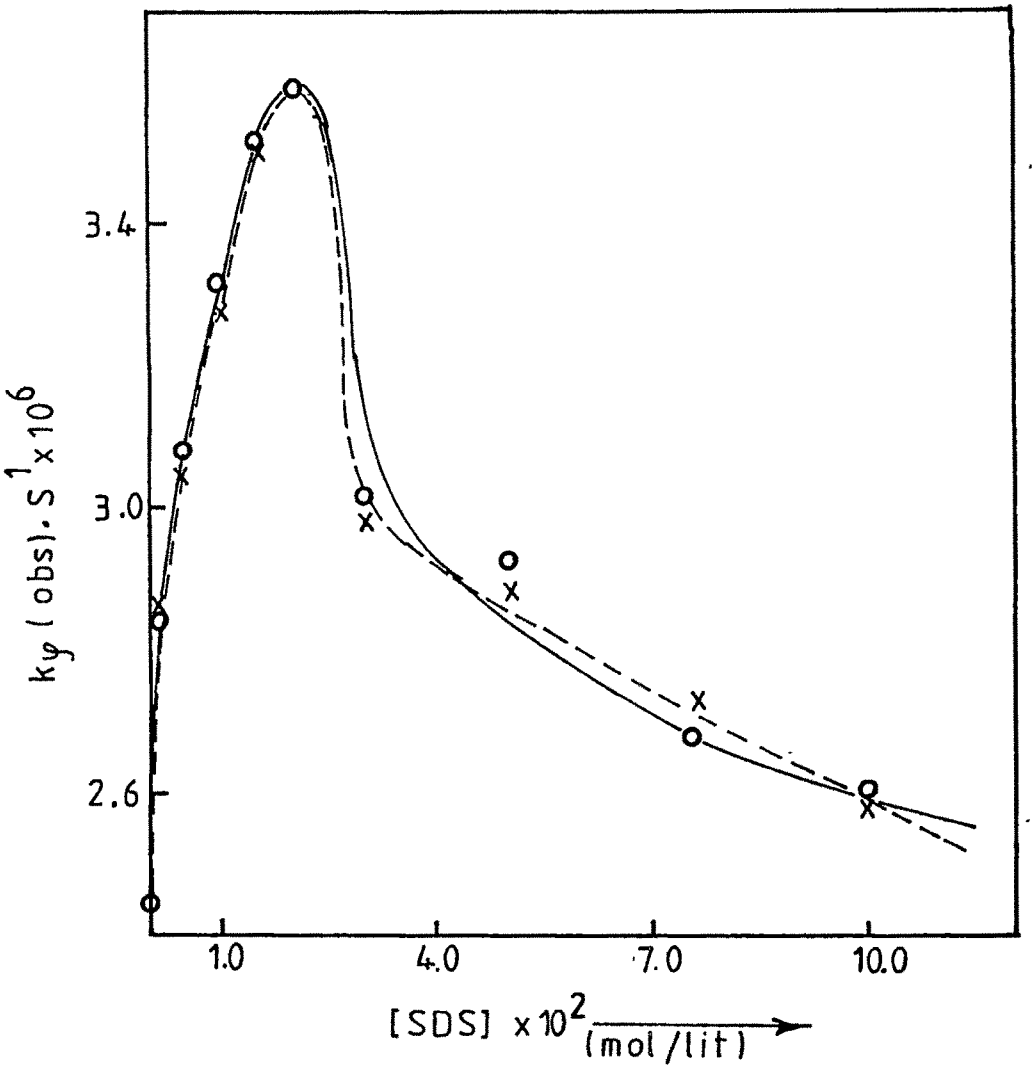


Fig. 20 PPIE simulation of kinetic data for MeGly hydrolysis in presence of SDS at pH 6.8 and at 40°C (O - $k_{\psi\,(observed)}$, X - $k_{\psi\,(calculated)}$)

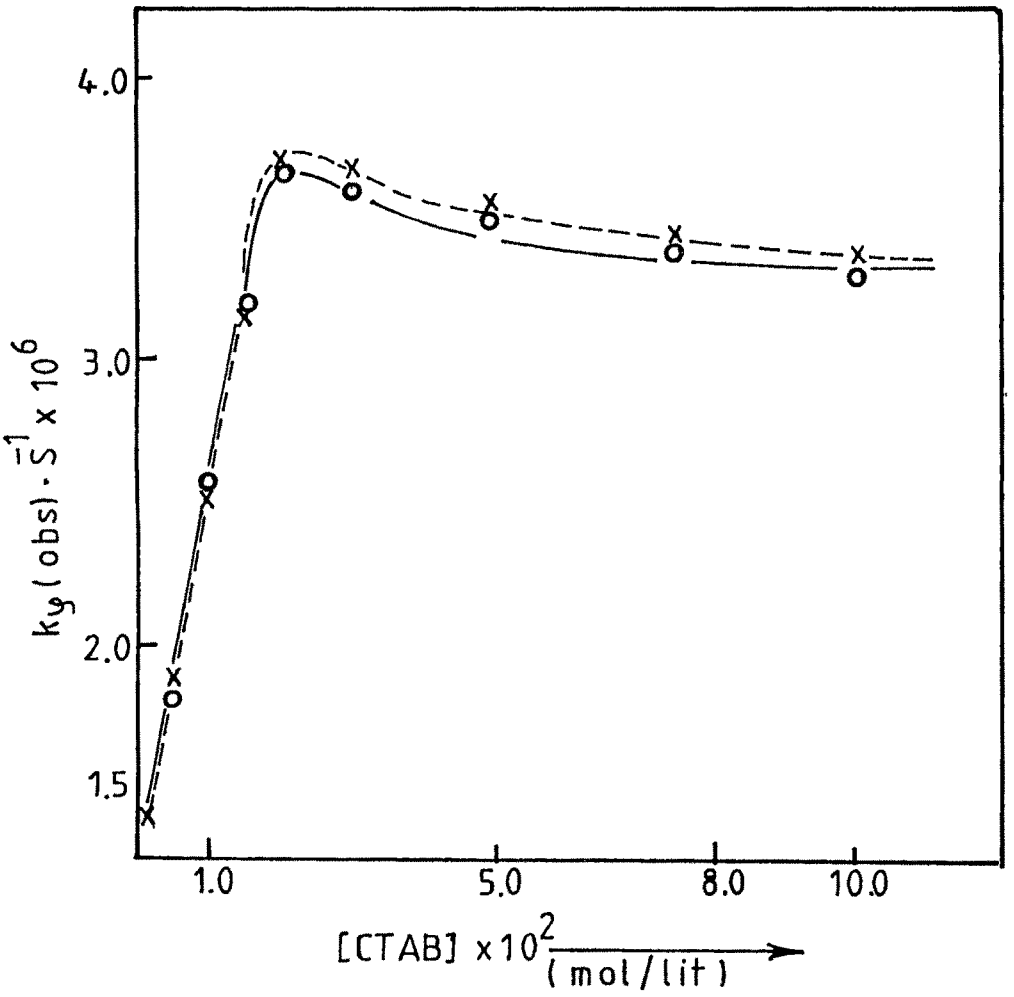


Fig 21 PPIE simulation of kinetic data for diMeGly hydrolysis in presence of CTAB at pH 6.8 and at 40°C (O - $k_{\varphi\,(observed)}$, X - $k_{\varphi\,(calculated)}$)

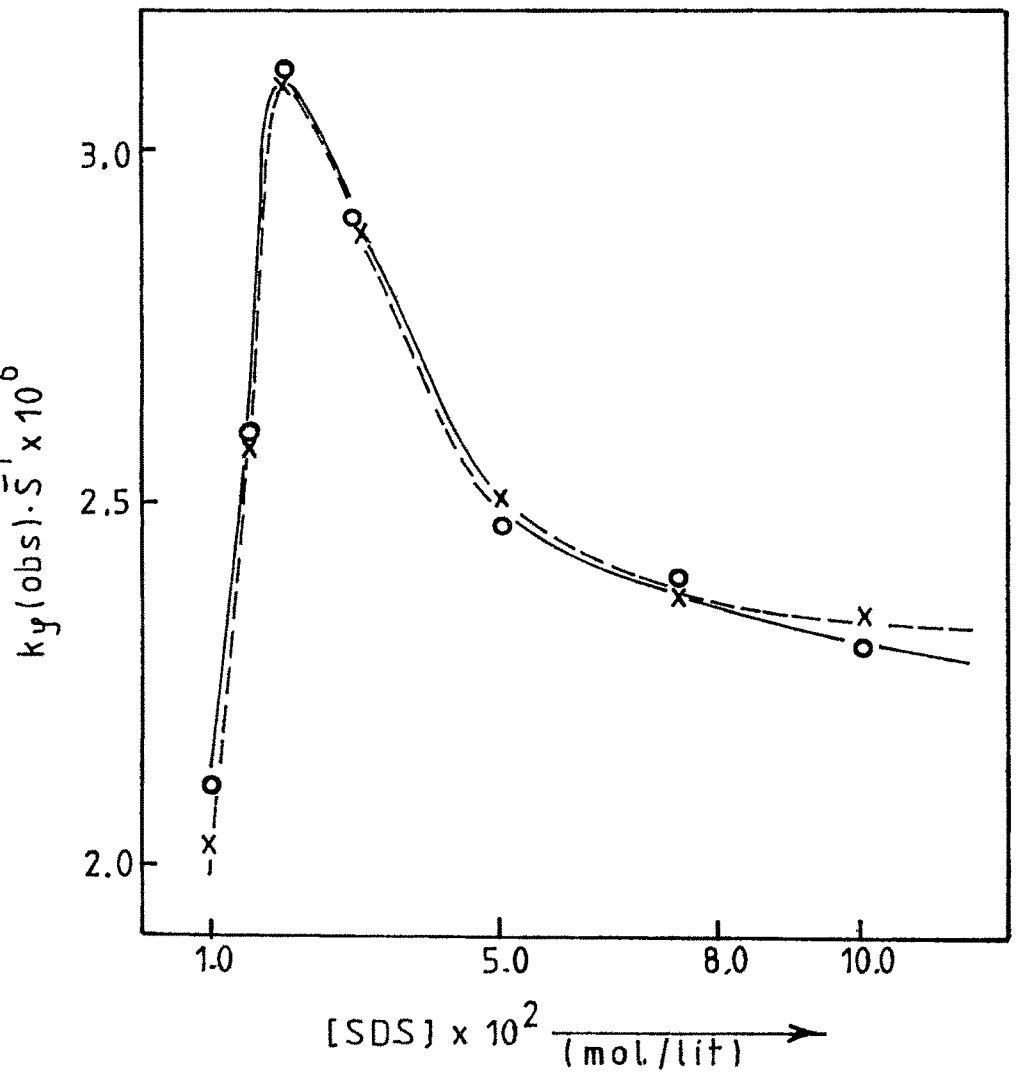


Fig. 22 PPIE simulation of kinetic data for diMeGly hydrolysis in presence of SDS at pH 6 8 and at 40°C (O - $k_{\varphi\,(observed)}$, X - $k_{\varphi\,(calculated)}$)

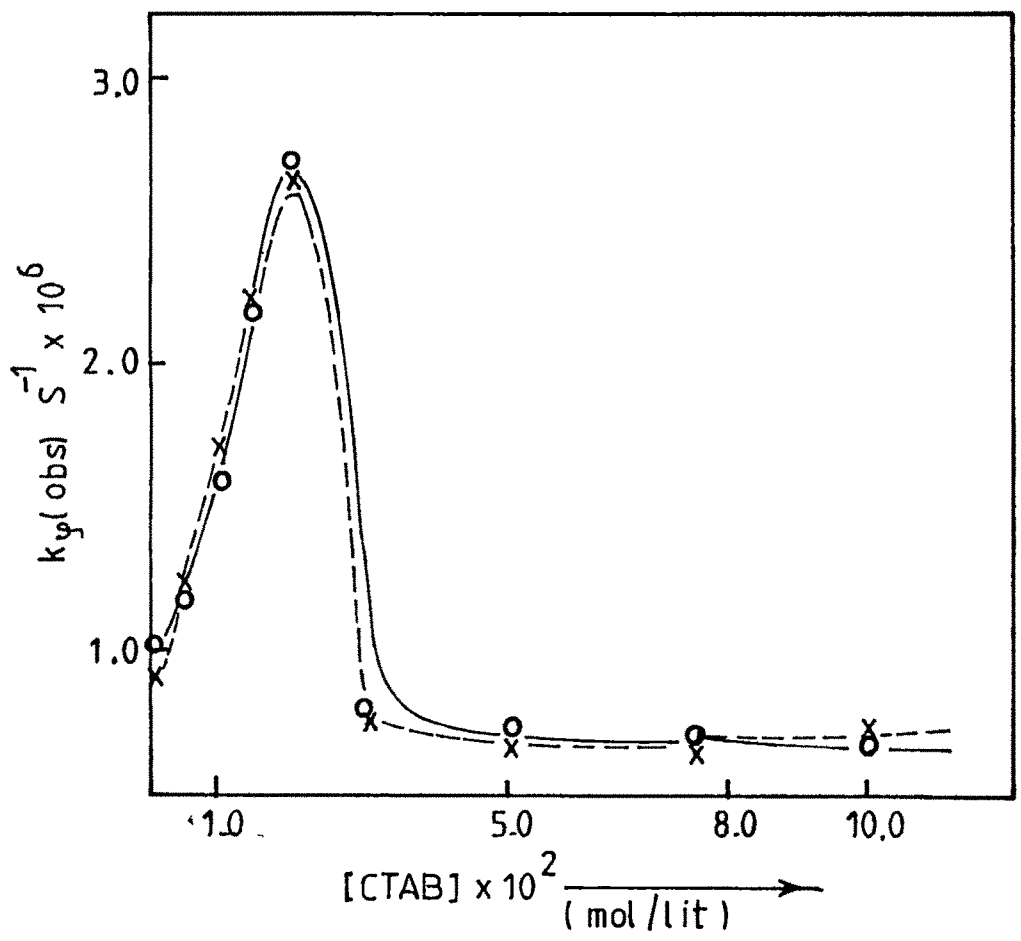


Fig. 23 PPIE simulation of kinetic data for PhGly hydrolysis in presence of CTAB at pH 6.8 and at 40°C (O - $k_{\psi\,(observed)}$, X - $k_{\psi\,(calculated)}$)

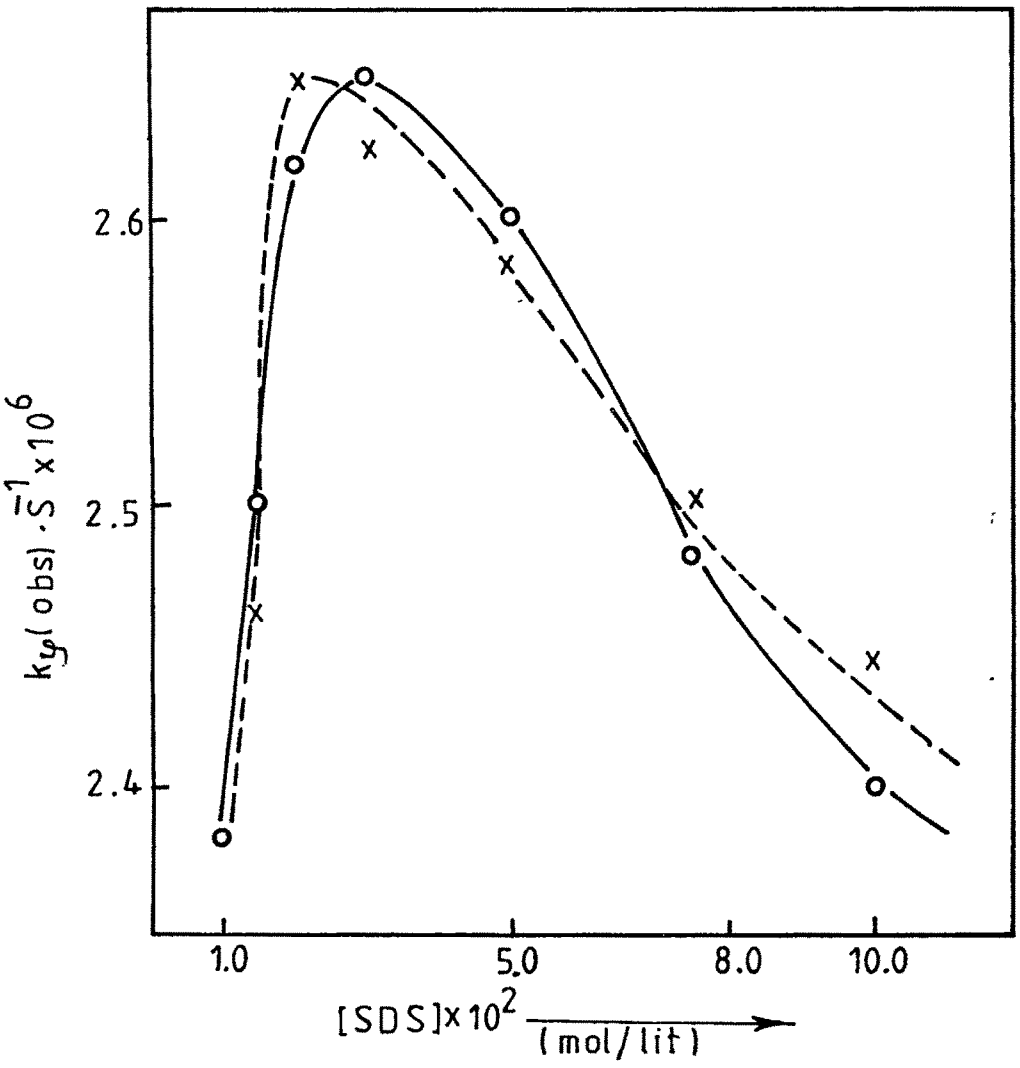


Fig. 24 PPIE simulation of kinetic data for PhGly hydrolysis in presence of SDS at pH 6.8 and at 40°C (O - $k_{\varphi\,(observed)}$, X - $k_{\varphi\,(calculated)}$)

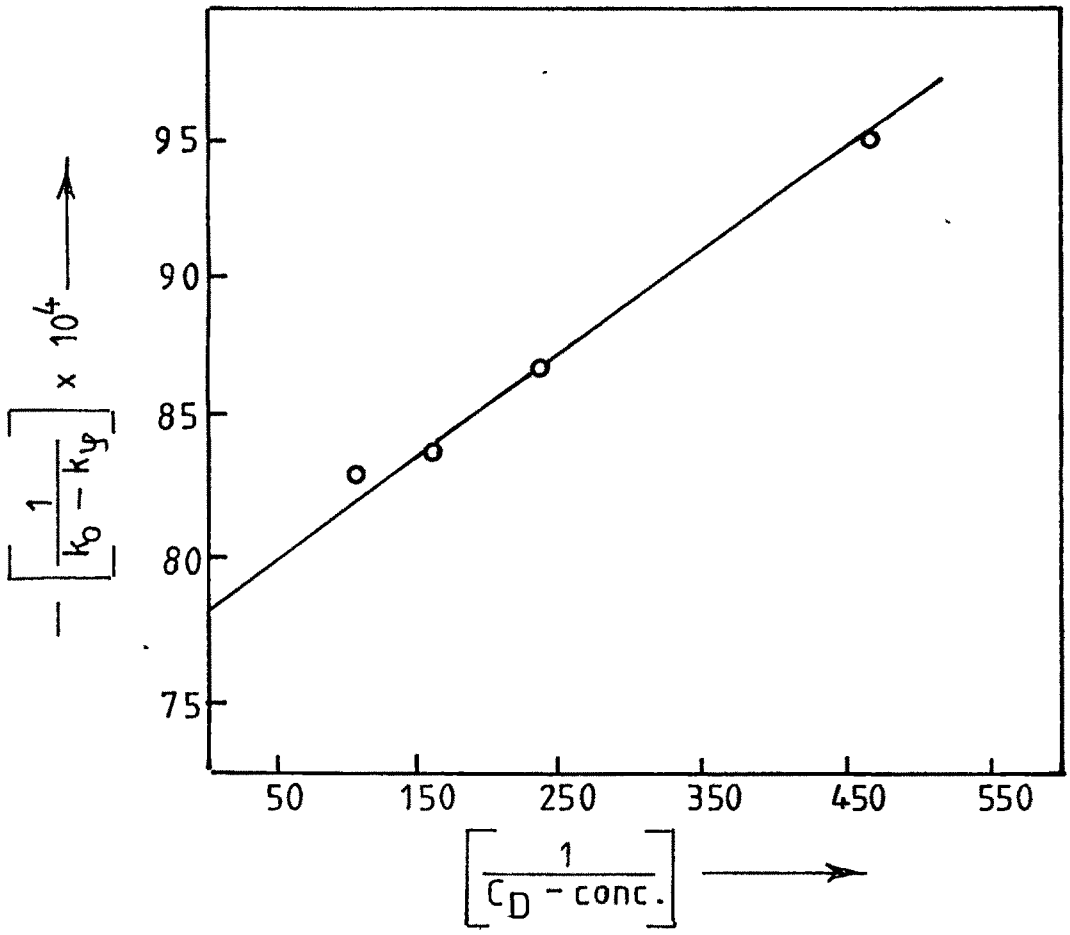


Fig. 25 Plot of $[1/k_0-k_\varphi]$ vs $[1/C_D\text{-CMC}]$ for EtGly hydrolysis at pH 6.8 and at 40°C

increasing and decreasing pattern of rate constant with increasing surfactant concentration, where as the use of equation (2 and 3) is found to be more satisfactory.

Temperature

The effect of temperature on the rate of hydrolysis of glycine esters was studied by carrying out the experiments at four different temperatures i.e. 30, 35, 40 and 45°C. Some of the observed data are shown in the plots of effect of surfactant concentration on rate constant at different temperatures (Fig. 26-29). A small increase in rate constant with increase in temperature was observed in all the cases. The results show that, the trend in rate profile (as it is obtained from the plot of $k_{\varphi(obs)}$ vs surfactant concentration) remained same at all temperatures studied, showing that the mechanism of the reaction is not affected when temperature is changing from 30 to 45°C.

Activation energy (Ea), activation entropy($\Delta S^{\pm}$) and activation enthalpy ($\Delta H^{\pm}$) for the hydrolysis of glycone esters in micellar medium have been determined. Representative plots of the effect of surfactant concentration on the activation energy (Ea) and activation entropy ($\Delta S^{\pm}$) are shown in fig (30-31). The Ea value decreased with increase in micellar concentration and reached a minimum value at the concentration of surfactant, where the rate of hydrolysis was found to be maximum. Similar observations were made by earlier workers also[32]. A plot of $\Delta H^{\pm}$ vs $\Delta S^{\pm}$ (fig 32) is a straight line following an equation,

$$\Delta H^{\pm} = k_1 + k_2 \Delta S^{\pm} \qquad (5)$$

showing that a linear compensation effect exists in this reaction.

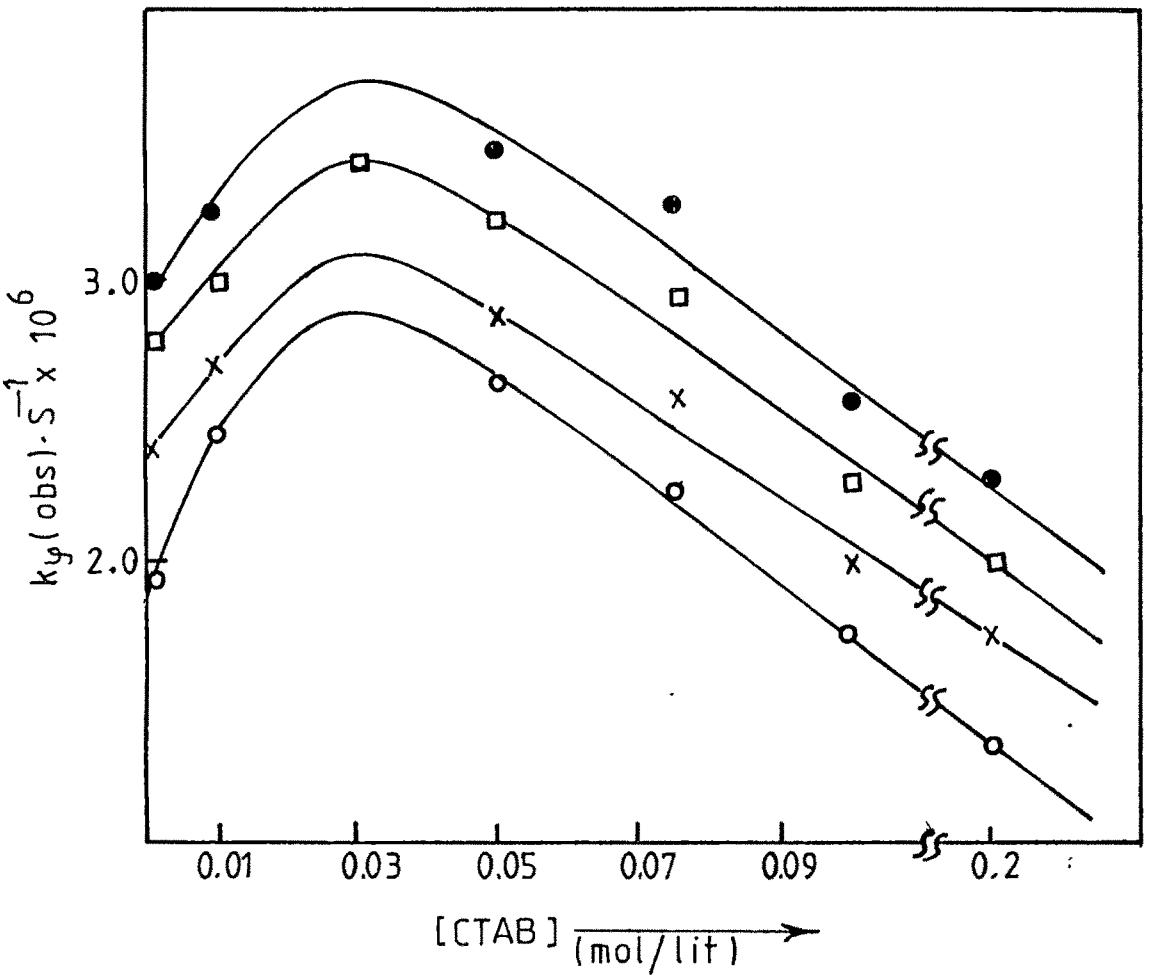


Fig 26 Effect of temperature and concentration of CTAB on EtGly hydrolysis at pH 6 8 : O - 30°C, X - 35°C, □ - 40°C, O - 45°C

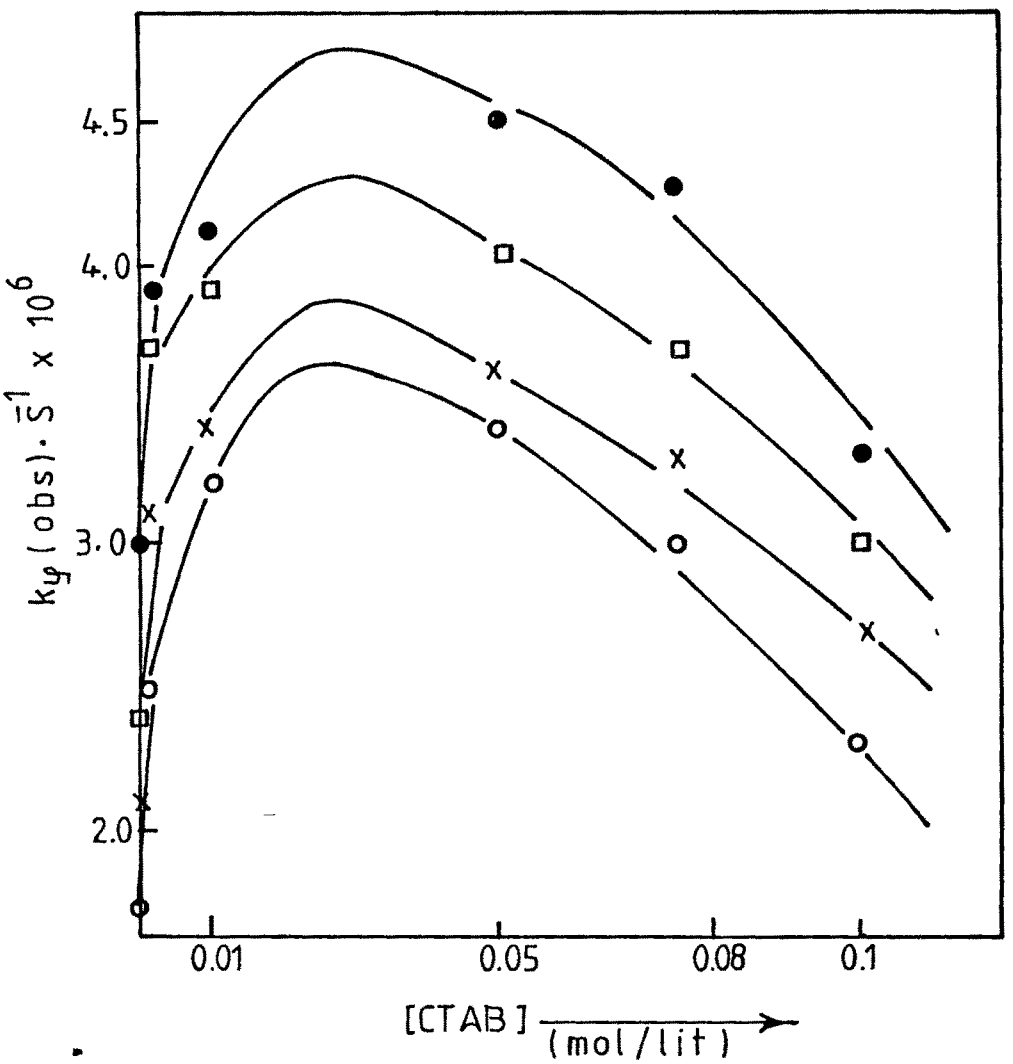


Fig. 27 Effect of temperature and concentration of CTAB on MeGly hydrolysis at pH 6.8 · O - 30°C, X - 35°C, □ - 40°C, O - 45°C

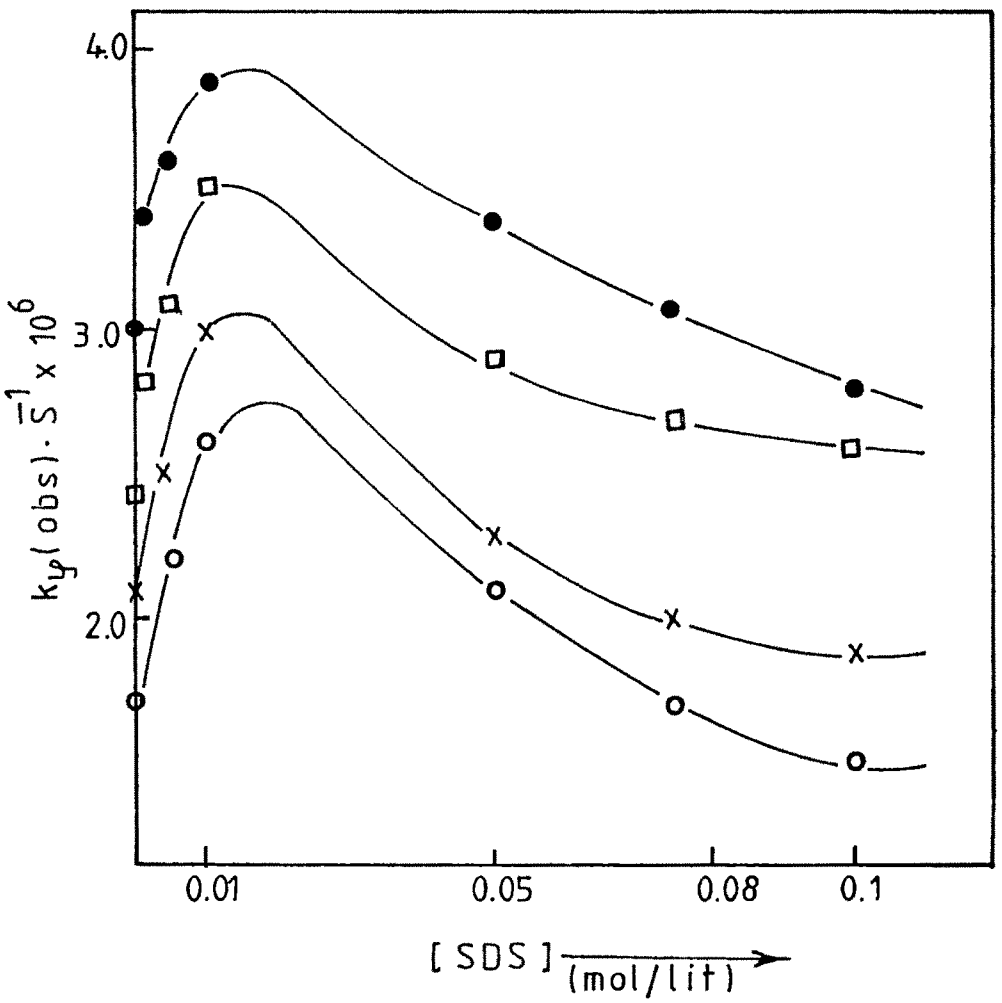


Fig 28 Effect of temperature and concentration of SDS on MeGly hydrolysis at pH 6.8 : O - 30°C, X - 35°C, □ - 40°C, O - 45°C

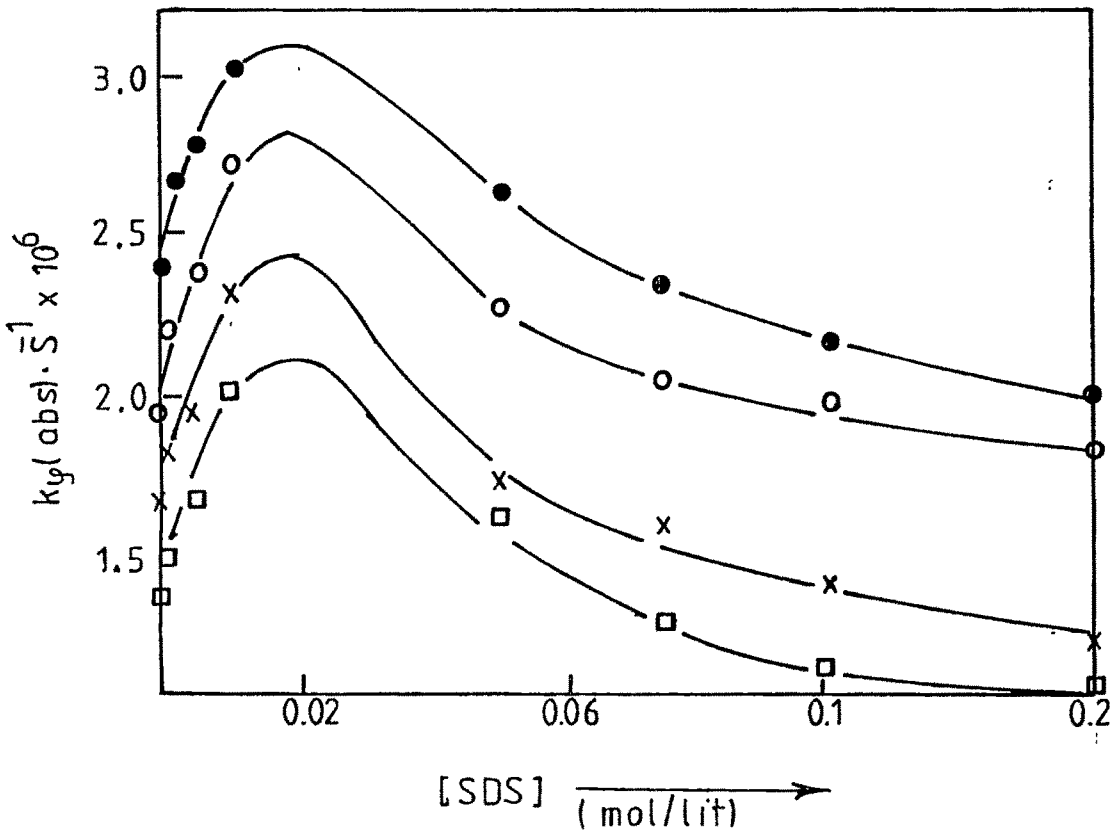


Fig. 29 Effect of temperature and concentration of SDS on EtGly hydrolysis at pH 6.8 : O - 30°C, X - 35°C, □ - 40°C, O - Δ45°C

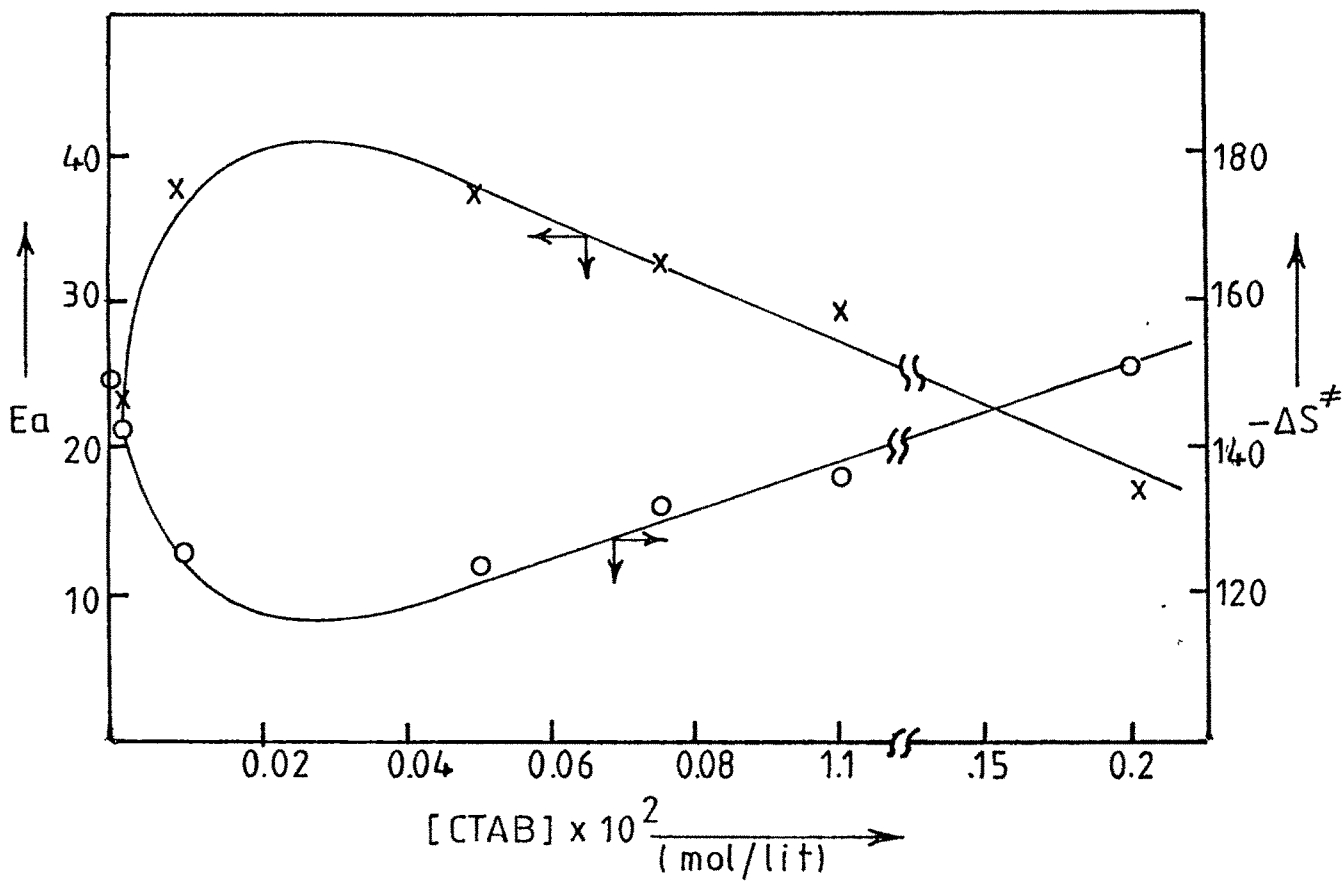


Fig. 30 Variation of activation energy and activation entropy for the hydrolysis of EtGly in presence of CTAB at different concentration : O - Ea, X - - $\Delta S^{\#}$

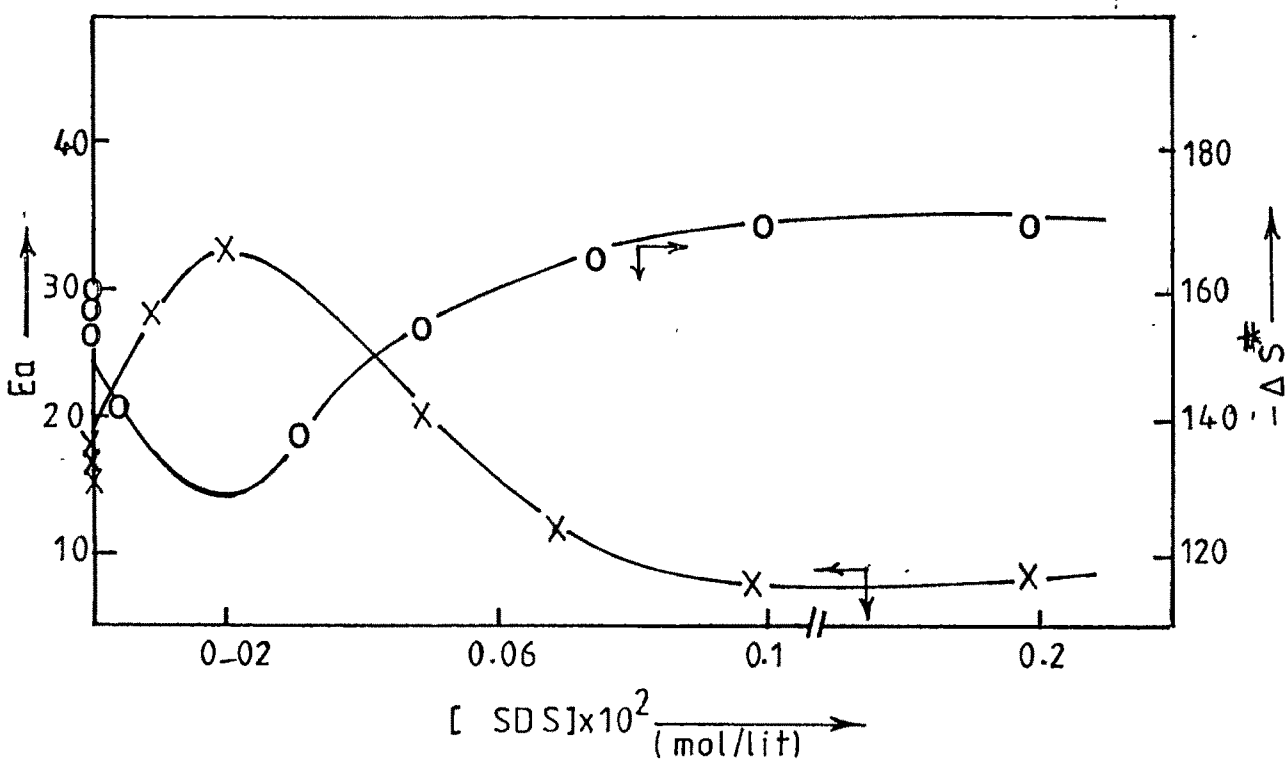


Fig 31 Variation of activation energy and activation entropy for the hydrolysis of EtGly in presence of SDS at different concentration · O - Ea, X - $-\Delta S^{\#}$

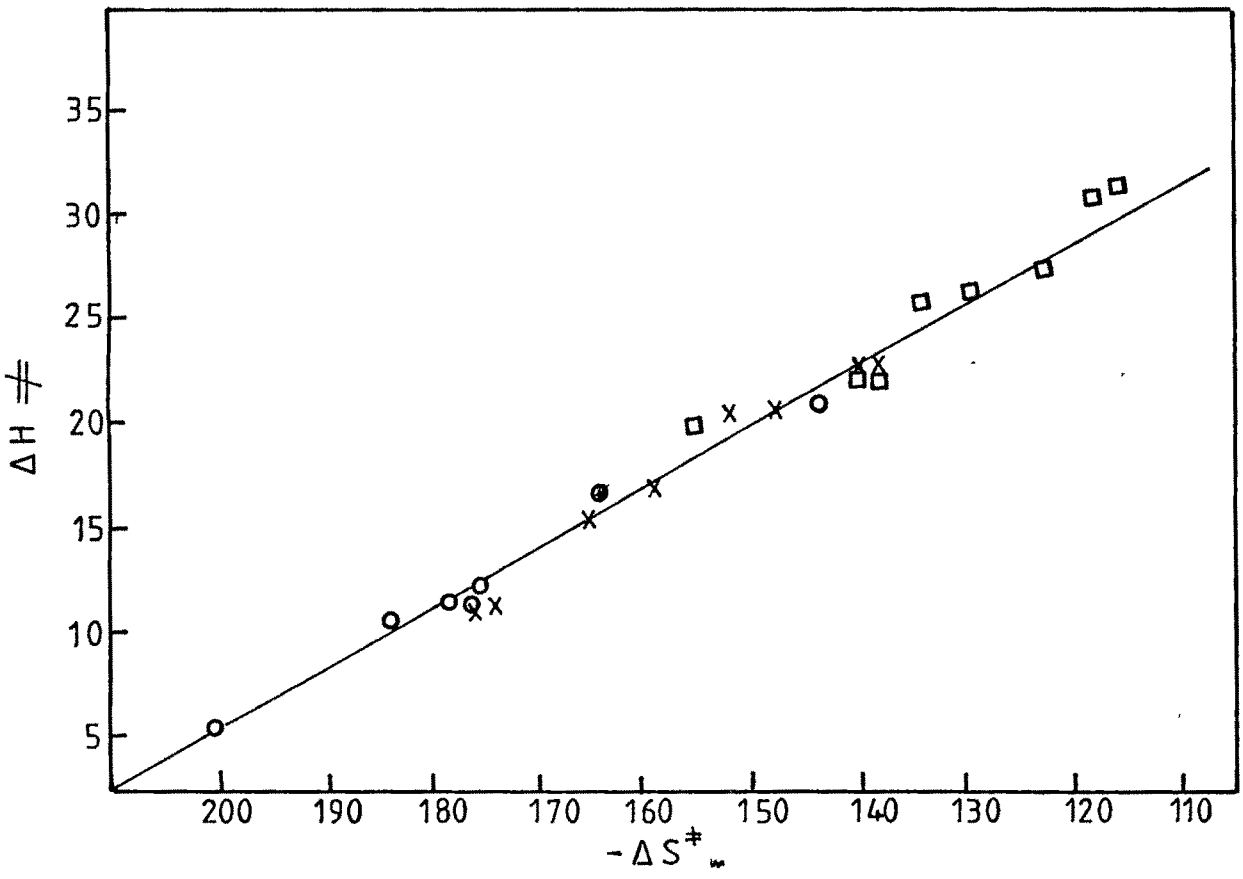


Fig 32 Variation of activation enthalpy and entropy of hydrolysis of ethylglycinate in presence of surfactants of various concentration : Δ- SDS, X - CTAB, O - Brij 35

3.2 Glycine ester hydrolysis in presence of metal complex in aqueous micellar medium

Metal ion promoted hydrolysis of aminoacid esters provide simple model for much more complex metalloenzymes[33-35], and the study of amino acid ester hydrolysis in micellar medium is also biologically important, as the micellar environment is similar to biological micro-environment.

Metals activating the enzymes in biological system are not present in free form, but are bound to an organic carrier ligand. Hence it is appropriate to study the catalytic effect of metal complexes on aminoacid ester hydrolysis in micellar medium.

Not much research work, regarding metal ion promoted hydrolysis of organic substrate in micellar medium has been cited in literature. In most cases studied, ligands of the metal complex, which are hydrophobic in character and capable of forming micellar aggregates have been used as effective catalysts and the studies were mainly concentrated on the pseudo-intramolecular attack of the metal ion coordinated OH^- group, to the micellar bound ester [31,36-38]. In the present section, the effort is to understand the individual as well as combined effect of cationic micelle CTAB and the metal ion or metal complex, on the hydrolysis of glycine esters in which, the OH^- are not bound to a ligand structure, but can be availed from the bulk phase.

The combined effect of metal complex and cationic surfactant CTAB on the hydrolysis of glycine esters (MeGly, EtGly, PhGly and diMeGly) were investigated under various conditions.

Pseudo First order rate constants k_0 (in absence of any catalyst), k_φ (in presence of CTAB), k_m (in presence of metal), $k_{\varphi m}$ (in presence of metal and CTAB), k_{mL} (in presence of metal complex), $k_{\varphi mL}$ (in presence of metal complex and CTAB) were determined. Metals and ligands used in this study were m_1 (Cu^{2+}) m_2 (Zn^{2+}), m_3 (Fe^{3+}), m_4(Mn^{2+}) and ligands L_1(bipyl) L_2 (O phen) and L_3 (DET)

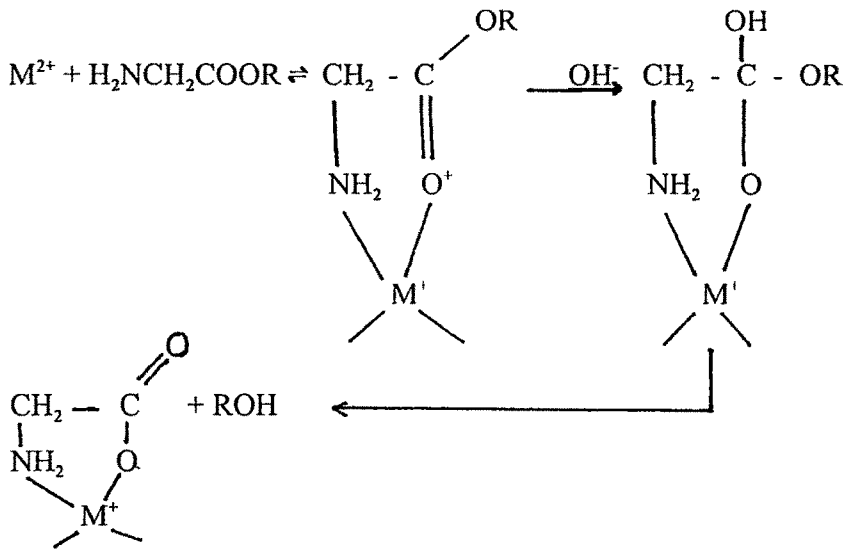
Most of the metal complexes are not stable at high pH. Therefore the hydrolysis catalysed by metal or metal complexes was studied at pH 4, 5 2 and 5 8 and the results are shown in Table (14-17)

Metal / Metal Complex

For hydrolysis of aminoacid esters, the path of reaction, could be through nucleophilic attack, by OH^- ion.

It is well known that, the metal ion forms a chelate with aminoacid esters which makes carbonyl carbon of the ester group more facile for the nucleophilic attack[39].

The mechanism of the hydrolysis can be shown as below [40].



At pH 5.2 all the glycine esters hydrolyse very slowly, their rate constants were of the order of 10^{-6} S^{-1}. When studied in presence of metal or metal complex (1:1) these reactions have higher rate constant (table 14-17). When compared not much difference was observed in the catalytic activity of the metals used and the enhancement in the rate of hydrolysis of different esters was approximately 25 to 40 times. Softness and hardness of the metal played a role in the catalytic activity of the metal. Knowledge of hardness or softness of metals have been used to understand various chemical and biochemical reactions involving metal or metal complexes [41-42]. The soft metal ion forms bonds with more covalent characters, via extensive back donation, than the hard metal ions. The back donation diminishes the effect of an electron donation from the ligand to the metal ion, thus making soft metal ions less sensitive to electron donation from attached ligands. Thus Cu and Zn being comparatively softer metals than Fe and Mn[41], it is observed that, their complexes show slightly higher catalytic activity.

Table 14 Effect of pH on Cu^{2+} /Cu complex catalysed hydrolysis of Glycine ester in presence and absence of CTAB (0 03M) at 40°C

	MeGly			EtGly			diMeGly			PhGly		
	k x 10^5 S^{-1}			k x 10^5 S^{-1}			k x 10^5 S^{-1}			k x 10^5 S^{-1}		
	pH 4	pH 5 2	pH 5.8	pH 4	pH 5 2	pH 5 8	pH 4	pH 5.2	pH 5.8	pH 4	pH 5 2	pH 5 8
-	81 00	0 20	0 22	68 00	0 11	0 12	48 41	0 08	0 08	45.33	0 08	0 08
Cu^{++}	105 40	4 71	5 07	82.81	3 35	3 69	59.06	2 67	2.94	57 04	2 60	2.94
Cu-bipyl	102 15	4 64	4 91	72 44	3.17	3 49	53.17	2 59	2 89	50 11	2.56	2.82
Cu-ophen	94 44	4 56	4 84	71 00	2 91	3.17	50.05	2.56	2 71	48 51	2.43	2.63
Cu-DET	103.65	4 70	5.09	75.40	3 25	3.54	55.71	2 65	2 86	52.45	2.58	2.86
CTAB	0 23	0 27	0 30	0.16	0.19	0.22	0 12	0 30	0.39	0.11	0.206	0.23
Cu-CTAB	3 90	6 13	6 30	2 81	5 51	5.69	2.16	8.84	9.17	2 07	6.06	6.37
[Cu-bipyl]-CTAB	3 80	6 01	6 21	2.74	5.24	5.49	2.10	8.71	9 04	1 94	5.91	6.20
[Cu-Ophen]-CTAB	3.65	5 88	6 01	2.54	5.05	5 27	1.84	8.38	8 69	1 80	5 73	5.97
[Cu-DET]-CTAB	3 86	5.94	6.18	2.61	5.17	5 34	2.14	8.76	9 10	1.97	5.94	6 15

Table 15 Effect of pH on Zn^{2+}/Zn complex catalysed hydrolysis of Glycine ester in presence and absence of CTAB (0.03M) at 40°C

	MeGly			EtGly			diMeGly			PhGly		
	k x 10^5 S^{-1}			k x 10^5 S^{-1}			k x 10^5 S^{-1}			k x 10^5 S^{-1}		
	pH 4	pH 5 2	pH 5 8	pH 4	pH 5.2	pH 5 8	pH 4	pH 5 2	pH 5 8	pH 4	pH 5 2	pH 5.8
-	-	0 20	0 22	68 00	0 11	0 12	48 41	0 08	0 08	45 35	0.08	0 08
Zn^{2+}	122 52	6.60	6 77	98 60	4 59	4.71	66.80	2 79	2 94	62.10	2.71	2 82
Zn-bipyl	117 14	6.30	6 54	89 42	4 44	4.65	57 52	2 70	2 85	53.07	2 60	2.75
Zn-ophen	112.41	6.51	6 44	75.46	4 17	4.56	50 17	2.64	2 70	48 47	2.57	2 60
Zn-DET	109 61	-	6 59	91 15	4 46	4 65	59 01	2 73	2 91	56.64	2.63	2 77
CTAB	0 23	0 27	0 30	0 16	0 19	0 22	0 12	0 29	0 39	0 11	0.21	0 23
Zn-CTAB	5.60	8 81	8 97	4.94	7.54	7 69	3.58	9 12	9 26	3.41	6.28	6 40
[Zn-bipyl]-CTAB	5 47	8 68	8 87	4 80	7.32	7 52	3.45	8.94	9 05	3.27	6.21	6 31
[Zn-Ophen]-CTAB	5 21	8.48	8 63	4.58	6.93	7 34	3 30	8.79	6 80	3.10	6 10	6 20
[Zn-DET]-CTAB	5.52	8.78	8 91	4.87	7 46	7 57	3.50	8 97	9 12	3.32	6 24	6 36

Table 16 Effect of pH on Fe^{3+} / Fe complex catalysed hydrolysis of Glycine ester in presence and absence of CTAB (0 03M) at 40°C

	MeGly			EtGly			diMeGly			PhGly		
	k x 10^5 S^{-1}			k x 10^5 S^{-1}			k x 10^5 S^{-1}			k x 10^5 S^{-1}		
	pH 4	pH 5 2	pH 5.8	pH 4	pH 5 2	pH 5 8	pH 4	pH 5.2	pH 5 8	pH 4	pH 5.2	pH 5 8
-	-	0 20	0 22	68 00	0.11	0.12	48 41	0 08	0 08	45 35	0.08	0.077
Fe^{3+}	91 25	4 13	4.21	77 00	3 27	3 35	54 70	2 52	2.61	51 24	2.44	2.48
Fe-bipyl	89 01	4 10	4 20	73 16	3 12	3 26	52.15	2.49	2.54	49 56	2.37	2.40
Fe-ophen	78.45	4 04	4 11	69.43	3.13	3 18	48.57	2 40	2.46	45.17	2.39	2.38
CTAB	0 23	0 27	0 30	0.16	0 19	0 22	0.12	0 29	0 39	0.11	0.21	0.23
Fe-CTAB	2.60	5 64	5.75	2.31	5 30	5 42	1.87	8 21	8 30	1.72	5 77	5.84
[Fe-bipyl]-CTAB	2.52	5 56	5.66	2.28	5.24	5 33	1.73	8 16	8.24	1.63	5 62	5.73
[Fe-Ophen]-CTAB	2.44	5.46	5 52	2.15	5 16	5 25	1.58	8.04	8 15	1 50	5.50	5.56

Table 17 Effect of pH on Mn^{2+}/Mn complex catalysed hydrolysis of Glycine ester in presence and absence of CTAB (0 03M) at 40°C

	MeGly			EtGly			diMeGly			PhGly		
	k x 10^5 S^{-1}			k x 10^5 S^{-1}			k x 10^5 S^{-1}			k x 10^5 S^{-1}		
	pH 4	pH 5 2	pH 5 8	pH 4	pH 5 2	pH 5.8	pH 4	pH 5 2	pH 5 8	pH 4	pH 5 2	pH 5 8
-	-	0.20	0.22	68.00	0 11	0.12	48.41	0 08	0 08	45.35	0 076	0 08
Mn^{2+}	97.05	4.23	4 28	79.40	3.20	3.33	57.12	2.47	2 36	52 15	2 35	2.30
Mn-bipyl	94 17	4.11	4 21	70.00	3 09	3.25	48.34	2.45	2.29	43.27	2.31	2.21
Mn-ophen	88 43	4.00	4 07	67 50	2 95	3 06	42.50	2 35	2.16	38.61	2.20	2.08
Mn-DET	96 41	4.16	4 25	72.17	3 11	3.22	51 47	2.47	2.31	45.52	2.32	2.25
CTAB	0 23	0.27	0 30	0 16	0.19	0.22	0 12	0.29	0.39	0.11	0 20	0 23
Mn-CTAB	2 85	5.71	5.84	2.50	5.37	5 47	2.04	8.34	8 46	1.85	5.88	5.96
[Mn-bipyl]-CTAB	2.72	5.60	5.73	2.41	5.27	5 38	1.90	8 27	8 39	1.80	5.80	5.90
[Mn-ophen]-CTAB	2 60	5.50	5.61	2.28	5.16	5.20	1.77	8.18	8.26	1.68	5.70	5.77
[Mn-DET]-CTAB	2.77	5.64	5 77	2.44	5.26	5.37	1.94	8 29	8.43	1.81	5.83	5.95

To see the effect of pH, these hydrolyses were carried out at pH 4 and pH 5.8 also. The rate constants were very high, due to high H^+ ion concentration at pH 4, as compared to that at pH 5.2. At pH 4, the metal complex catalysed the hydrolysis to a small extent The maximum enhancement at low pH could be due to the fact that the complexes (binary / ternary) formed with glycine esters are not very stable at this pH The stability of the metal complexes studied were found to be maximum in the pH range 4.8 to 5.6.

The rate constants at pH 5.8 were slightly higher than that at pH 5.2, which may be due to a small increase in OH^- ion concentration But when compared the increase in rate constant values at pH 5.2 and 5.8 due to metal complex, it was observed that, the enhancement was almost same in some cases or slightly less than that at pH 5.2, which is probably due to the lower stability of the complex between the substrate and the catalyst at this pH. For example, copper-bipyl complex is most stable around pH 5, and it was observed that for McGly, the rate enhancement in presence of Copper or copper-bipyl complex was more (23.5 times) at pH 5.2 than that at pH 5.8 (22 6 times). Nearly same difference has been observed for all the esters and all the copper complexes studied.

Metal complexes were found to have lower catalytic activity than free metal ions, which may be the result of slight electron withdrawing capacity of metal due to prior formation of complex.

Metal ion as well as cationic micelle (eg. CTAB) can catalyse the hydrolysis of aminoacid esters, while the former can polarize the carboxylic group of the esters and facilitate an attack of nucleophile on carbonyl carbon, the latter is able to bring the nucleophile and the ester in close proximity with each other Therefore one can expect a combined effect, if they are used together as catalyst for the hydrolysis.

Metal / Metal Complex and Surfactants

At pH 4, the presence of CTAB caused an inhibition in the hydrolysis rate of glycine esters to an extent of 400 times. In absence of surfactant, metal complexes enhanced the rate of ester hydrolysis, but when the same experiment was carried out in presence of CTAB, rate cosntant was found to be very much reduced For example, in case of EtGly at pH 4, the rate constant was 6.8×10^{-4} S^{-1}, in presence of 0 03 M CTAB, it was

1 6 x 10^{-6} S^{-1}, in presence of Cu-bipyl (1·1) it was 7 2 x 10^{-1} S^{-1} and in presence of Cu-bipyl and CTAB it was 2.74 x 10^{-5} S^{-1}. As explained in the earlier section, the inhibition in presence of CTAB was caued by the electrostatic repulsion of H^+ ion by CTAB, thus making the substrate deprived of attacking protons In the absence of surfactant, the metal complex enhances the rate, only ≈1.2 times Now if we compare the rate constants in micellar medium in presence of metal complexe to that in absence of metal complex, it was about 20 times more It means that, the catalytic activity of the same metal complex at pH 4 was much higher in micellar environment, as compared to that without micelle. This may be explained as follows, the substrate - metal binding becomes more stable in this environment, as it is possible that the pH in the micellar medium may increase due to the repulsion of H^+ ion by CTAB. Thus inspite of the catalytic effect of metal complex, the overall result was a reduction in the rate of hydrolysis by ≈30 times, due to an overwhelming inhibiting effect of CTAB at pH 4

At pH 5 2 there is predominance of OH^- ion attack on ester As OH^- ion is attracted by CTAB, slight enhancement in the rate was observed, when hydrolysis was carrid out in cationic micellar medium The small enhancement is due to very low OH^- ion concentration at this pH. Presence of metal complex showed a significant enhancement (≈ 30 times) in the hydrolysis rate as compared to that of pH 4, due to the stability of metal complex at pH 5.2. It is observed that this enhancement due to metal complex was smaller in the micellar medium. As such CTAB attracts OH^- ion, so one expected higher enhancement, but it is possible that there may be a slight decrease in stability of the binding between the ester and the metal due to a small increase in the pH in the micellar medium

However, at pH 5 8, the rate constant in presence of CTAB was slightl;y higher than that at pH 5.2 due to the availability of more OH^- ions, the rate enhancement due to metal complex (k_M/k_0) was found to be less than or equal to that at pH 5.2. Once again, the lower stability of metal complex at this pH, could be the reason for this observation.

The combined catalytic effect of metal complex and CTAB on glycine ester hydrolysis was found to be quite high at pH 5 2 (Table 18). The values of combined rate

Table 18 Effect of Metal/Metal complex and CTAB (0 03M) on Glycine ester hydrolysis at 40°C and pH 5 2

	MeGly	EtGly	diMeGly	PhGly
$k_0 x 10^6$	0 197	0 114	0.08	0.076
$k_{\varphi m1}/k_0$	31 12	48 33	110.50	79.74
$k_{\varphi m1L1}/k_0$	30 51	45.96	108 87	77.76
$k_{\varphi m1L2}/k_0$	29 85	44 30	104 75	75 39
$k_{\varphi m1L3}/k_0$	30.15	45 61	109 50	78.16
$k_{\varphi m2}/k_0$	44 72	66 14	114 00	82.63
$k_{\varphi m2L1}/k_0$	44 06	64 21	111 75	81.71
$k_{\varphi m2L2}/k_0$	43 05	60 79	109 87	80.26
$k_{\varphi m2L3}/k_0$	44 56	65.44	112.13	82.10
$k_{\varphi m3}/k_0$	28 63	46 49	102.62	75.92
$k_{\varphi m3L1}/k_0$	28 22	45 96	102 00	73.94
$k_{\varphi m3L2}/k_0$	27 71	45 26	100.50	72.37
$k_{\varphi m4}/k_0$	28 98	47 10	104.25	77.37
$k_{\varphi m4L1}/k_0$	28 43	46.23	103.37	76 32
$k_{\varphi m4L2}/k_0$	27 92	45.26	102.25	75.00
$k_{\varphi m4L3}/k_0$	28.63	46.14	103.62	76.71

$m_1 \rightarrow Cu^{++}$ $m_2 \rightarrow Zn^{++}$ $m_3 \rightarrow Fe^{++}$ $m_4 \rightarrow Mn^{++}$
$L_1 \rightarrow$ 2,2'Bipyridyl $L_2 \rightarrow$ O-Phenanthrolene
$L_3 \rightarrow$ Diethylene triamine

enhancement was nearly equal to the product of the enhancement due to each one, when used separately

i.e., $k_{\varphi mL} / k_{mL} \times k_{mL}/k_0 \approx k_{\varphi mL}/k_0$ ..... (1)

and $k_{\varphi} / k_0 \times k_{mL}/k_0 \approx k_{\varphi mL}/k_0$ (2)

For diMeGly hydrolysis, the rate enhancement in presence of Zn-bipyl and CTAB at pH 5.2 was nearly 110 times, whereas the individual catalytic effect of Zn-bipyl and CTAB were nearly 30 and 3.30 times respectively It indicated that, there was a synergetic effect of metal complex and CTAB on glycine ester hydrolysis, when they were used together as catalyst.

From eqn (1) and (2), we can say,

$k_{\varphi mL} / k_{mL} \approx k_{\varphi mL}/k_0$ ..... (3)

Eqn (3) shows that, the effect of micelle on the rate of hydrolysis should be nearly same in absence and presence of metal complexes, and it was observed that at a particular pH, the values of $k_{\varphi mL} / k_{mL}$ and k_{φ}/k_0 were nearly constant (Table 19). When the values of k_{mL}/k_0 (Table 20) and $k_{\varphi mL}/k_{\varphi}$ (Table 21) were compared, they were also nearly same. These observations indicate that the mechanisms by which metal complex and surfactant catalyse the hydrolysis of ester when used seperately are not affected or changed by the presence of each other when they are used together.

The rate enhancement for glycine ester hydrolysis in presence of both metal complex and CTAB together were in the following order.

diMeGly > PhGly > EtGly > MeGly

(Table 19). This is in the same order as that in absence of metal complex and as observed in the previous section.

The effect of concentration of CTAB, on the hydrolysis of glycine esters in presence of all the four metals or their complexes in micellar medium were studied in the range of 1×10^{-2} to 1×10^{-1} M CTAB at pH 5.2 (Fig. 33-48). The rate profile of glycine ester hydrolysis in presence of different CTAB concentrations remained more or less same as that at 6.8 pH, i e., a slight enhancement in rate was observed with increase in concentration of surfactant, attained a limit around 0.03 M CTAB, followed by a decrease in rate with further addition of surfactant.

Table 19: Effect of CTAB (0 03M) on hydrolysis of Glycine esters in presence and absence of Metal/Metal complexes at 40°C and pH 5.2

	MeGly	EtGly	DiMeGly	PhGly
$k_{0 \times 10}^{6}$	0 197	0114	0.08	0.076
$k_{\varphi} x10^{6}$	0.269	0.189	0.294	0.206
k_{φ}/k_{0}	1 34	1.66	3.68	2 71
$k_{\varphi m1}/k_{m1}$	1 30	1.64	3.31	2.34
$k_{\varphi m1L1}/k_{m1L1}$	1 30	1.65	3.36	2.31
$k_{\varphi m1L2}/k_{m1L2}$	1 29	1 73	3.27	2.36
$k_{\varphi m1L3}/k_{m1L3}$	1 26	1 60	3.31	2 30
$k_{\varphi m2}/k_{m2}$	1.33	1 64	3.27	2.31
$k_{\varphi m2L1}/k_{m2L1}$	1.34	1.65	3.31	2.39
$k_{\varphi m2L2}/k_{m2L2}$	1.35	1.66	3.33	2.37
$k_{\varphi m2L3}/k_{m2L4}$	1.35	1.67	3.29	2.37
$k_{\varphi m3}/k_{m3}$	1.36	1.62	3.26	2.36
$k_{\varphi m3L1}/k_{m3L1}$	1 35	1.68	3.28	2.37
$k_{\varphi m3L2}/k_{m3L2}$	1.35	1.65	3.35	2.30
$k_{\varphi m4}/k_{m4}$	1.35	1.68	3.37	2.50
$k_{\varphi m4L1}/k_{m4L1}$	1 36	1.70	3.36	2.51
$k_{\varphi m4L2}/k_{m4L2}$	1.37	1.73	3.48	2.58
$k_{\varphi m4L3}/k_{m4L3}$	1 36	1.69	3.36	2.51

$m_1 \rightarrow Cu^{++}$ $m_2 \rightarrow Zn^{++}$ $m_3 \rightarrow Fe^{++}$ $m_4 \rightarrow Mn^{++}$
$L_1 \rightarrow$ 2,2'Bipyridyl $L_2 \rightarrow$ O-Phenanthrolene
$L_3 \rightarrow$ Diethylene triamine

Table 20: Effect of Metal/Metal complex on hydrolysis of Glycine esters at pH 5.2 and 40°C

	MeGly	EtGly	DiMeGly	PhGly
$k_0 x 10^6$	0.197	0.114	0.08	0.076
k_{M1}/k_0	31.51	29.38	33.37	34.20
k_{M1L1}/k_0	30.51	27.80	32.37	33.68
k_{M1L2}/k_0	29 85	25.53	32.00	31.97
k_{M1L3}/k_0	30.15	28.50	33.12	33.94
k_{M2}/k_0	33.50	40.26	34.87	35.75
k_{M2L1}/k_0	32.80	38.90	33.75	34.21
k_{M2L2}/k_0	31.97	36.57	33.00	33.81
k_{M2L3}/k_0	33.04	39 12	34.12	34.60
k_{M3}/k_0	20.96	28.68	31.50	32.10
k_{M3L1}/k_0	20.81	27.37	31.12	31.18
k_{M3L2}/k_0	20.50	27.46	30 00	31.44
k_{M4}/k_0	21.47	28.07	30.87	30.92
k_{M4L1}/k_0	20.86	27.11	30.63	30 39
k_{M4L2}/k_0	20.30	25.88	29.37	28.94
k_{M4L3}/k_0	21.11	27 28	30.87	30.52

$m_1 \rightarrow Cu^{++}$ $m_2 \rightarrow Zn^{++}$ $m_3 \rightarrow Fe^{++}$ $m_4 \rightarrow Mn^{++}$
$L_1 \rightarrow$ 2,2'Bipyridyl $L_2 \rightarrow$ O-Phenanthrolene
$L_3 \rightarrow$ Diethylene triamine

Table 21. Effect of Metal/Metal complex on Glycine esters hydrolysis in presence of CTAB (0 03M) at pH 5 2 and 40°C

	MeGly	EtGly	DiMeGly	PhGly
$k_{\varphi} \times 10^{6}$	0 269	0 189	0 294	0.206
$k_{\varphi m1}/k_{\varphi}$	22 79	29 15	30 07	29.42
$k_{\varphi m1L1}/k_{\varphi}$	22 34	27 72	29 63	28.69
$k_{\varphi m1L2}/k_{\varphi}$	21 86	26 72	28 50	27.82
$k_{\varphi m1L3}/k_{\varphi}$	22 08	27 35	29 79	28 83
$k_{\varphi m2}/k_{\varphi}$	32 75	39 89	31 02	30 48
$k_{\varphi m2L1}/k_{\varphi}$	32 27	38 73	30.41	30.14
$k_{\varphi m2L2}/k_{\varphi}$	31.52	36 67	29 89	29 61
$k_{\varphi m2L3}/k_{\varphi}$	32 64	40 76	30 51	30 29
$k_{\varphi m3}/k_{\varphi}$	20 96	28 04	27.93	28 01
$k_{\varphi m3L1}/k_{\varphi}$	20 67	27 72	27.76	27.28
$k_{\varphi m3L2}/k_{\varphi}$	20 30	27 30	27 35	26 70
$k_{\varphi m4}/k_{\varphi}$	21 22	28.41	28 37	28 54
$k_{\varphi m4L1}/k_{\varphi}$	20 82	27 88	28 13	28.16
$k_{\varphi m4L2}/k_{\varphi}$	20.45	27.30	27 82	27.67
$k_{\varphi m4L3}/k_{\varphi}$	20 97	27 83	28 20	28.30

$m_1 \rightarrow Cu^{++}$ $m_2 \rightarrow Zn^{++}$ $m_3 \rightarrow Fe^{++}$ $m_4 \rightarrow Mn^{++}$
$L_1 \rightarrow$ 2,2'Bipyridyl $L_2 \rightarrow$ O-Phenanthrolene
$L_3 \rightarrow$ Diethylene triamine

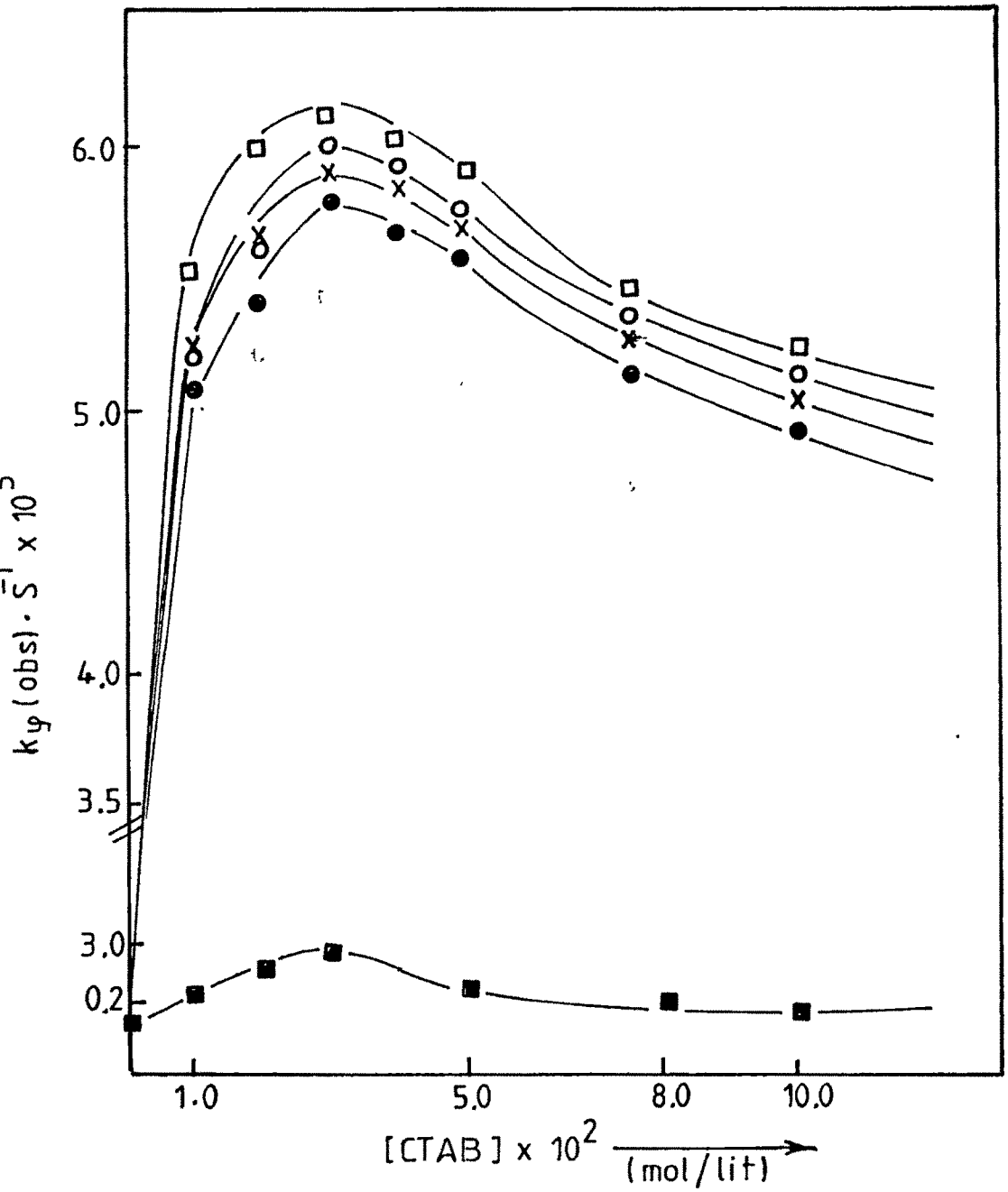


Fig 33 Effect of concentration of CTAB on hydrolysis of MeGly⁻ ■, in presence of Cu^{2+} - □ , Cu-bipyl - O, Cu-DET - X, Cu-Ophen - ●.

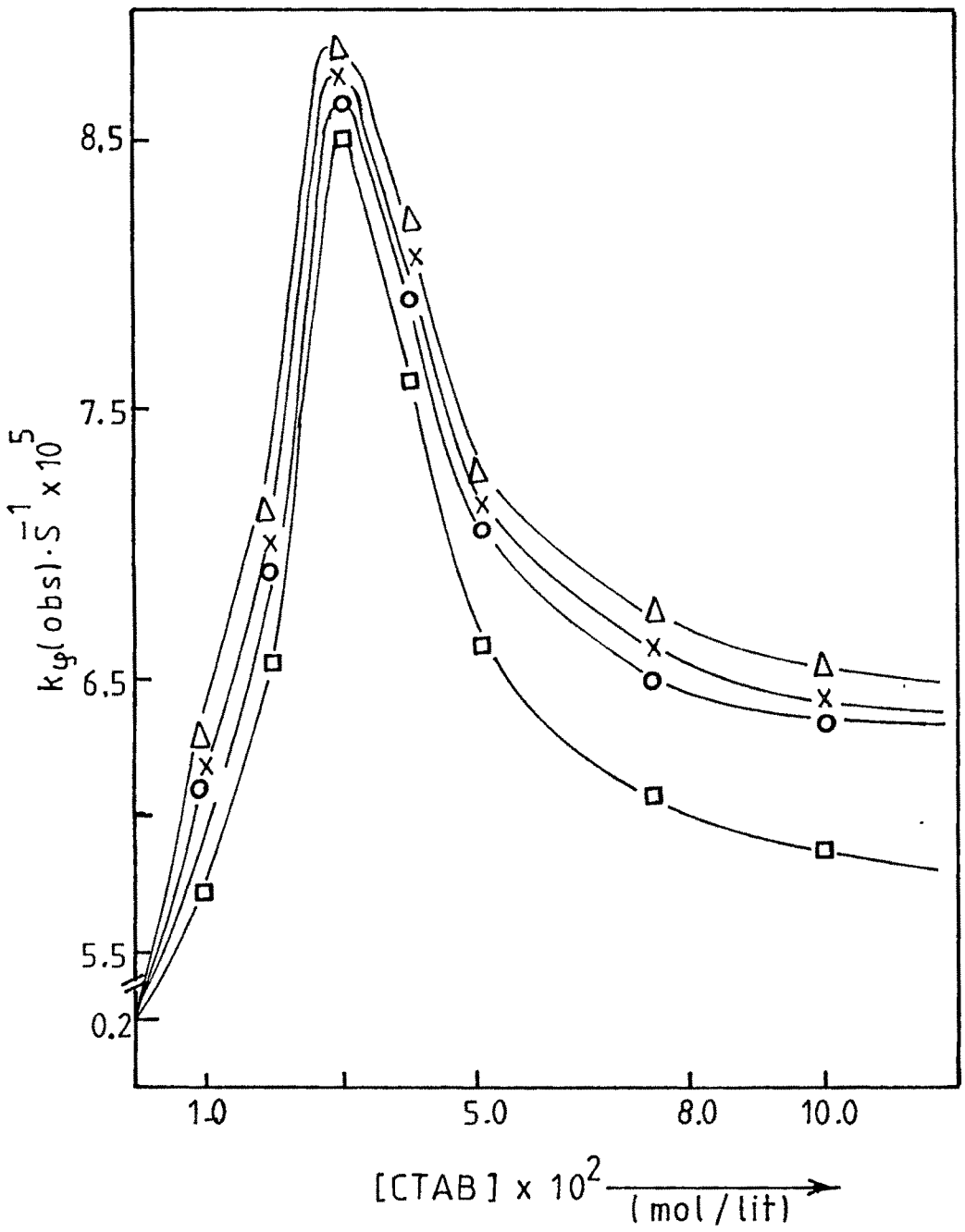


Fig 34 Effect of concentration of CTAB on hydrolysis of MeGly - · · in presence of Zn^{2+} - Δ , Zn-bipyl - O,Zn-DET - X, Zn-Ophen - □

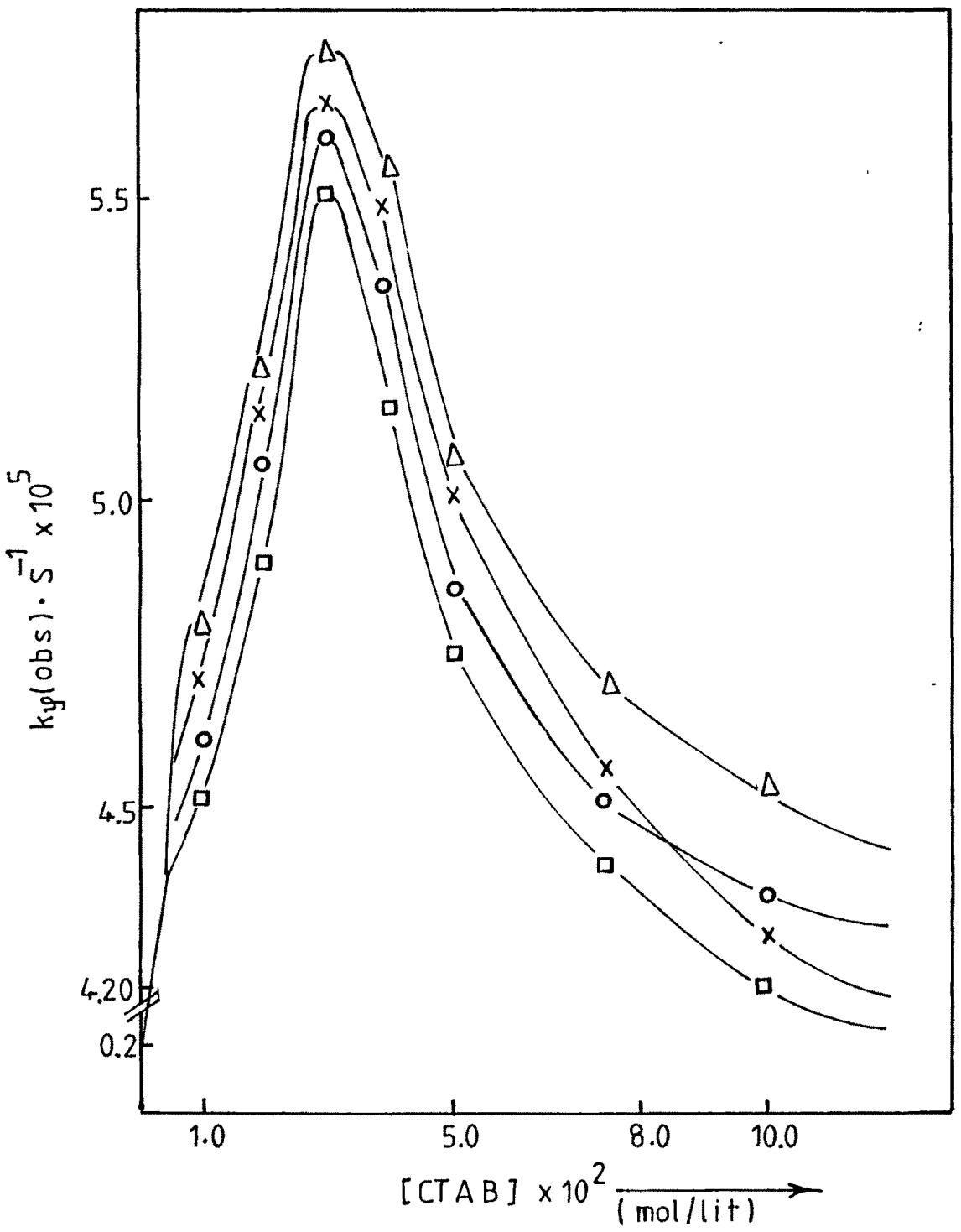


Fig 35 Effect of concentration of CTAB on hydrolysis of MeGly , in presence of Mn^{2+} - Δ, Mn-bipyl - O, Mn-DET - X, Mn-Ophen - □

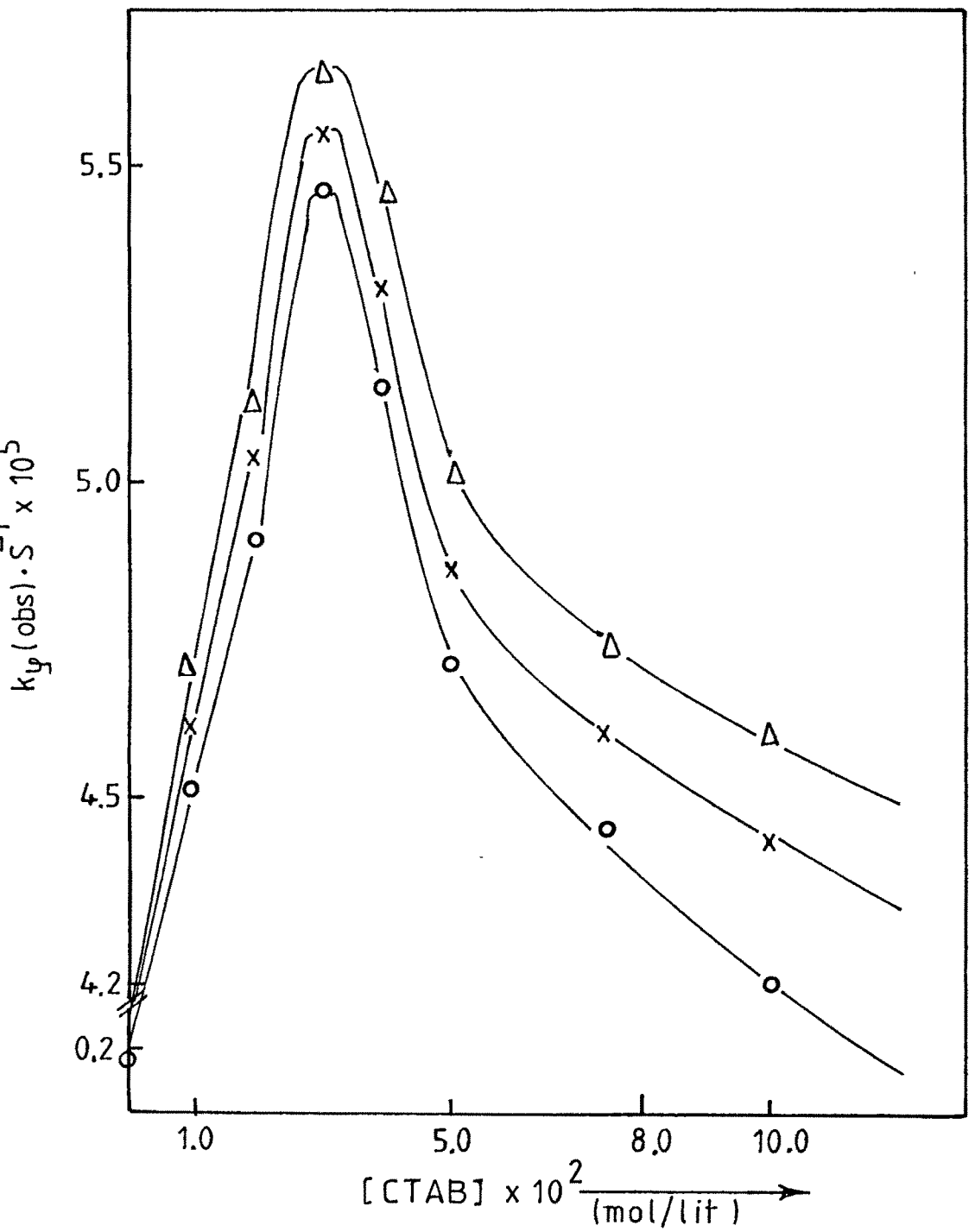


Fig 36 Effect of concentration of CTAB on hydrolysis of MeGly · , in presence of Fe^{3+} - Δ, Fe-bipyl - X, Fe-Ophen - O

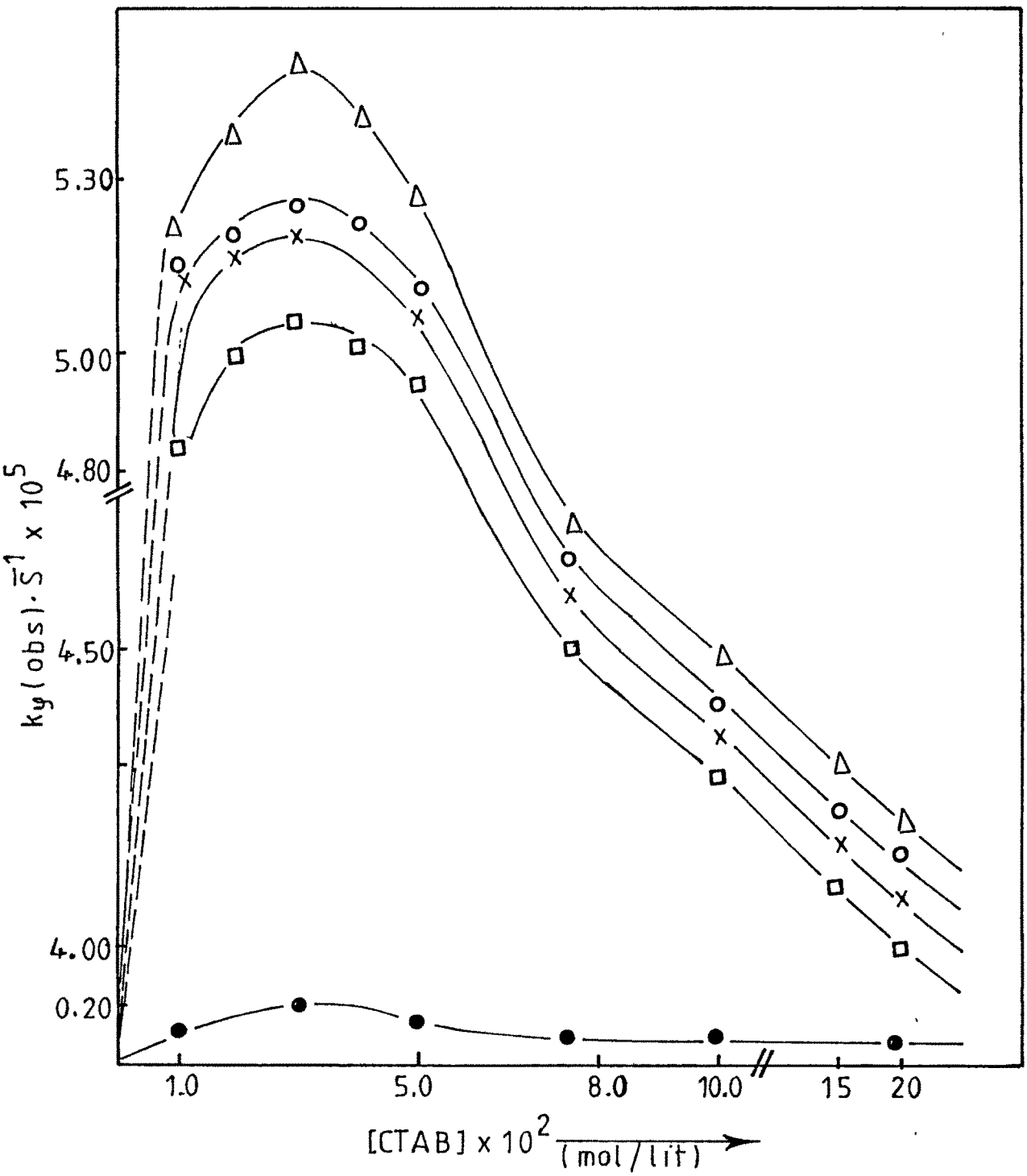


Fig 37 Effect of concentration of CTAB on hydrolysis of EtGly - ●, in presence of Cu^{2+} - Δ, Cu-bipyl - O, Cu-DET - X, Cu-Ophen - □

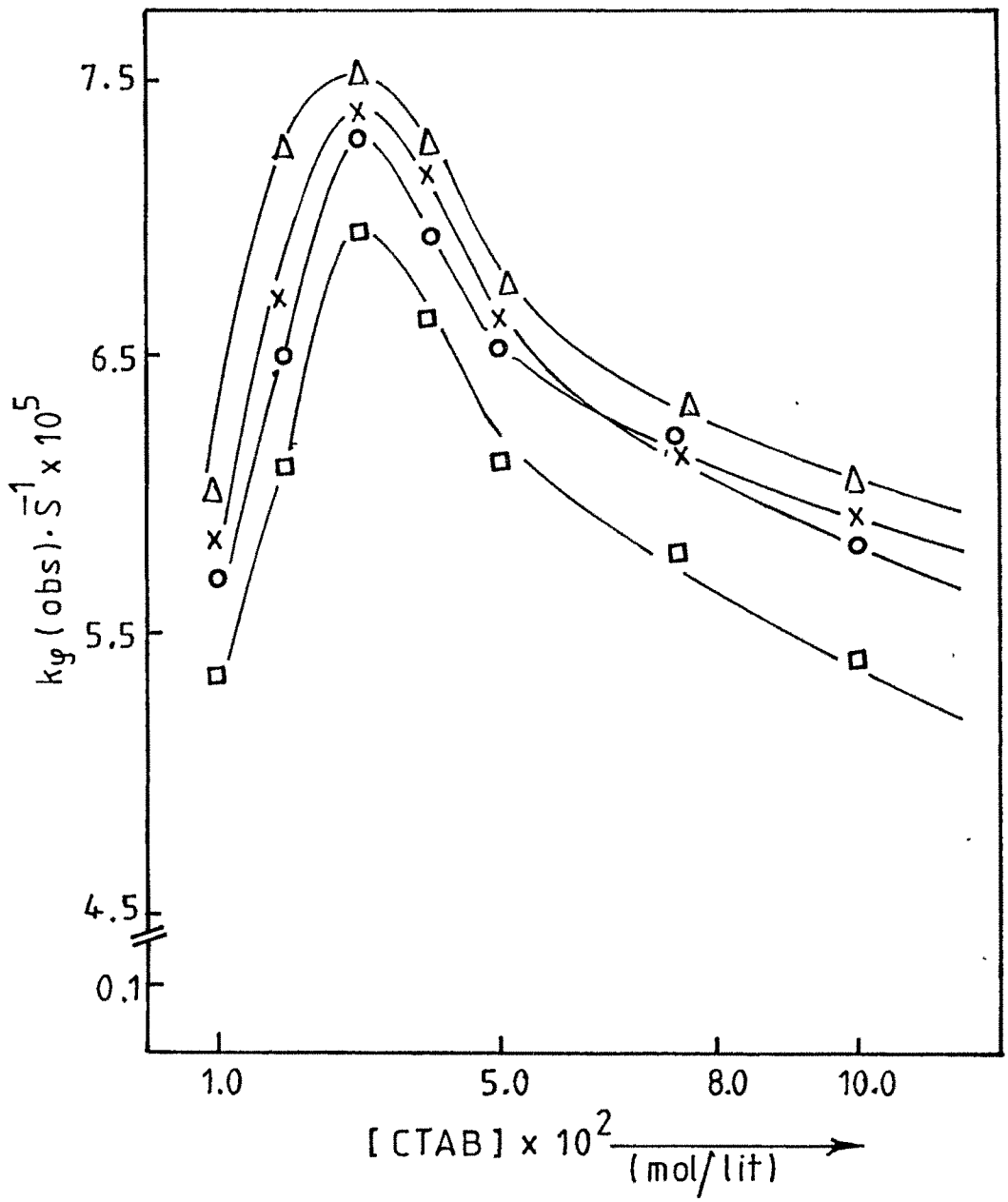


Fig 38 Effect of concentration of CTAB on hydrolysis of EtGly :, in presence of Zn^{2+} - Δ , Zn-bipyl - O,Zn-DET - X, Zn-Ophen - □.

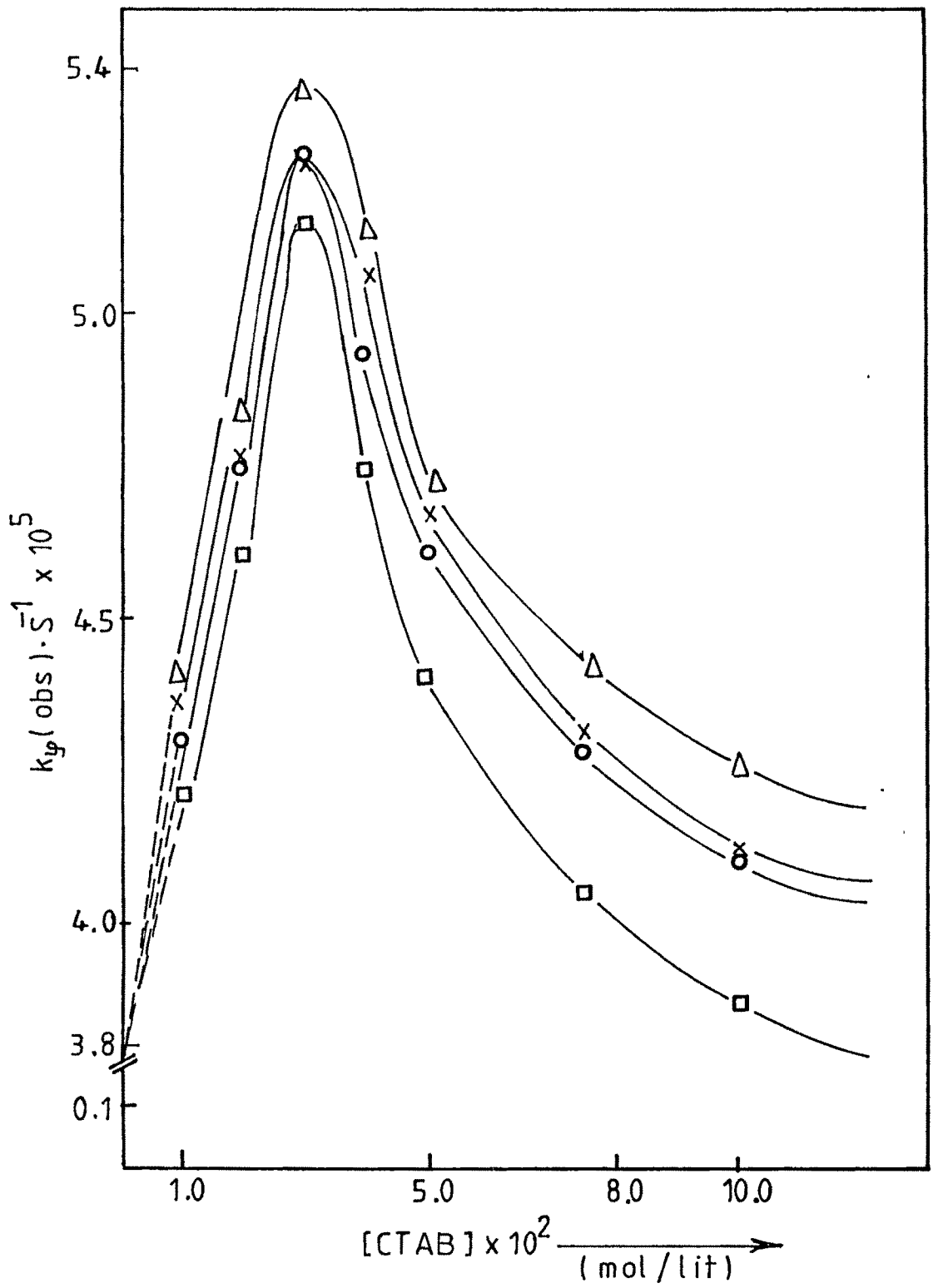


Fig 39 Effect of concentration of CTAB on hydrolysis of EtGly . , in presence of Mn^{2+} - Δ , Mn-bipyl - O, Mn-DET - X, Mn-Ophen - □

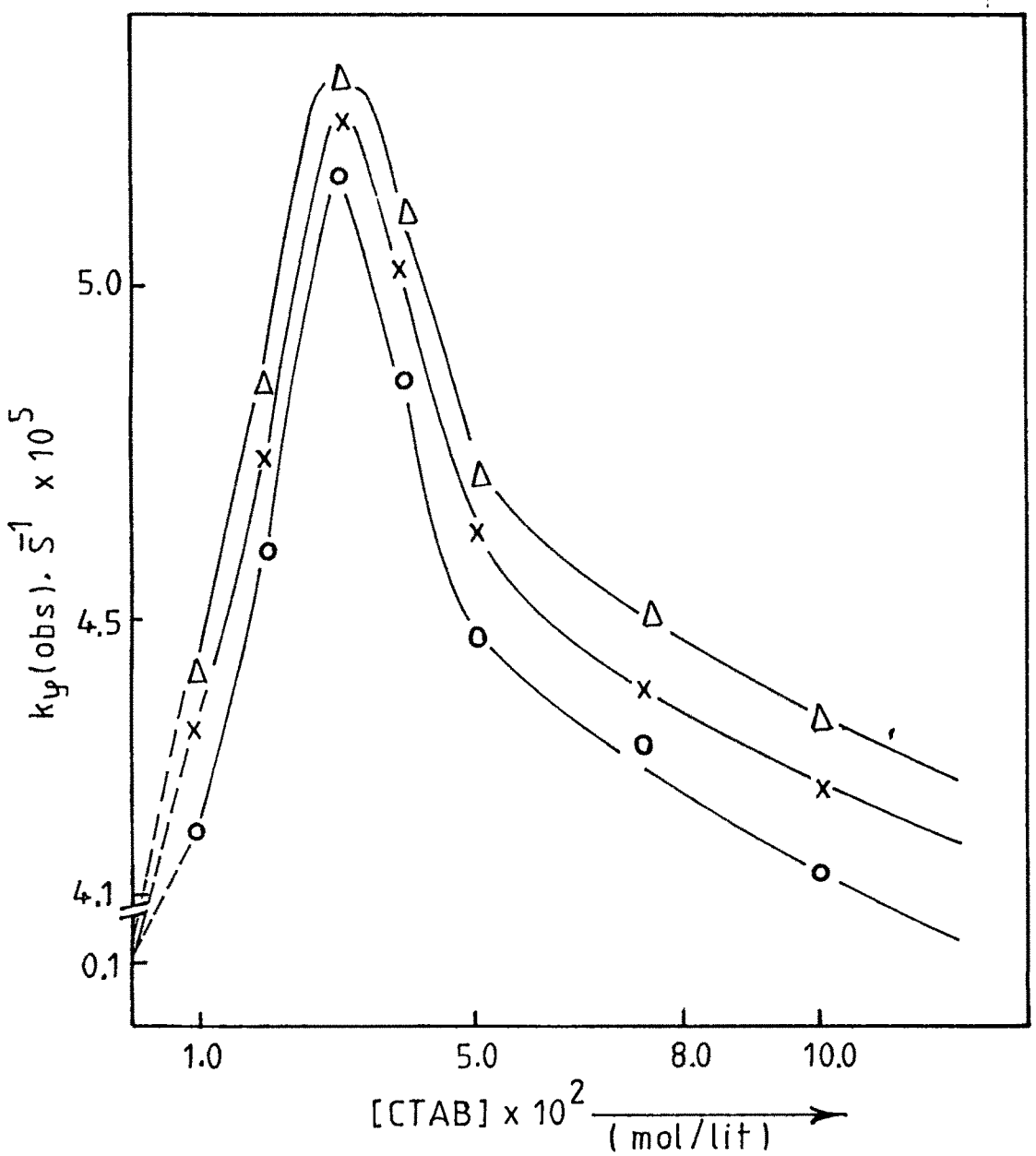


Fig. 40 Effect of concentration of CTAB on hydrolysis of EtGly ., in presence of Fe^{2+} - Δ, Fe-bipyl - X, Fe -Ophen - O

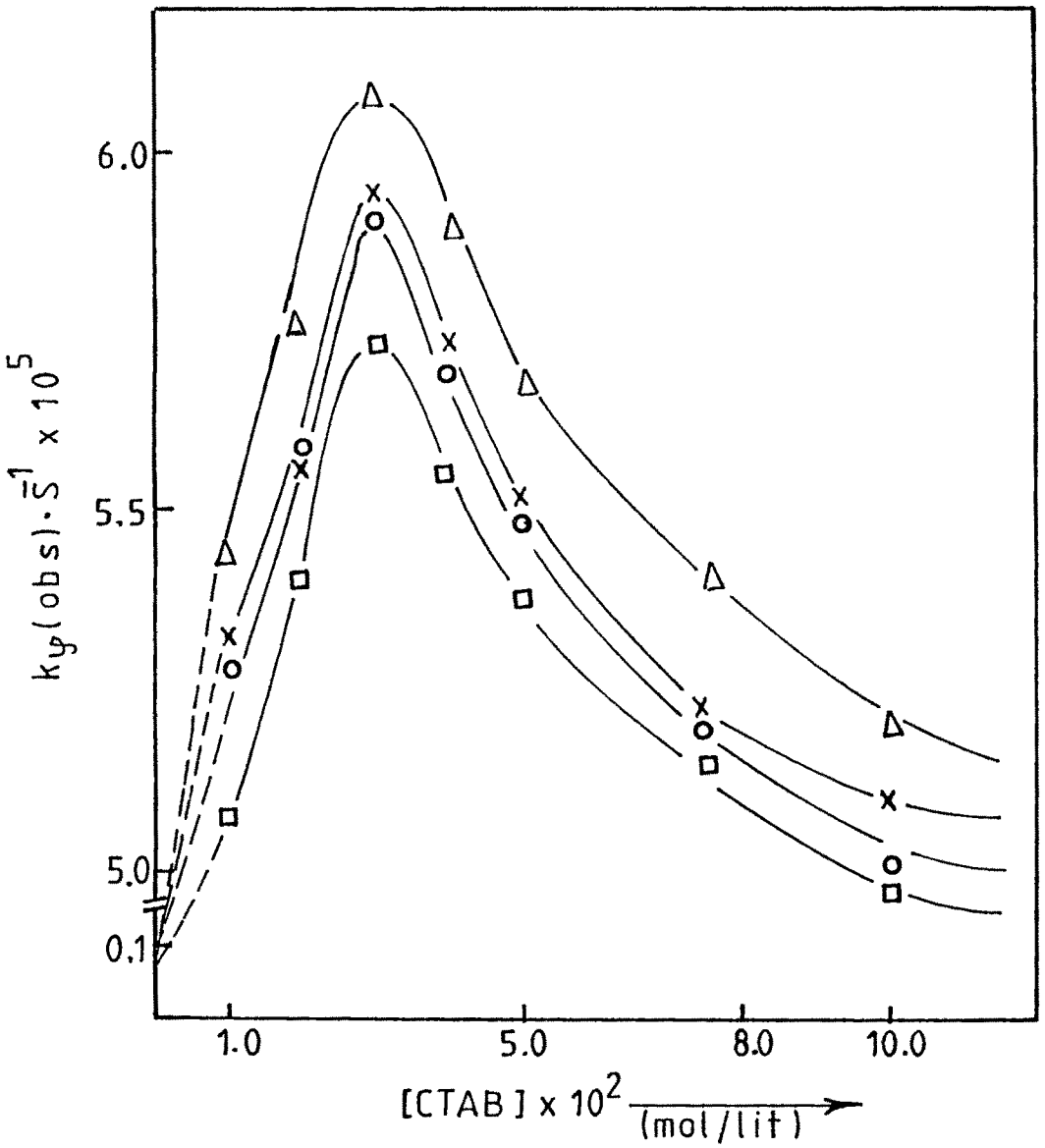


Fig 41 Effect of concentration of CTAB on hydrolysis of PhGly , in presence of Cu^{2+} - Δ , Cu-bipyl - O, Cu-DET - X, Cu-Ophen - □

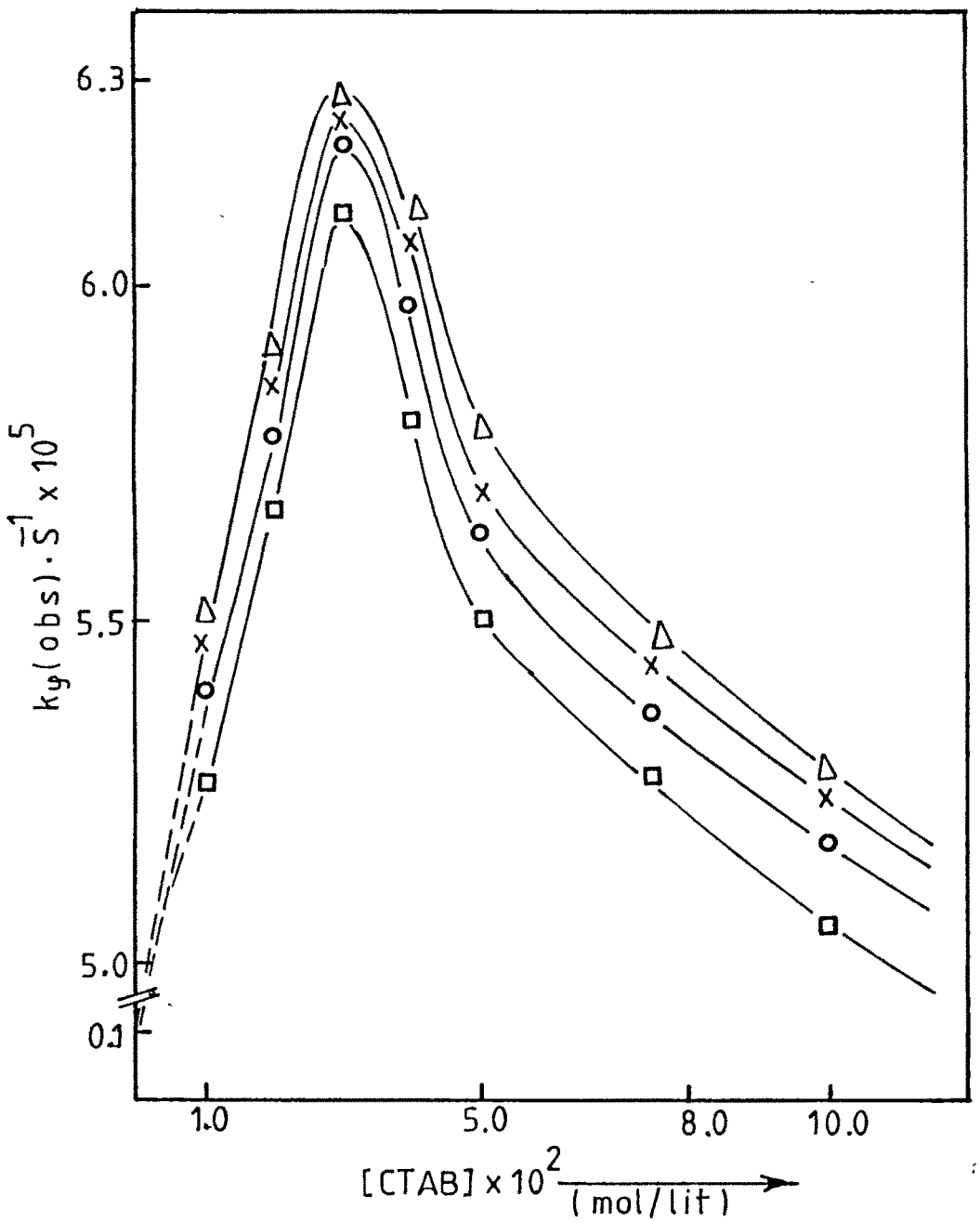


Fig 42 Effect of concentration of CTAB on hydrolysis of PhGly , in presence of Zn^{2+} - Δ , Zn-bipyl - O, Zn-DET - X, Zn-Ophen - □

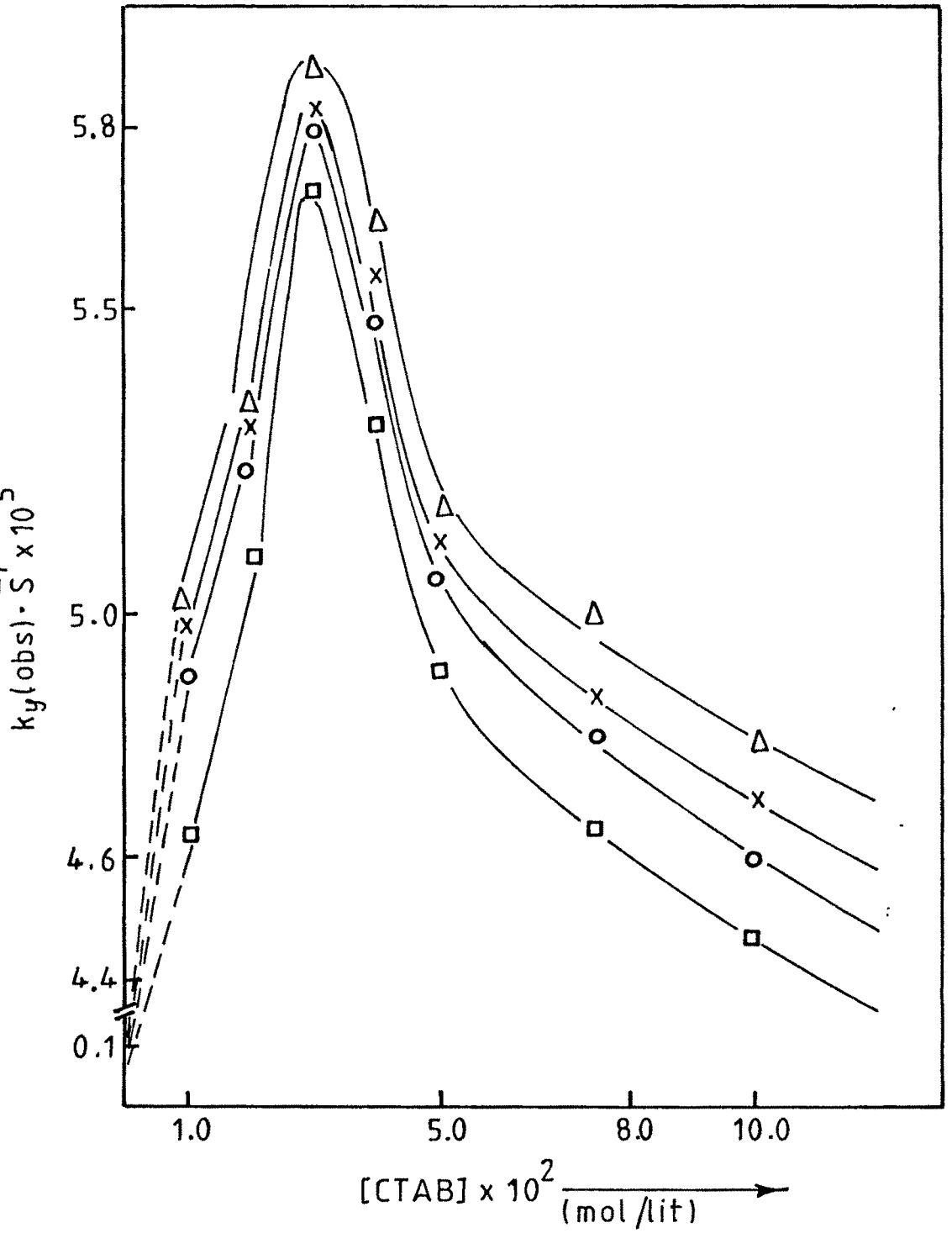


Fig 43 Effect of concentration of CTAB on hydrolysis of PhGly , in presence of Mn^{2+} - Δ , Mn-bipyl - O, Mn-DET - X, Mn-Ophen - □

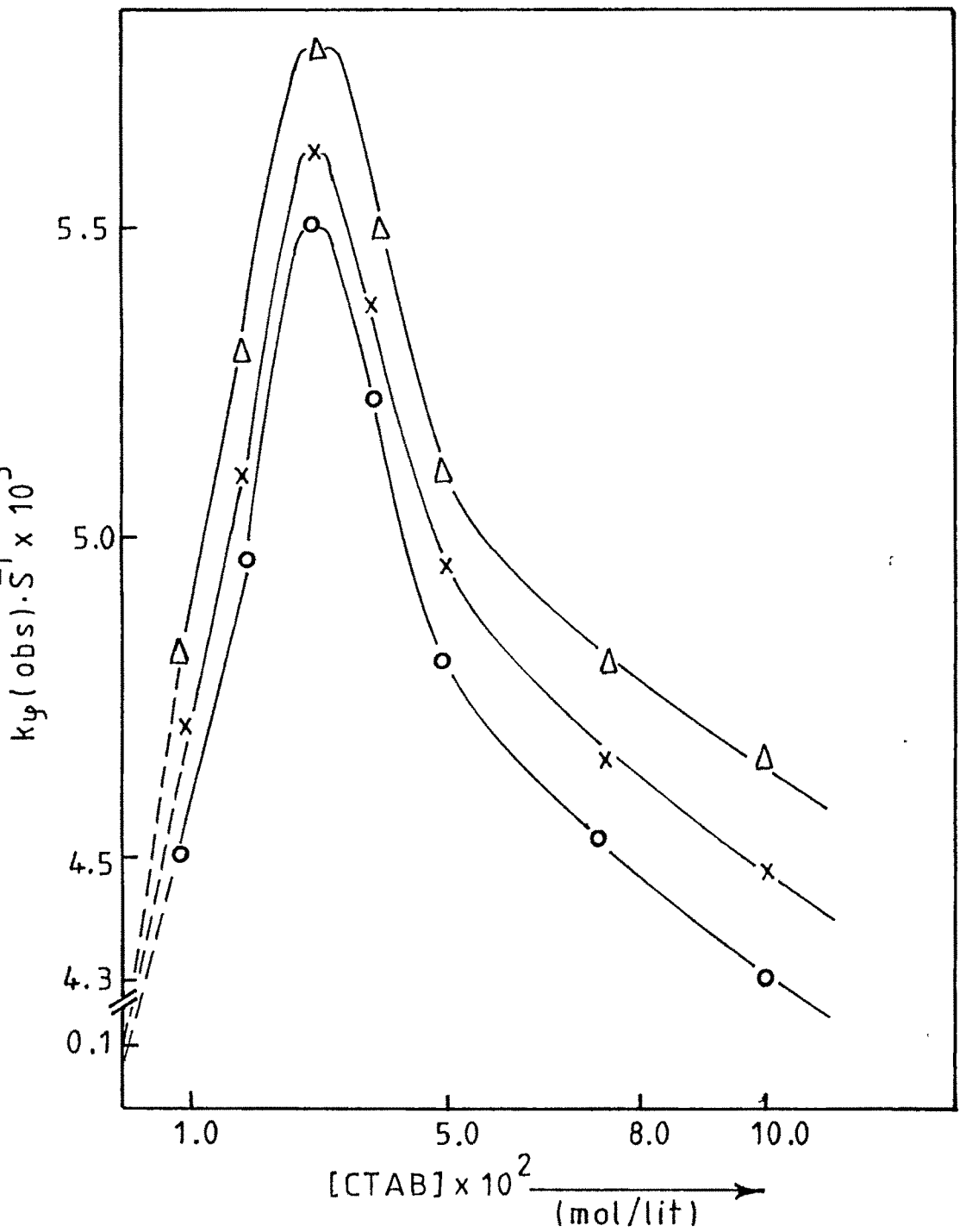


Fig 44 Effect of concentration of CTAB on hydrolysis of PhGly , in presence of Fe^{3+} - Δ , Fe-bipyl - X, Fe-Ophen -O

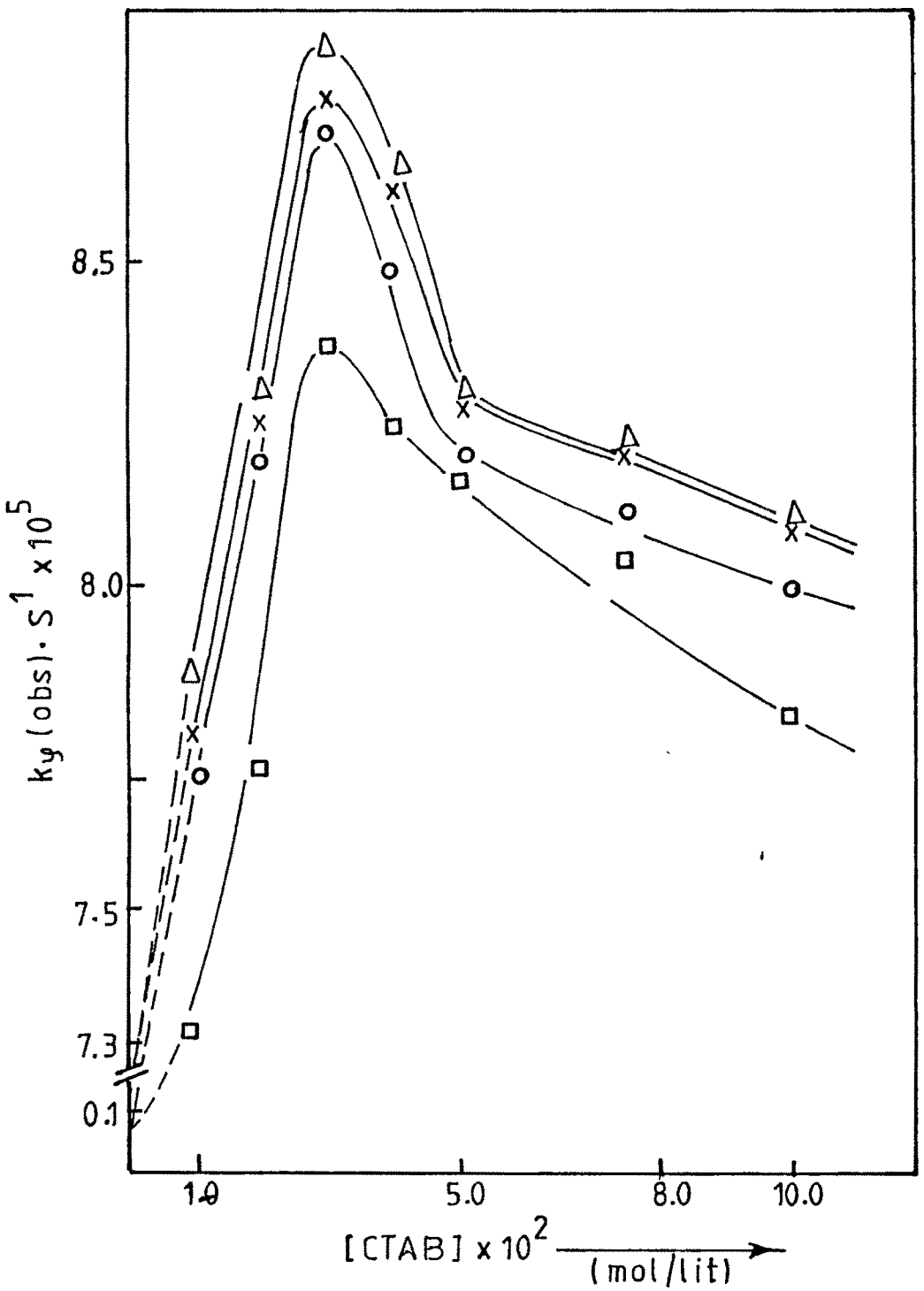


Fig 45 Effect of concentration of CTAB on hydrolysis of diMeGly , in presence of Cu^{2+} - Δ , Cu-bipyl - O, Cu-DET - X, Cu-Ophen - □.

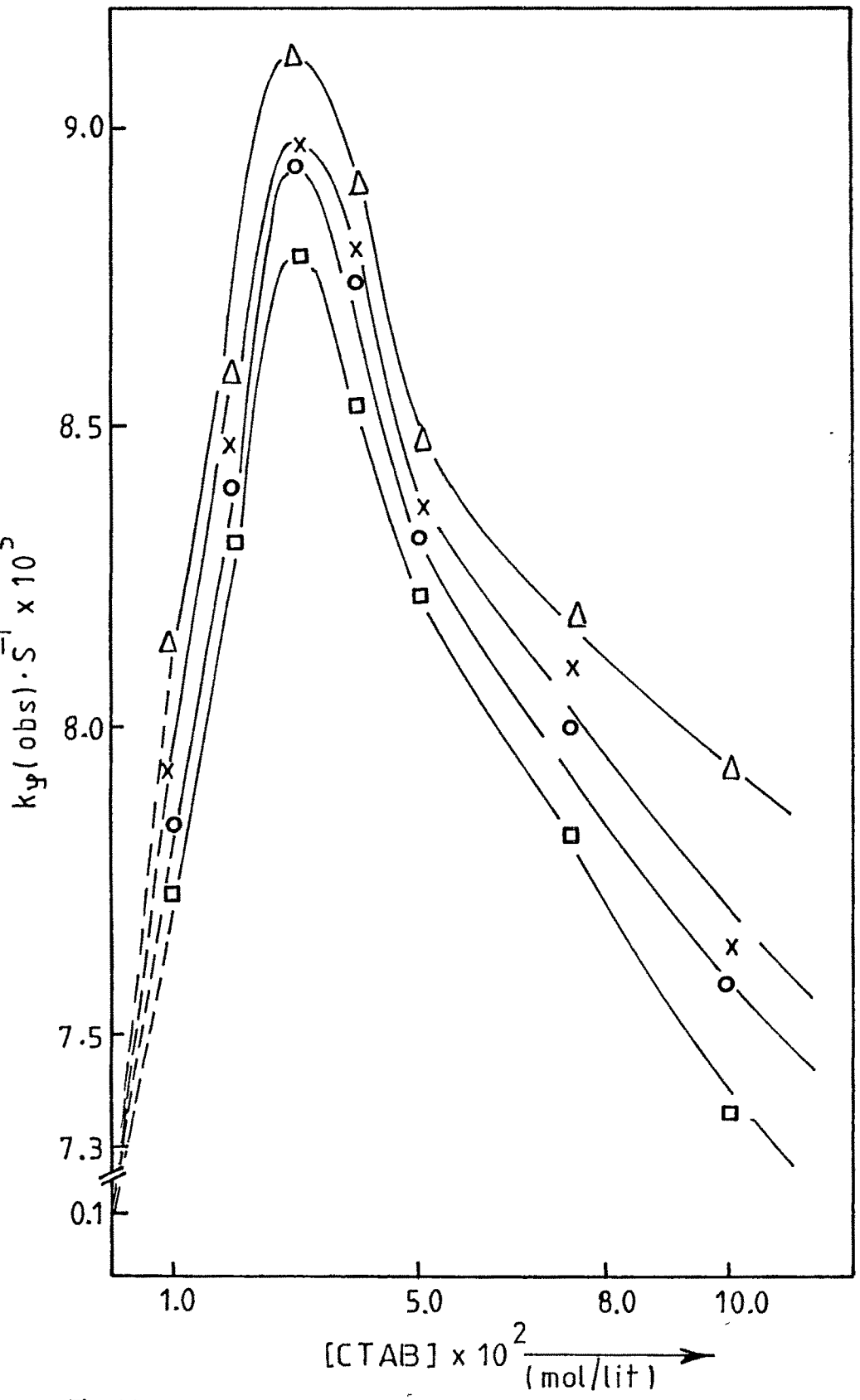


Fig. 46 Effect of concentration of CTAB on hydrolysis of diMeGly , in presence of Zn^{2+} - Δ , Zn-bipyl - O, Zn-DET - X, Zn-Ophen - □

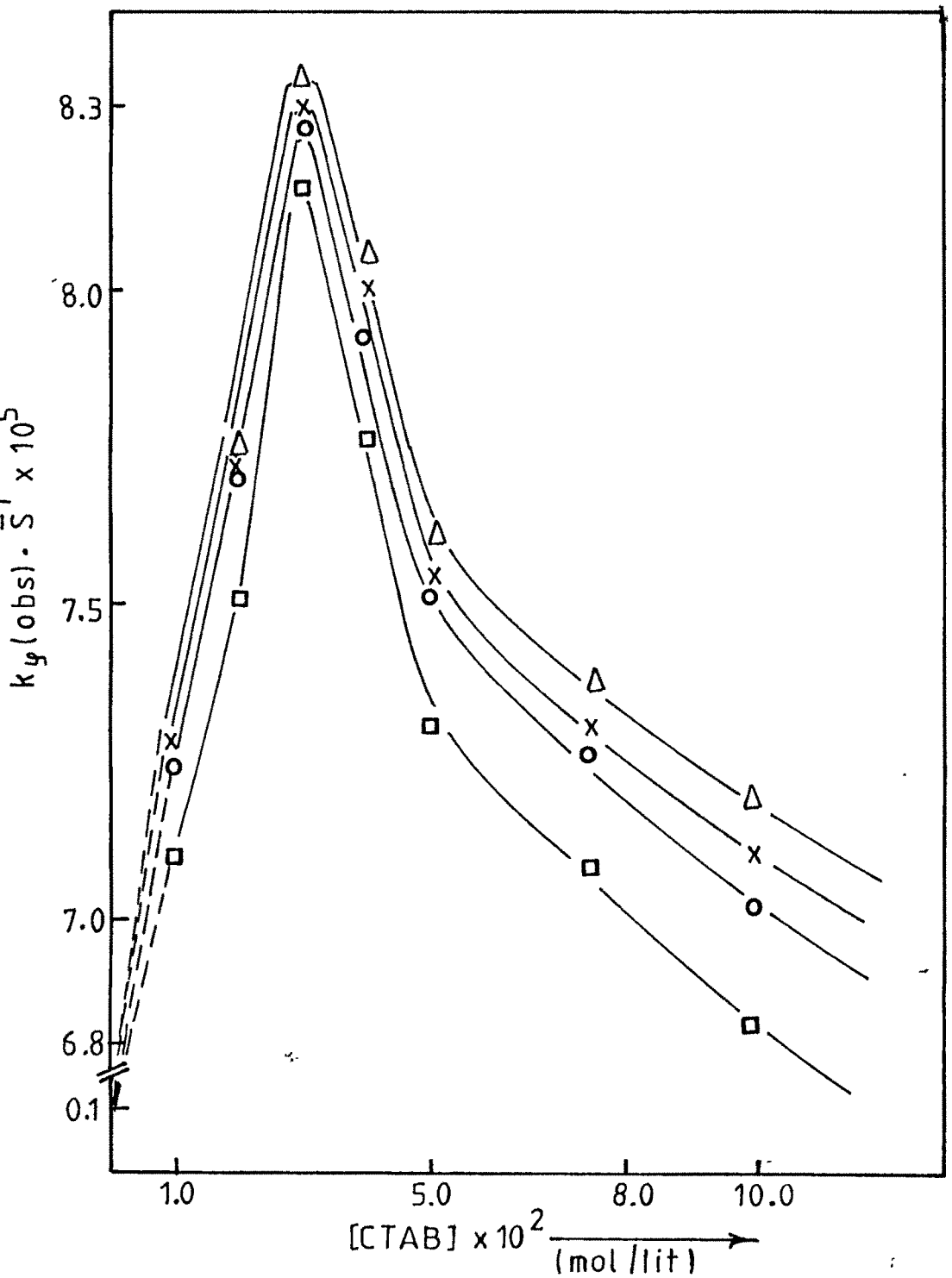


Fig 47 Effect of concentration of CTAB on hydrolysis of diMeGly - , in presence of Mn^{2+} - Δ , Mn-bipyl - O, Mn-DET - X, Mn-Ophen - □.

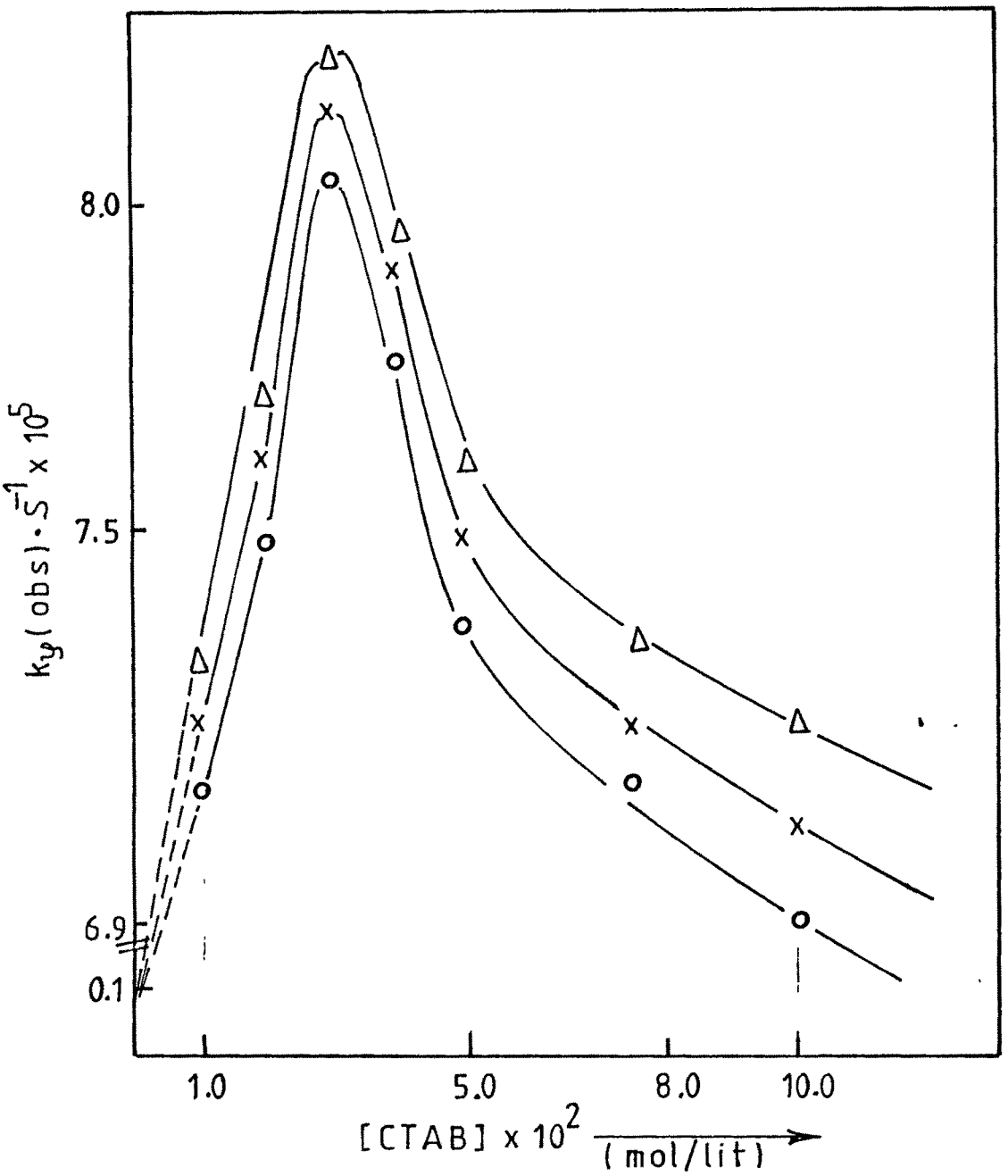


Fig 48 Effect of concentration of CTAB on hydrolysis of diMeGly , in presence of Fe^{3+} - Δ, Fe-bipyl - X, Fe-Ophen - O

The observed kinetic behaviour could be explained by PPIE model, which is explained in detail int he previous section Applying the model we can say that

Here, $k_{\varphi mL(obs)} = \alpha k_{MW}[D] + k_M (1 - \alpha)$ ..... . (4)

where,

$k_{\varphi mL}$: rate constant in presence of metal complex and CTAB

k_{MW} : rate constant due to additional attack on ester from aqueous pseudophase

k_M : rate constant in micellized pseudophase

D : surfactant concentration

α : the degree of micellar dissociation

CMC for CTAB in presence of different metal complexes coordinated with glycine ester as well as in presence of only glycine esters were determined by surface tension method. No significant change in CMC of CTAB was observed in any of the case studied For example CMC for CTAB in presence of Me Gly and Me Gly (Cu-bipyl) were found to be 8 96 x 10^{-4} mole/lit and 8.9 x 10^{-4} mole/lit respectively. The CMC values were close to that given in literature. α was determined by conductivity method The α value was found to be constant only upto 0.03 M CTAB and then slowly increased with further increase in concentration of CTAB. Therefore the rate constant $k_{\varphi mL}$ depends on α, k_{MW}, k_M and D.

At pH 5.2, as the concentration of micelle increases, initially, more and more OH ions are brought to micellar surface due to electrostatic attraction and thus make the way for attack of OH^- ions on glycine ester As the reaction was proceeding at constant pH of the bulk, the availability of OH^- ion in bulk would remain same, while the concentration of micelle increases. Beyond 0.03 M CTAB, the amount of counter ions around the micelle might be increased to such an extent that, it almost prevents the attack of OH^- ions from the aqueous phase to the micellar bound glycine ester, i e.; the value of k_{MW} should become zero at this point and therefore, the equation (4) becomes,

$$k_{\varphi mL(obs)} = k_M (1-\alpha) \qquad \text{..... ....} \qquad (5)$$

It was observed that, the value of α increased with concentration of CTAB, above 0.03 M, but k_M was nearly constant and therefore the $k_{\varphi ML}$ value decreased with increase in concentration of CTAB.

The equation (4) could be rearranged to,

$$k_{\varphi ML(obs)} /1-\alpha = \alpha/1-\alpha\ [D]\ k_{MW} + k_M \quad (6)$$

k_{MW} and k_M values were calculated from the slope and intercept of the plot of $[k_{\varphi ml\ (obs)} /1-\alpha]$ vs $(\alpha/1-\alpha) \times D]$ Two straight line plots were obtained in the range of 1×10^{-2} to 1×10^{-1} M CTAB for the hydrolysis of EtGly in presence of metal complexes (Fig 49) The same type of plots were obtained for other esters also.

k_{MW} and k_M values up to 0.03 M CTAB for glycine ester metal complex system were found to be in the range of 10^{-5} and 10^{-3}. And above 0.03 M CTAB, k_{MW} for all the systems were zero and k_M values were in the range 10^{-5} The values of k_{MW} above 0.03 M CTAB in all the cases of hydrolysis, support the statement that the attack of OH^- ion from aqueous pseudophase towards the bound aminoacid ester was shielded by the presence of large amount of counter ions of CTAB. Using these values of α, k_M and k_{MW} (Table 22-25), k_{mL} values were calculated and presented in (Table 26-33). The model applied in this study was found to be in good agreement with the experimental data (Fig. 50-61) as it is in the case of glycine ester hydrolysis in presence of only surfactants. As the same model using the same arguements is applicable for both the systems, it shows that metal complex is not interfering or affecting the mechanism of micellar catalysis.

When the effect of temprature was studied, it showed the effect was similar to that observed in the absence of metal complexes. Some of the observed data are presented in Figures (62-65). Temperature and rate constant follow the Arrhenious relationship Though a small increase int he rate constant is observed with increase in temperature, it does not make any change int he trend of variation of rate constant with concentration of CTAB, showing the mechanism is not affected by change in temperature from 30-45°C.

Table 22· α, k_M and k_{MW} values for the hydrolysis of Glycine esters in presence of Cu^{2+}/Cu complexes

		α						$k_M \times 10^5$		$k_{MW} \times 10^3$
Ester	[CTAB]→ Metal Complex	0 01M	0 02M	0 03M	0 05M	0.075M	0 1M	≤0.03M	>0.03M	≤0.03M
MeGly	Cu-bipyl	0.23	0 23	0 23	0 25	0 30	0.32	6.33	7 65	1.75
	Cu-Ophen	0 23	0 23	0 23	0 25	0 30	0 32	5.68	7 42	2.43
	Cu-DET	0 23	0 23	0 23	0 25	0 30	0 32	6.40	7 60	1.47
	Cu-bipyl	0 22	0 22	0 22	0 23	0 28	0 35	6 56	6 60	0.14
EtGly	Cu-Ophen	0 22	0 22	0 22	0 23	0 26	0 34	6 10	6 45	0 37
	Cu-DET	0 22	0 22	0 22	0 24	0 29	0 36	6.55	6 55	0 14
	Cu-bipyl	0 19	0 19	0 19	0 21	0 22	0 23	8.76	10.4	2.72
diMeGly	Cu-Ophen	0.19	0 19	0.19	0 21	0 22	0 25	8.34	10 3	2.72
	Cu-Dien	0.19	0 19	0.19	0 21	0 22	0 25	8.80	10 4	2.73
	Cu-bipyl	0 21	0.21	0 21	0 24	0 28	0 30	6.28	7.25	1.51
PhGly	Cu-Ophen	0 21	0.21	0.21	0 24	0 28	0 30	6.01	7 07	1 56
	Cu-DET	0 21	0 21	0 21	0 24	0 28	0 30	6.31	7.24	1.49

Table 23· α, k_M and k_{MW} values for the hydrolysis of Glycine esters in presence of Zn^{2+} /Zn complexes

		α						$k_M \times 10^5$		$k_{MW} \times 10^3$
Ester	[CTAB] → Metal Complex	0 01M	0 02M	0.03M	0 05M	0 075M	0 1M	≤0.03M	>0 03M	≤0 03M
MeGly	Zn-bipyl	0 23	0 23	0 23	0 25	0 30	0.32	6 02	9 43	5.61
	Zn-Ophen	0 23	0 23	0.23	0 25	0 30	0 32	5.40	8 75	6 00
	Zn-DET	0 23	0 23	0.23	0 25	0 30	0 32	6.30	9 47	5 46
	Zn-bipyl	0 22	0.22	0.22	0 24	0 27	0 31	6 38	8 55	3.48
EtGly	Zn-Ophen	0 22	0 22	0 22	0 24	0 27	0 31	5 90	7 96	3 43
	Zn-DET	0 22	0 22	0.22	0 24	0 27	0 31	6 58	8 56	3.48
	Zn-bipyl	0 19	0 19	0.19	0 21	0 22	0 25	9 01	10 3	2 81
DiMeGly	Zn-Ophen	0 19	0 19	0 19	0 21	0 22	0 25	8 88	10.4	2.91
	Zn-DET	0 19	0 19	0.19	0 21	0 22	0 25	9.08	10 3	2 85
	Zn-bipyl	0 21	0 21	0.21	0 24	0.28	0 30	6.32	7 44	1 92
PhGly	Zn-Ophen	0 21	0 21	0.21	0 24	0 28	0 30	6 13	7.25	1 93
	Zn-DET	0 21	0.21	0.21	0.24	0.28	0 30	6 43	7 50	1 85

Table 24. α, k_M and k_{MW} values for the hydrolysis of Glycine esters in presence of Fe^{3+} /Fe complexes

		α						$k_M \times 10^5$		$k_{MW} \times 10^3$
Ester	[CTAB] → Metal Complex	0.01M	0 02M	0.03M	0.05M	0.075M	0 1M	≤0.03M	>0 03M	≤0 03M
MeGly	Fe-bipyl	0.23	0.23	0.23	0.25	0 31	0.32	4.91	6.47	2.56
	Fe-Ophen	0.22	0.23	0.23	0.25	0 30	0 32	5 21	6 27	2 06
EtGly	Fe-bipyl	0.22	0 22	0.22	0.24	0 28	0 31	4.99	6.08	2.02
	Fe-Ophen	0.22	0.22	0 22	0.24	0 28	0.31	4.52	5.88	3 12
DiMeGly	Fe-bipyl	0.19	0.19	0.19	0.21	0 23	0 25	8 25	9.41	2.57
	Fe-Ophen	0 19	0 19	0.19	0.21	0.22	0 25	8.15	9 25	2.47
PhGly	Fe-bipyl	0.21	0.21	0.21	0.24	0.28	0 30	5.35	6.48	2.18
	Fe-Ophen	0.21	0 21	0.21	0.25	0.28	0 31	5.08	6.38	2 34

Table 25: α, k_M and k_{MW} values for the hydrolysis of Glycine esters in presence of Mn^{2+} /Mn complexes

		α						$k_M \times 10^5$		$k_{MW} \times 10^3$
Ester	[CTAB] → Metal Complex	0.01M	0.02M	0.03M	0.05M	0.075M	0.1M	≤0.03M	>0.03M	≤0.03M
MeGly	Mn-bipyl	0.23	0 23	0.23	0.25	0.30	0 32	5 37	6 48	2.11
	Mn-Ophen	0 23	0 23	0.23	0 25	0.30	0 32	5 19	6.31	2.39
	Mn-DET	0.23	0 23	0.23	0 25	0 30	0.32	5.48	6.50	2.30
	Mn-bipyl	0 22	0 22	0.22	0 24	0.27	0.31	4 87	6.01	2.22
EtGly	Mn-Ophen	0.22	0.22	0.22	0.24	0 28	0 31	4.67	5.65	2.38
	Mn-DET	0.22	0.22	0.22	0.24	0 28	0 30	4 99	5.95	2.04
	Mn-bipyl	0.19	0.19	0.19	0 21	0 22	0.25	8.32	9 51	2.64
diMeGly	Mn-Ophen	0.19	0 19	0.19	0.21	0 23	0.25	8.05	9 24	2.83
	Mn-DET	0.19	0.19	0.19	0.21	0 22	0 26	8.40	9.32	2.53
	Mn-bipyl	0 21	0.21	0.21	0.24	0.29	0 31	5.59	6.70	2.15
PhGly	Mn-Ophen	0.21	0 21	0.21	0.24	0.28	0 30	5.17	6.46	2.52
	Mn-DET	0.21	0.21	0.21	0.24	0 28	0.30	5.59	6 70	2.15

Table 26· Observed (obs) and Calculated (cal) rate constants for MeGly and EtGly hydrolysis in presence of Cu complexes and CTAB at 40°C and 5 2 pH

[CTAB] M	Me Gly						EtGly					
	$k_{\varphi m1L1}x10^5\ S^{-1}$		$k_{\varphi m1L2}x10^5\ S^{-1}$		$k_{\varphi m1L3}x10^5\ S^{-1}$		$k_{\varphi m1L1}x10^5\ S^{-1}$		$k_{\varphi m1L2}x10^5\ S^{-1}$		$k_{\varphi m1L3}x10^5\ S^{-1}$	
	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal
0 01	5 16	5 15	4 84	4 83	5.14	5 14	5 21	5 27	5.10	4 95	5 24	5 26
0 02	5 29	5 18	5 02	4 92	5 17	5 18	5.58	5 65	5 40	5 48	5 65	5 61
0 03	5 24	5.21	5 05	5 01	5.20	5.20	6 01	6 06	5 88	6 05	5 94	5 94
0 05	5 10	5 08	4 96	4 97	5 07	5 01	5 75	5 74	5 58	5 56	5.69	5 70
0 075	4 14	4 03	4.75	4.77	4 63	4 67	5 37	5 40	5 17	5 19	5 26	5 30
0 1	3 75	3 65	4.18	4 25	4.15	4.21	5.14	5 20	4 95	5 04	5 14	5 16

$m_1 \rightarrow Cu^{2+}$, L_1 →bipyl. L_2 →ophen and L_3 →DET

Table 27 Observed (obs) and Calculated (cal.) rate constants for diMeGly and PhGly hydrolysis in presence of Cu complexes and CTAB at 40°C and 5 2 pH

[CTAB] M	diMeGly						PhGly					
	$k_{cpm1L1}x10^5$ S^{-1}		$k_{cpm1L2}x10^5.S^{-1}$		$k_{cpm1L3}x10^5$ S^{-1}		$k_{cpm1L1}x10^5$ S^{-1}		$k_{cpm1L2}x10^5$ S^{-1}		$k_{cpm1L3}x10^5$ S^{-1}	
	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal
0 01	7 71	7.62	7 31	7 28	7.78	7 66	5.28	5 28	5.07	5 08	5 32	4 99
0 02	8.21	8 14	7.72	7 78	8.26	8 17	5 59	5 60	5.40	5 40	5.58	5.61
0 03	8 71	8 65	8 38	8 31	8.76	8 69	5 91	5.90	5.73	5 74	5 94	5 92
0 05	8 24	8 22	8.17	8 14	8 30	8 24	5 48	5 51	5.37	5 35	5 51	5 50
0 075	8 16	8 12	8 06	8 04	8.14	8.12	5 22	5 20	5.15	5 09	5.20	5 21
0 1	8 03	8.01	7 80	7 73	7.72	7.80	5 04	5 07	5 01	4 95	5 10	5 07

$m_1 \rightarrow Cu^{2+}$, L_1 →bipyl. L_2 →ophen and L_3 →DET

Table 28: Observed (obs) and Calculated (cal.) rate constants for MeGly and EtGly hydrolysis in presence of Zn complexes and CTAB at 40°C and 5 2 pH

	MeGly						EtGly					
	$k_{\varphi m2L_1}x10^5\ S^{-1}$		$k_{\varphi m2L_2}x10^5.S^{-1}$		$k_{\varphi m2L_3}x10^5.S^{-1}$		$k_{\varphi m2L_1}x10^5.S^{-1}$		$k_{\varphi m2L_2}x10^5\ S^{-1}$		$k_{\varphi m2L_3}x10^5\ S^{-1}$	
	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal
0 01	5.72	5.74	5.35	5 36	5 86	5.89	6.10	5 93	5.72	5.56	6 27	6.15
0 02	6 51	6 50	6.09	6 11	6.67	6.66	6 87	7 21	6.55	6.90	7.04	7.30
0 03	7 32	7 28	6.93	6 87	7.46	7.43	8 68	8.52	8 48	8.34	8.78	8 62
0 05	6.54	6.50	6 07	6.05	6 65	6.51	7 08	7 07	6 59	6.56	7.12	7.10
0 075	6 20	6.24	5 78	5 81	6.20	6.25	6.54	6 60	6.08	6.12	6.61	6 62
0 1	5 80	5.89	5.40	5 49	5 38	5.92	6.35	6 41	5.89	5.95	6 40	6.43

$m_2 \rightarrow Zn^{2+}$, $L_1 \rightarrow$bipyl, $L_2 \rightarrow$ophen and $L_3 \rightarrow$ DET

Table 29 Observed (obs) and Calculated (cal.) rate constants for diMeGly and PhGly hydrolysis in presence of Zn complexes and CTAB at 40°C and 5.2 pH

[CTAB] M	diMeGly						PhGly					
	$k_{\psi m2L_1}x10^5\ S^{-1}$		$k_{\psi m2L_2}x10^5\ S^{-1}$		$k_{\psi m2L_3}x10^5.S^{-1}$		$k_{\psi m2L_1}x10^5.S^{-1}$		$k_{\psi m2L_2}x10^5\ S^{-1}$		$k_{\psi m2L_3}x10^5.S^{-1}$	
	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal
0 01	7.84	7.83	7.72	7 74	7.91	7.90	5.40	5.39	5.27	5.25	5 47	5 47
0 02	8.40	8 37	8 31	8 30	8.47	8.45	5.78	5.80	5.66	5.65	5.85	5 86
0.03	8 94	8.91	8.79	8 84	8 97	8 98	6 21	6.20	6 10	6 06	6.24	6.25
0 05	8.31	8 14	8 22	8 21	8.36	8.14	5.63	5.65	5.51	5.51	5.69	5 70
0 075	8.03	8.03	8.01	8.10	8.10	8.05	5.37	5 36	5.28	5 22	5.45	5 40
0 1	7.58	7.70	7.36	7 80	7 63	7.70	5.19	5 21	5.05	5 07	5.26	5.25

$m_2 \rightarrow Zn^{2+}$, $L_1 \rightarrow$bipyl, $L_2 \rightarrow$ophen and $L_3 \rightarrow$DET

Table 30. Observed (obs) and Calculated (cal.) rate constants for MeGly and EtGly hydrolysis in presence of Fe compleces and CTAB at 40°C and pH 5.2

[CTAB] M	MeGly				EtGly			
	$k_{\varphi m3L1} x10^5 S^{-1}$		$k_{\varphi m3L2} x10^5 S^{-1}$		$k_{\varphi m3L1} x10^5 S^{-1}$		$k_{\varphi m3L2} x10^5 .S^{-1}$	
	obs	cal	obs	cal	obs	cal	obs	cal
0 01	4.35	4 34	4 19	4 21	4 60	4 37	4.51	4.49
0 02	4.74	4 78	4 60	4.89	5.05	4 96	4 90	4.95
0 03	5 24	5.23	5.16	5 57	5.56	5 55	5 46	5 43
0 05	4 62	4.62	4 47	4 47	4.85	4 85	4 70	4.70
0.075	4.40	4.38	4.22	4 23	4.60	4 46	4.45	4.39
0.1	4 26	4.20	4.13	4 06	4.43	4.40	4.21	4.26

$m_3 \rightarrow Fe^{2+}$, $L_1 \rightarrow$bipyl and $L_2 \rightarrow$ophen

Table 31 Observed (obs) and Calculated (cal.) rate constants for diMeGly and PhGly hydrolysis in presence of Fe complexes and CTAB at 40°C and pH 5.2

[CTAB] M	diMeGly				PhGly			
	$k_{pm3L_1}x10^5\ S^{-1}$		$k_{pm3L_2}x10^5.S^{-1}$		$k_{pm3L_1}x10^5.S^{-1}$		$k_{pm3L_2}x10^5.S^{-1}$	
	obs	cal	obs	cal	obs	cal	obs	cal
0 01	7.20	7.17	7.10	7.07	4.70	4.68	4.51	4.50
0 02	7 60	7.65	7.48	7.54	5.10	5 14	4 97	4.99
0 03	8.16	8.15	8 04	8.01	5.62	5.60	5 50	5.49
0 05	7.48	7.43	7.35	7.31	4.95	4 92	4 80	4.79
0 075	7.20	7.24	7.11	7.21	4.65	4.67	4 53	4 59
0.1	7.05	7 05	6.90	6.94	4.47	4.53	4 30	4.40

$m_3 \rightarrow Fe^{2+}$, $L_1 \rightarrow$bipyl and $L_2 \rightarrow$ophen

Table 32· Observed (obs) and Calculated (cal) rate constants for MeGly and EtGly hydrolysis in presence of Mn complexes and CTAB at 40°C and 5.2 pH

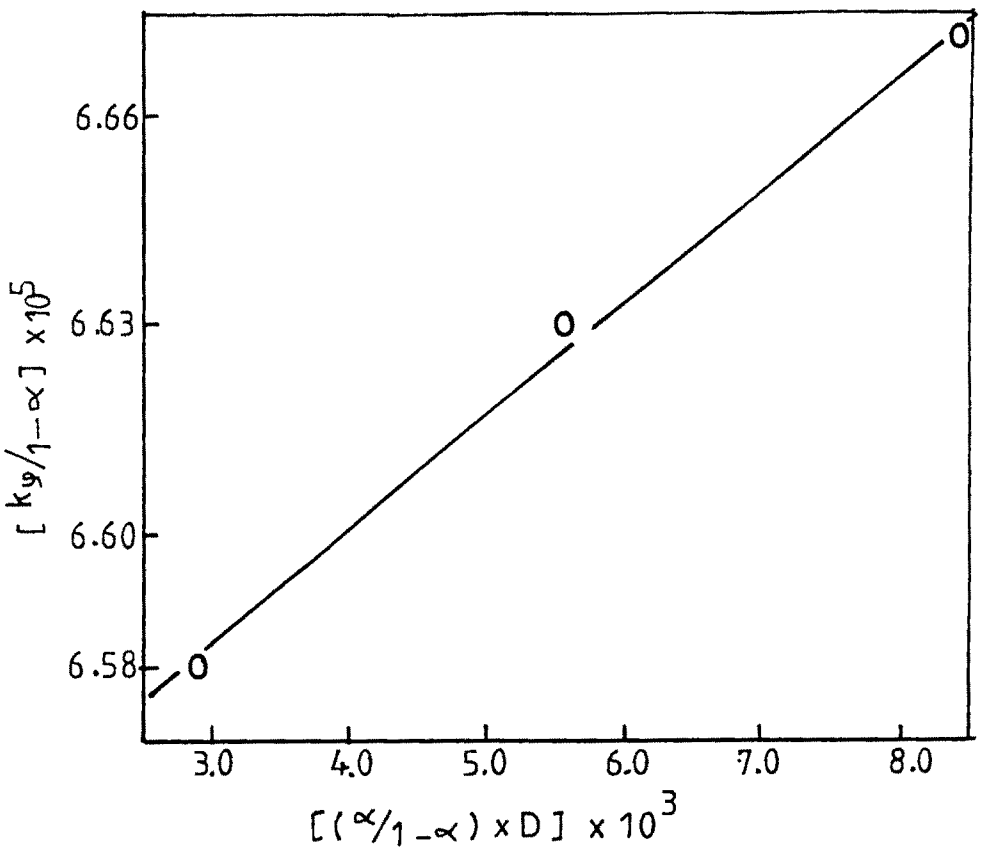
[C TAB] M	MeGly						EtGly					
	$k_{\varphi m4L1}x10^5\ S^{-1}$		$k_{\varphi m4L2}\ S^{-1}x10^5$		$k_{\varphi m4L3}x10^5\ S^{-1}$		$k_{\varphi m4L1}x10^5\ S^{-1}$		$k_{\varphi m4L2}x10^5\ S^{-1}$		$k_{\varphi m4L3}x10^5\ S^{-1}$	
	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal
0 01	4 30	4 29	4 21	4 17	4 36	4.34	4 63	4 62	4.52	4 54	4 70	4 74
0 02	4.75	4 77	4 60	4 69	4 76	4 78	5 08	5.10	4 90	5 07	5.14	5.27
0 03	5 27	5 26	5 16	5 21	5 26	5 24	5 60	5.59	5.50	5.62	5 64	5 80
0 05	4 61	4 57	4 41	4,30	4 48	4 51	4.87	4 86	4 75	4 73	4 91	4 88
0 075	4 28	4 35	4 05	4 06	4 25	4 28	4.52	4.54	4 40	4 41	4 54	4.55
0 1	4 12	4 14	3 87	3 89	4 08	4 16	4.35	4.40	4 21	4 29	4.28	4 40

$m_4 \rightarrow Mn^{2+}$, $L_1 \rightarrow$bipyl, $L_2 \rightarrow$ophen and $L_3 \rightarrow$DET

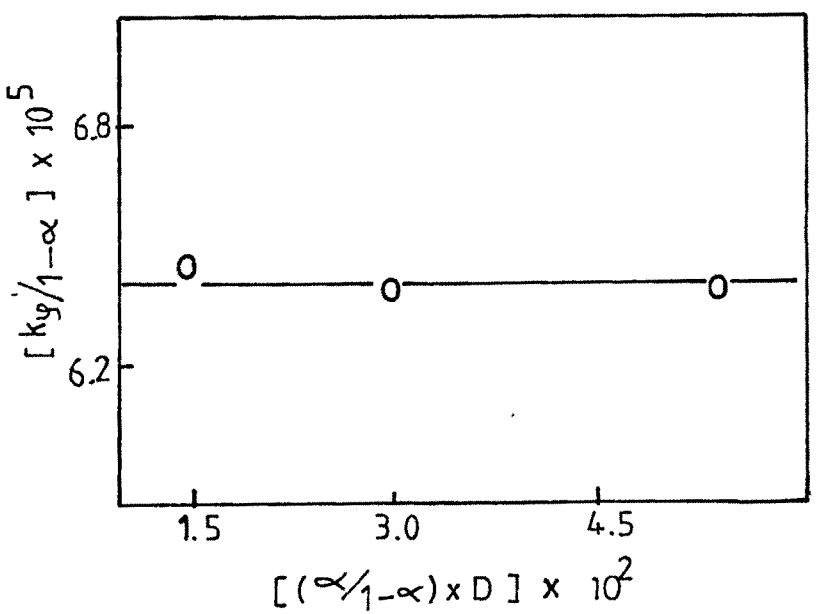
Table 33· Observed (obs) and Calculated (cal) rate constants for diMeGly and PhGly hydrolysis in presence of Mn complexes and CTAB at 40°C and 5.2 pH

[C TAB] M	diMeGly						PhGly					
	$k_{\varphi m4L1}x10^5\ S^{-1}$		$k_{\varphi m4L2}\ S^{-1}x10^5$		$k_{\varphi m4L3}x10^5.S^{-1}$		$k_{\varphi m4L1}x10^5\ S^{-1}$		$k_{\varphi m4L2}x10^5\ S^{-1}$		$k_{\varphi m4L3}x10^5.S^{-1}$	
	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal
0 01	7 26	7.24	7 10	7 06	7 30	7.28	4 90	4 87	4.64	4.61	4.90	4 87
0 02	7.70	7 74	7 51	7 59	7 73	7 76	5.26	5 30	5.10	5 14	5 31	5 32
0 03	8 27	8 24	8.18	8 14	8.29	8 25	5.80	5 77	5 70	5 68	5 83	5 77
0 05	7 52	7.51	7 30	7 30	7 35	7.36	5 07	5 09	4.91	4.91	5.14	5.09
0 075	7.28	7 40	7 10	7 11	7 30	7.27	4.80	4 76	4.65	4.65	4.85	4 76
0 1	7 03	7 12	6 84	6 90	7 10	6 90	4 63	4.62	4.48	4 52	4 70	4 63

$m_4 \rightarrow Mn^{2+}$, $L_1 \rightarrow$bipyl, $L_2 \rightarrow$ophen and $L_3 \rightarrow$DET



a) [CTAB] = 1 x 10^{-2} M to 3 x 10^{-2} M



b) [CTAB] => 3 x 10^{-2} M

Fig. 49 Plot of [$k_{\varphi mL3}$ /α1-α] vs [(α/1-α) x D] for EtGly hydrolysis in presence of Cu-DET complex and CTAB,

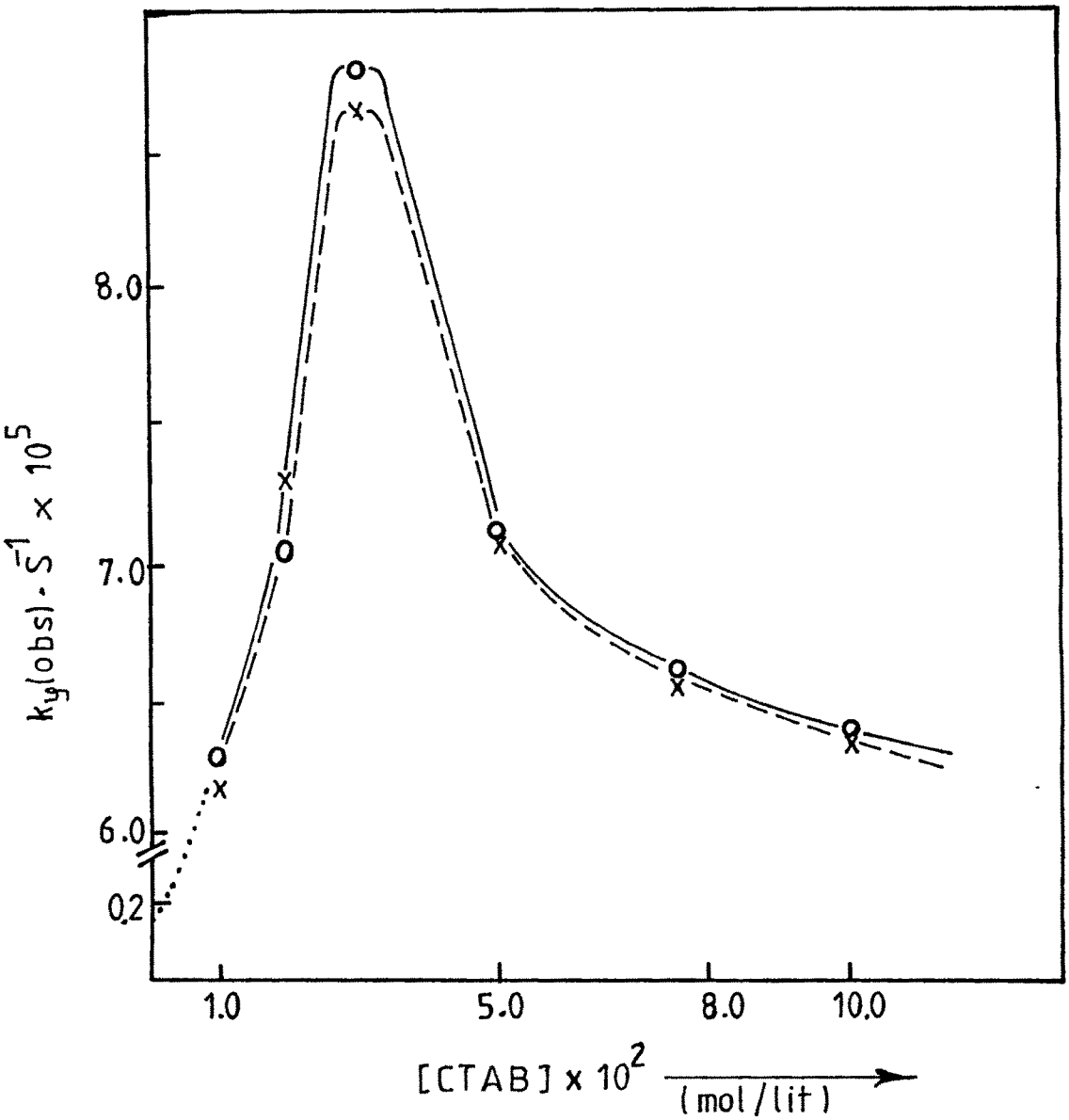


Fig 50 PPIE simulation of kinetic data for [MeGly - Zn-DET] - CTAB system at pH 5 2 and 40°C . O - $k_{\psi\ mL3\ observed}$, X - $k_{\psi\ mL3\ calculated}$

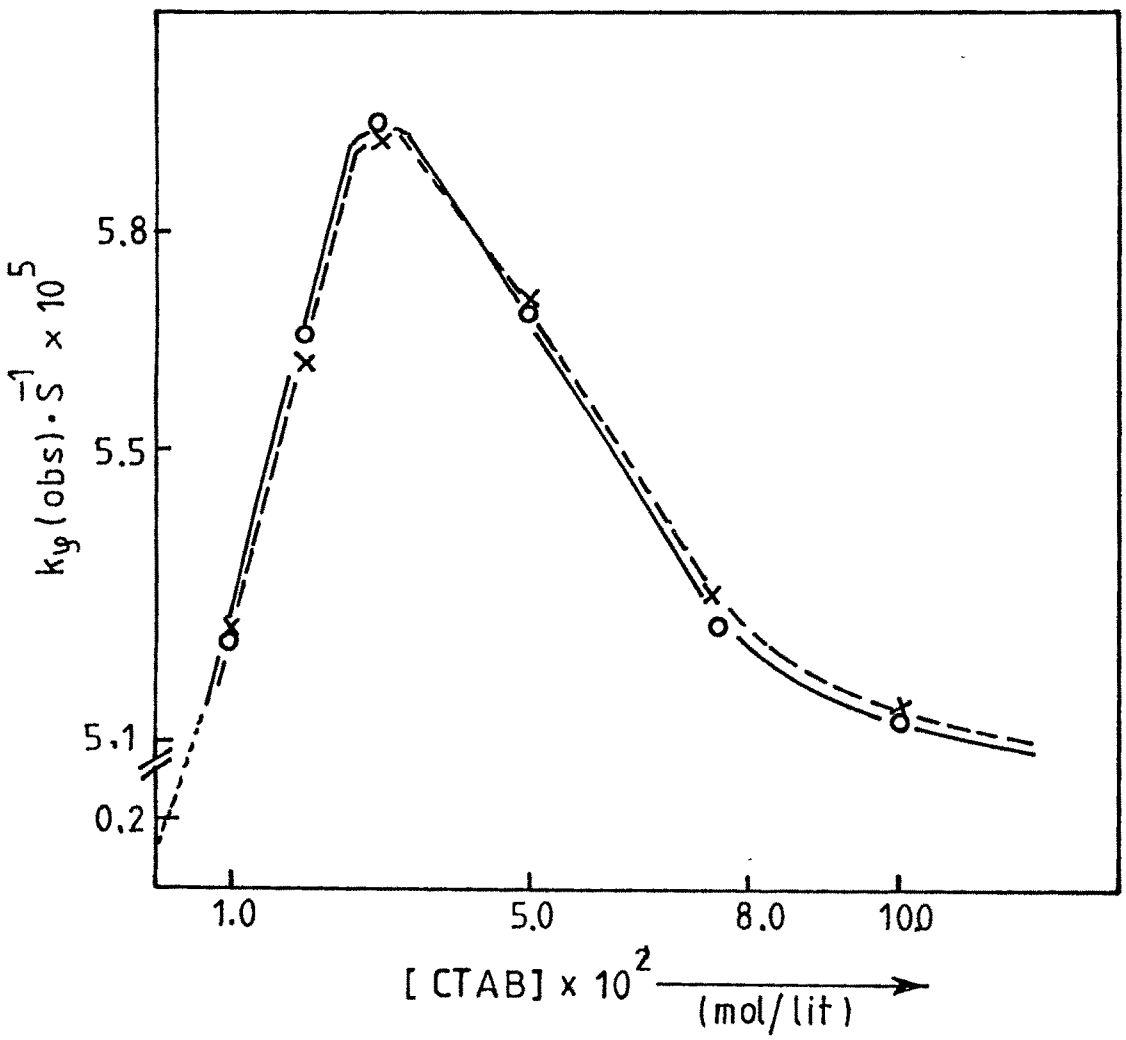


Fig 51 PPIE simulation of kinetic data for [MeGly - Cu-DET] - CTAB system at pH 5 2 and 40°C · O - $k_{\varphi\, mL3 observed}$, X - $k_{\varphi\, mL3\ calculated}$

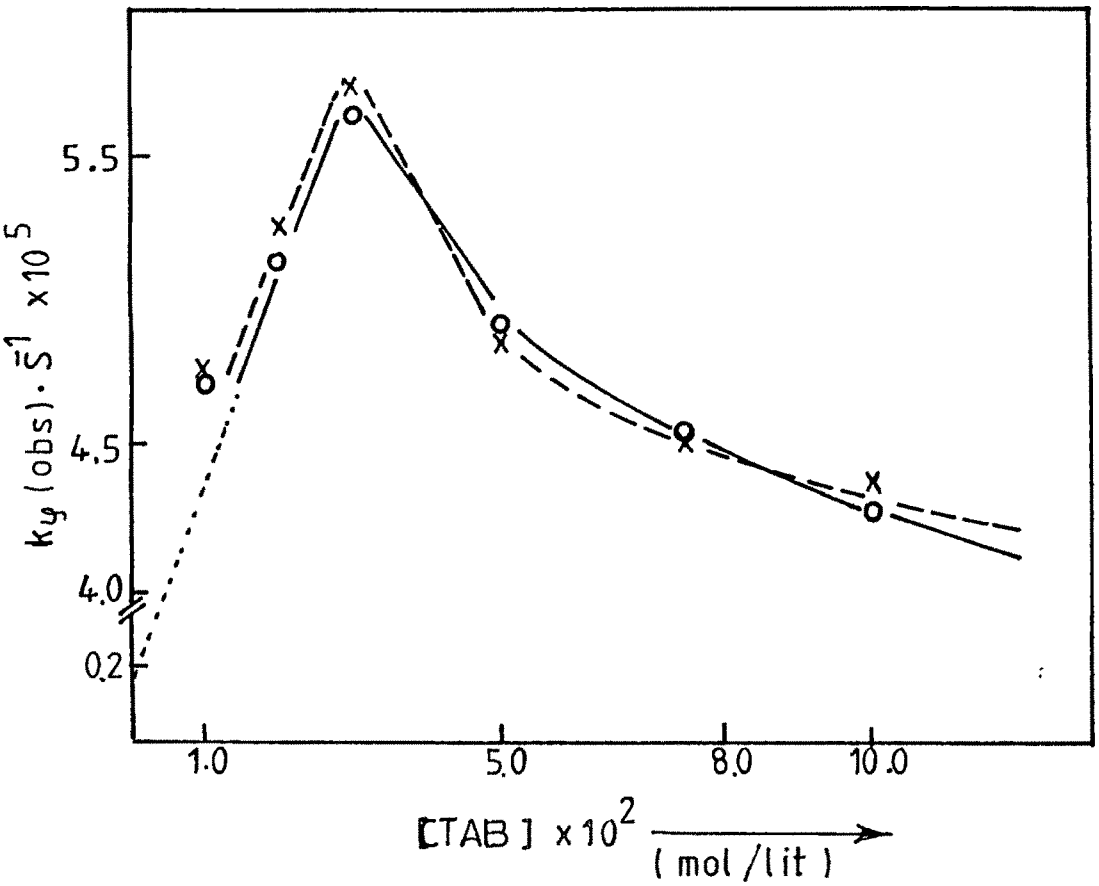


Fig 52 PPIE simulation of kinetic data for [MeGly - Mn-DET] - CTAB system at pH 5.2 and 40°C · O - $k_{\psi\ mL3\ observed}$, X - $k_{\psi\ mL3 calculated}$

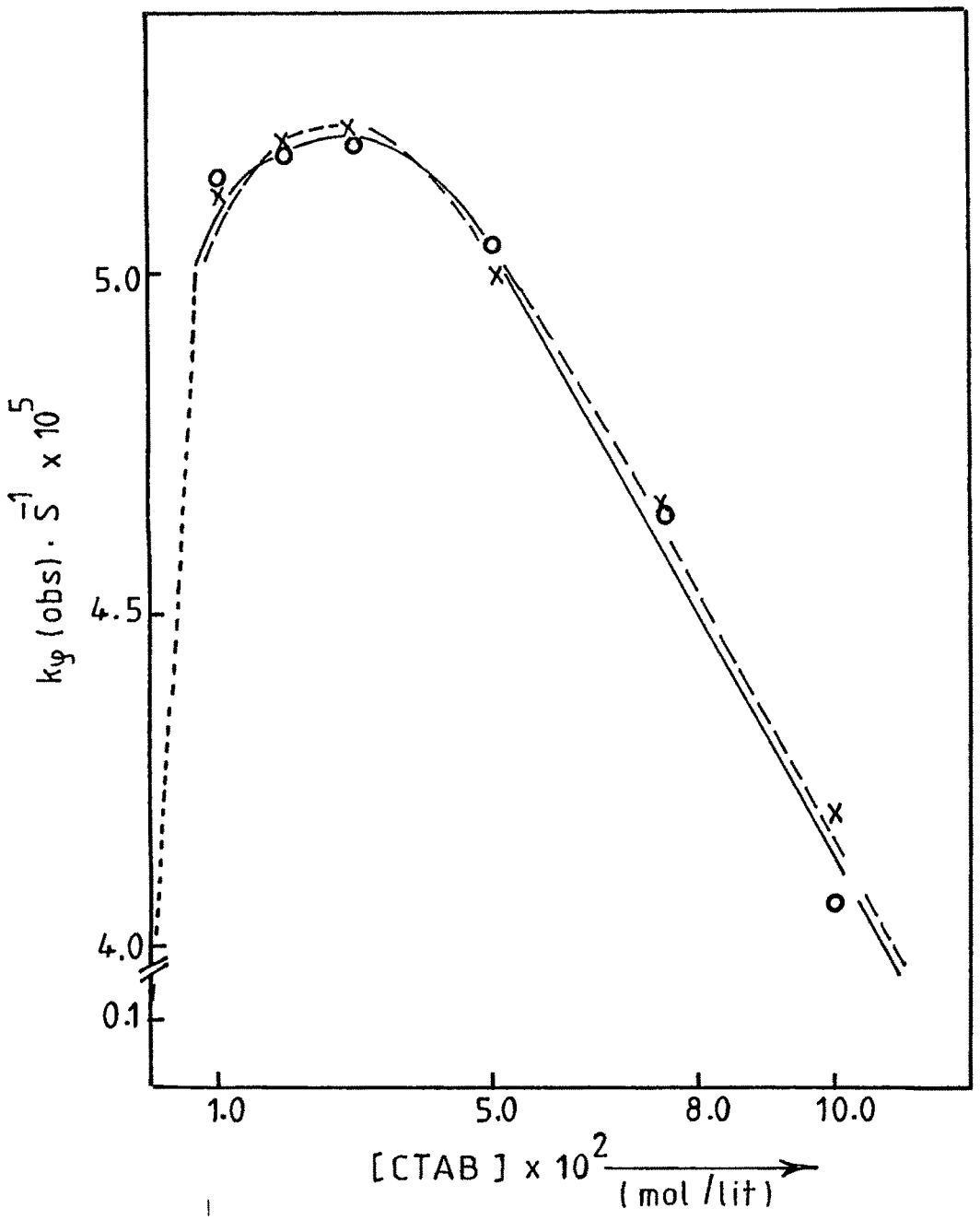


Fig 53 PPIE simulation of kinetic data for [EtGly - Cu-DET] - CTAB system at pH 5 2 and 40°C · O - $k_{\varphi\ ml.3observed}$, X - $k_{\varphi\ ml.3calculated}$

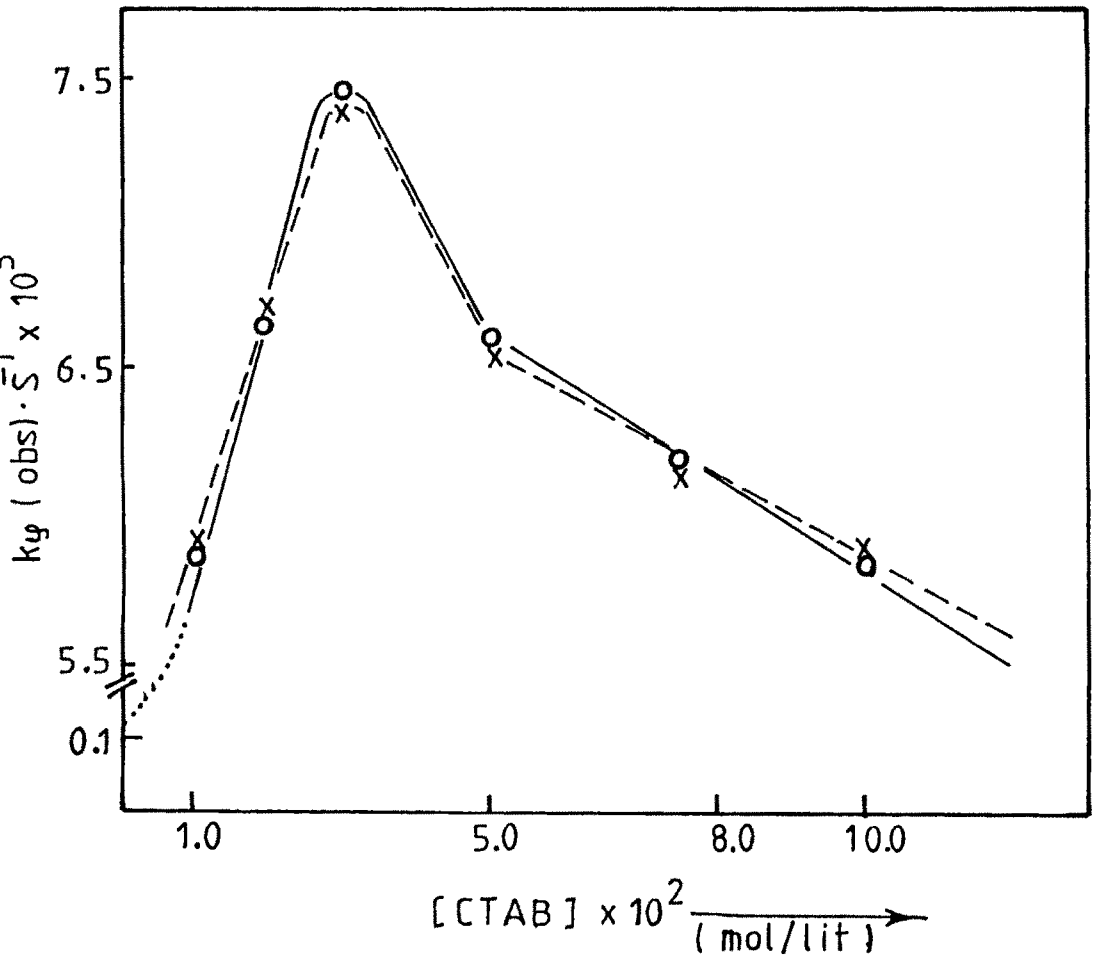


Fig 54 PPIE simulation of kinetic data for [EtGly - Zn-DET] - CTAB system at pH 5 2 and 40°C : O - $k_{\varphi\ mL3 observed}$, X - $k_{\varphi\ mL3\ calculated}$

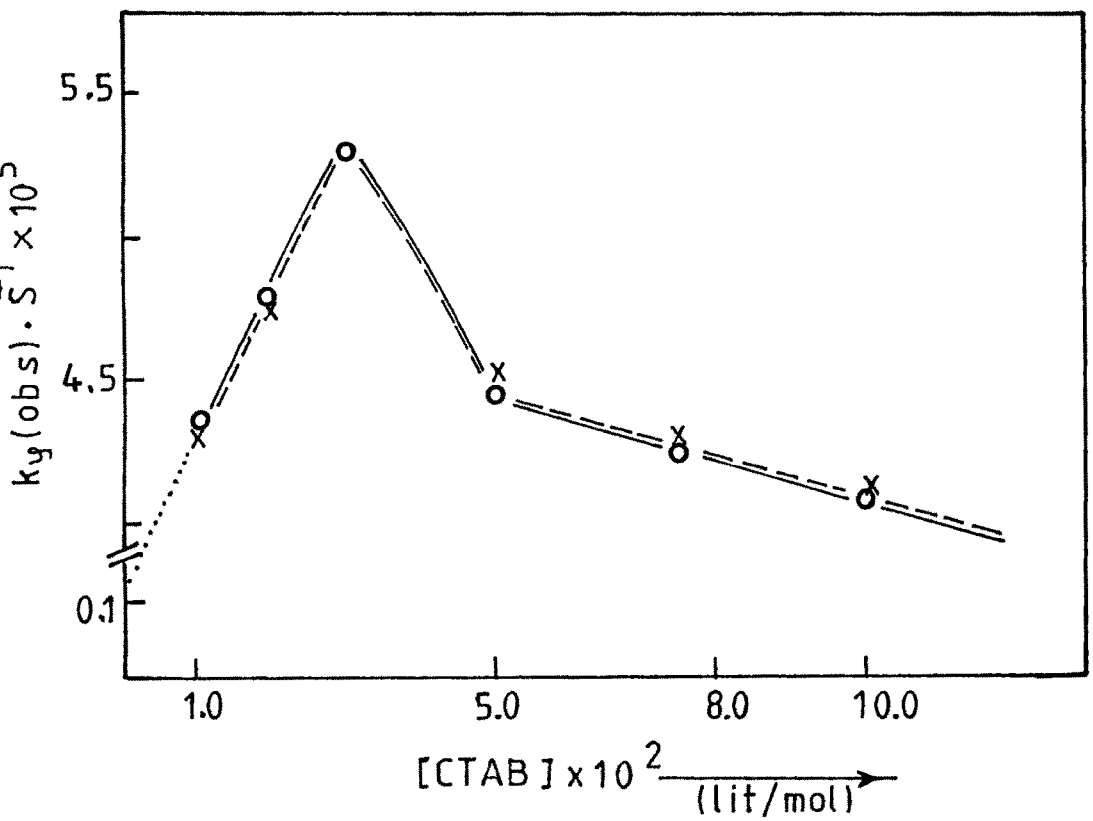


Fig. 55 PPIE simulation of kinetic data for [EtGly -Mn-DET] - CTAB system at pH 5.2 and 40°C : O - $k_{\varphi\ mL3\ observed}$, X - $k_{\varphi\ mL3\ calculated}$

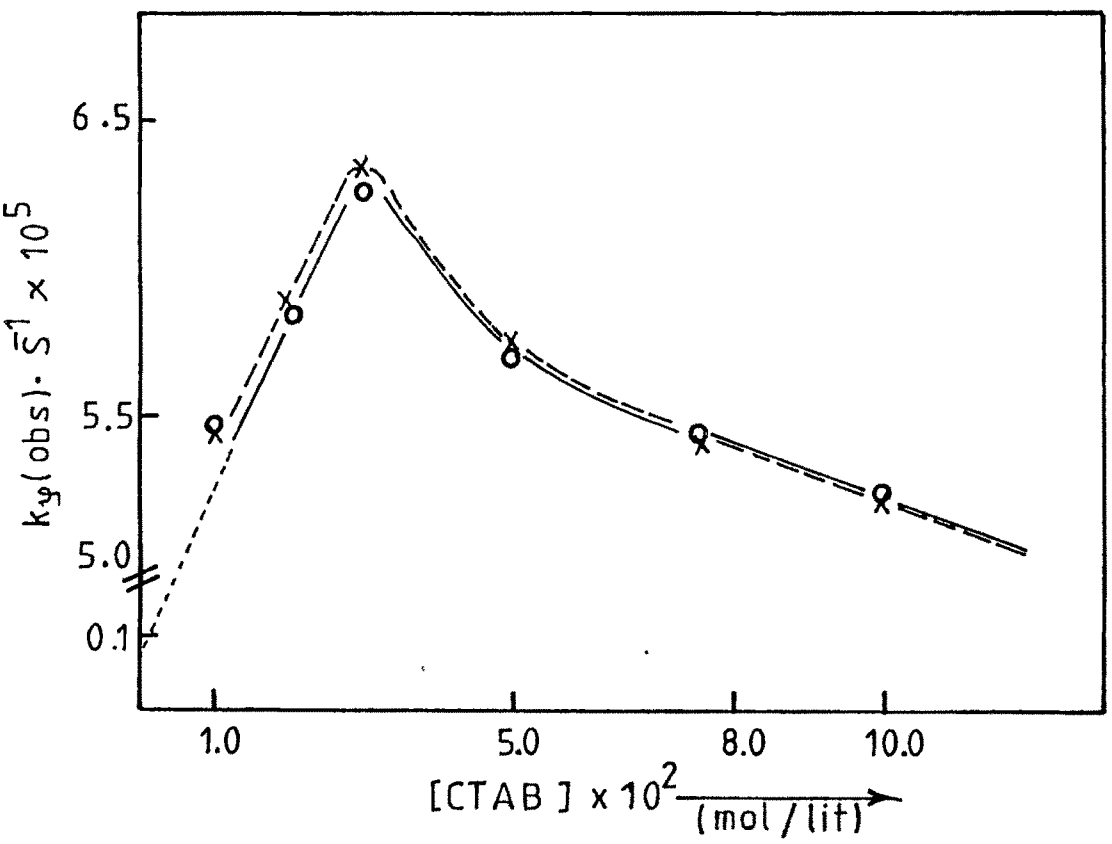


Fig. 56 PPIE simulation of kinetic data for [PhGly - Zn-DET] - CTAB system at pH 5.2 and 40°C · O - $k_{\varphi\ mL3observed}$, X - $k_{\varphi\ mL3calculated}$

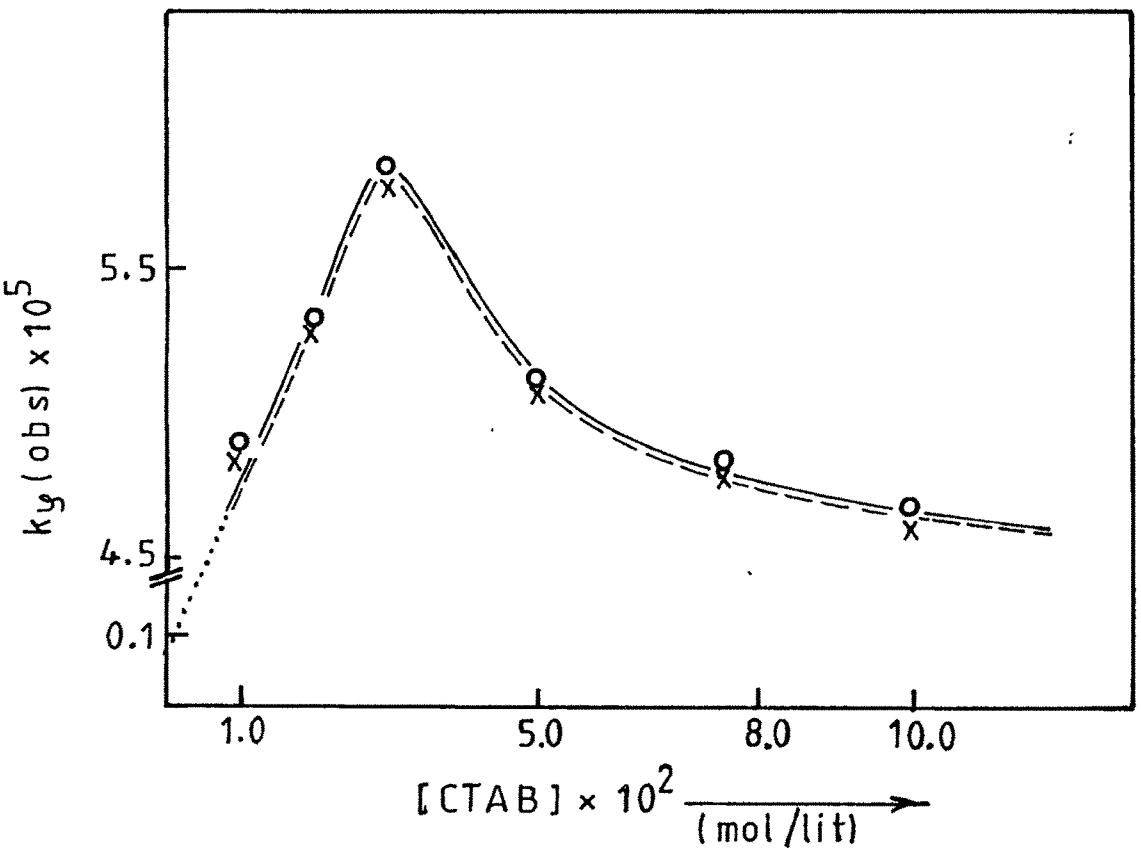


Fig 57 PPIE simulation of kinetic data for [PhGly - Mn-DET] - CTAB system at pH 5 2 and 40°C O - $k_{\psi\,mL3\,observed}$, X - $k_{\psi\,mL3calculated}$

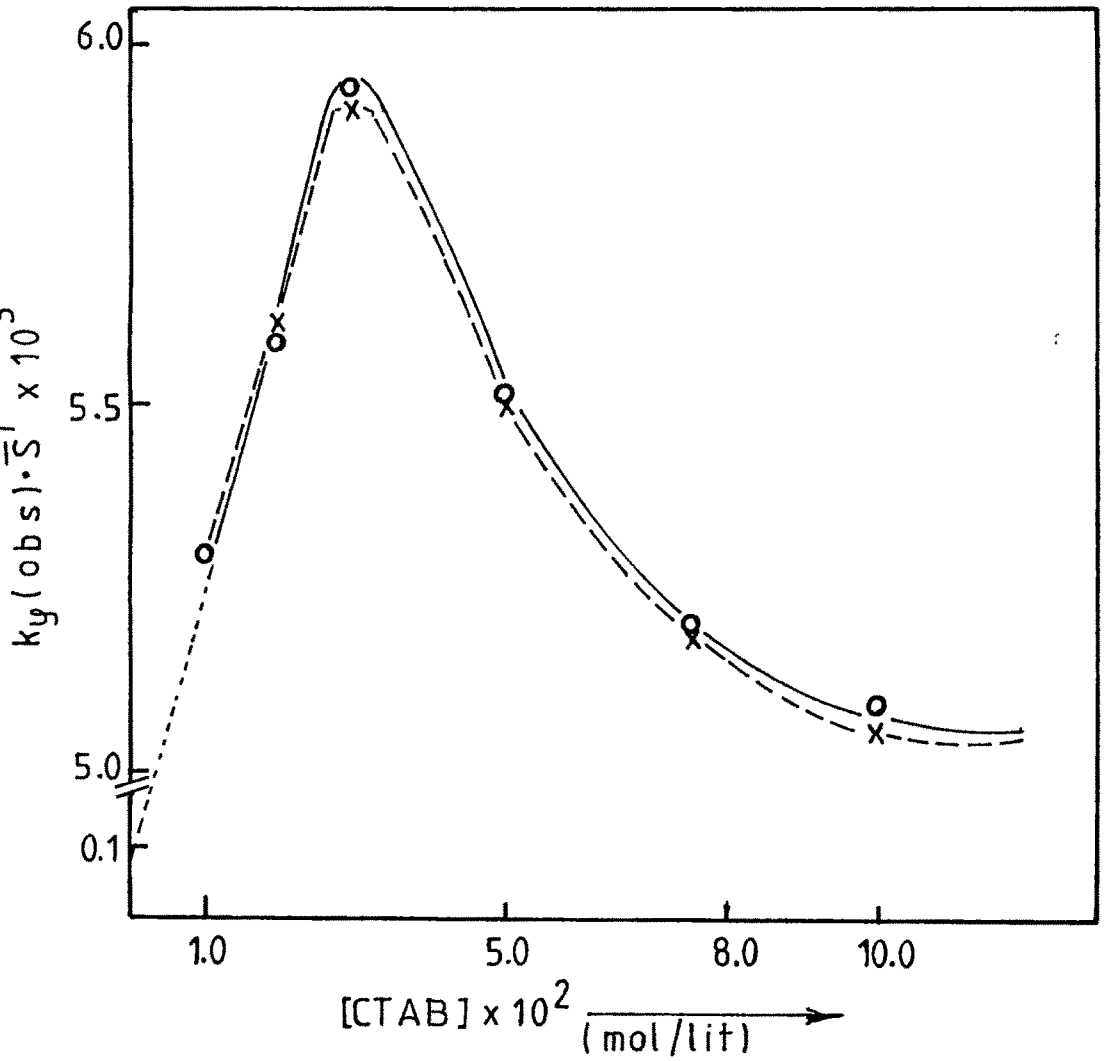


Fig 58 PPIE simulation of kinetic data for [PhGly - Cu-DET] - CTAB system at pH 5 2 and 40°C · O - $k_{\varphi\ ml.3observed}$, X - $k_{\varphi\ mL3\ calculated}$

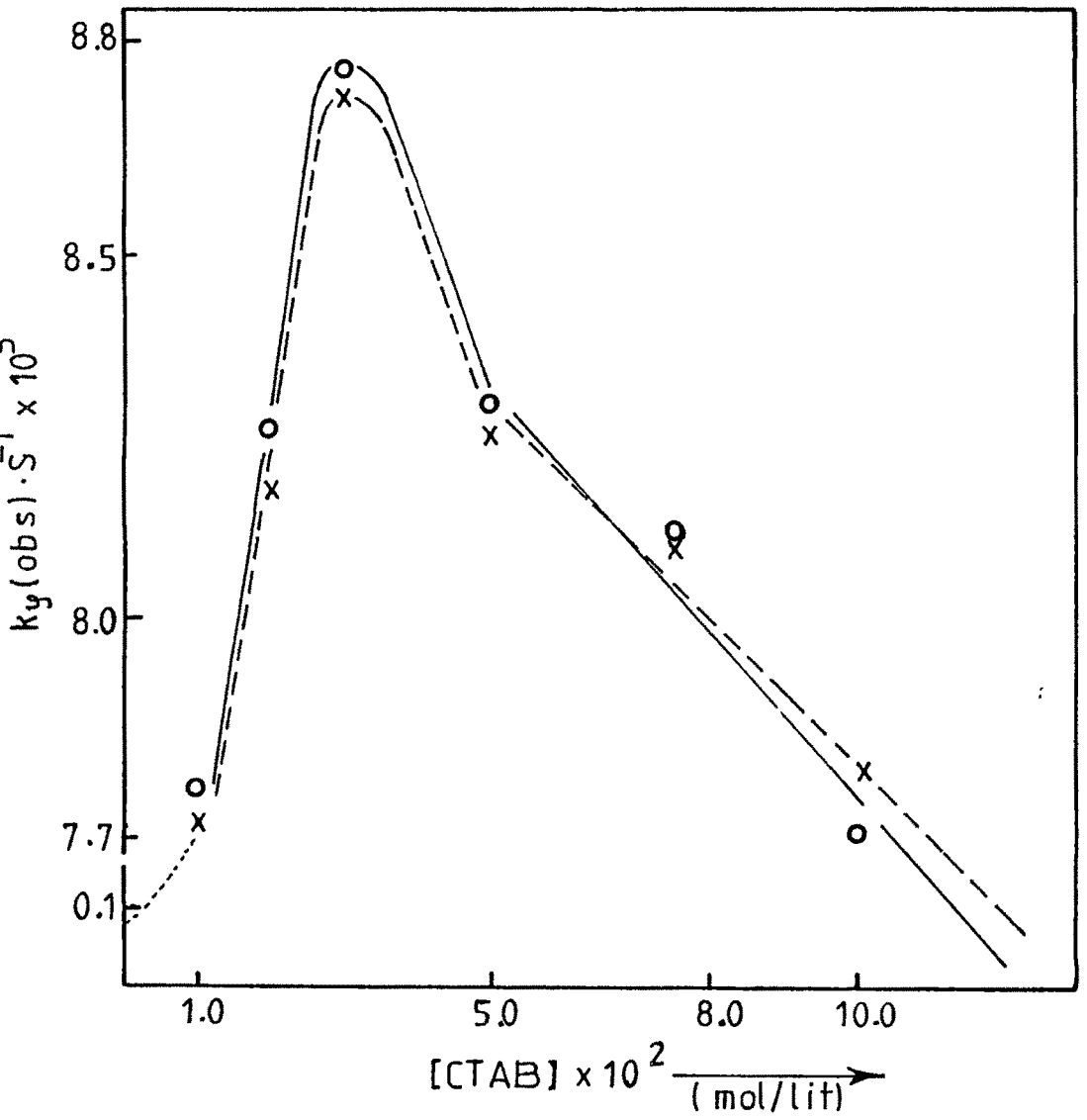


Fig. 59 PPIE simulation of kinetic data for [diMeGly - Cu-DET] - CTAB system at pH 5 2 and 40°C O - $k_{\varphi\ mL3 observed}$, X - $k_{\varphi\ mL3\ calculated}$

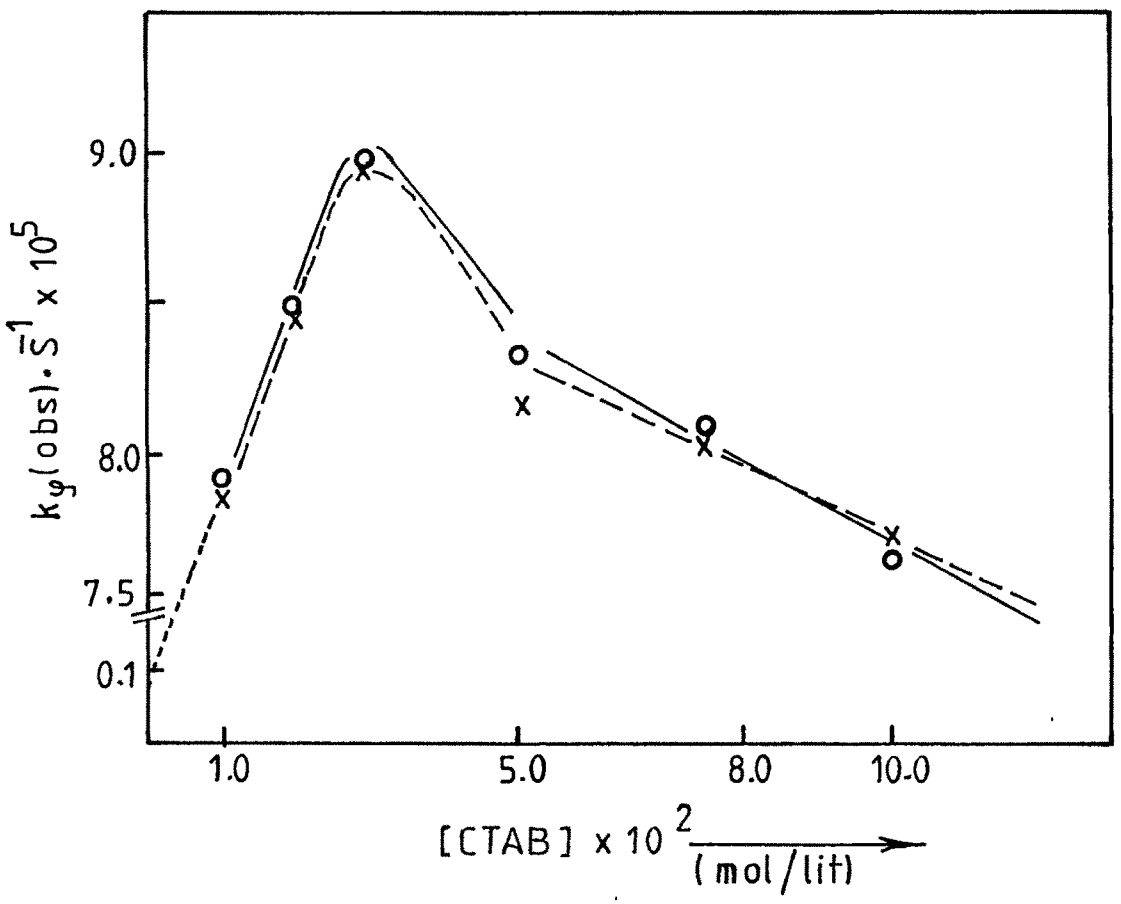


Fig 60 PPIE simulation of kinetic data for [diMeGly - Zn-DET] - CTAB system at pH 5 2 and 40°C : O - $k_{\varphi\ mL3observed}$, X - $k_{\varphi\ mL3calculated}$

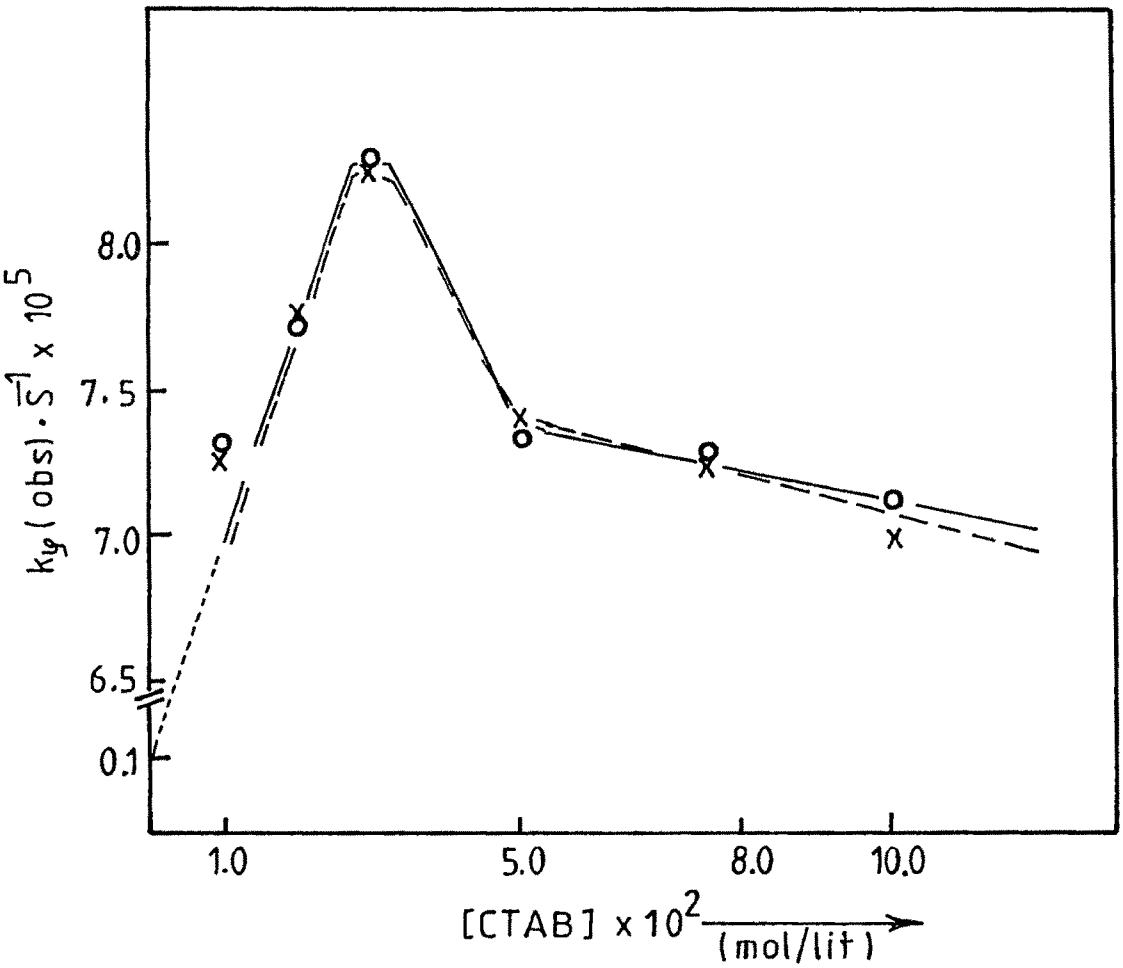


Fig. 61 PPIE simulation of kinetic data for [diMeGly - Mn-DET] - CTAB system at pH 5 2 and 40°C · O - $k_{\varphi\ mL3\ observed}$, X - $k_{\varphi\ mL3calculated}$

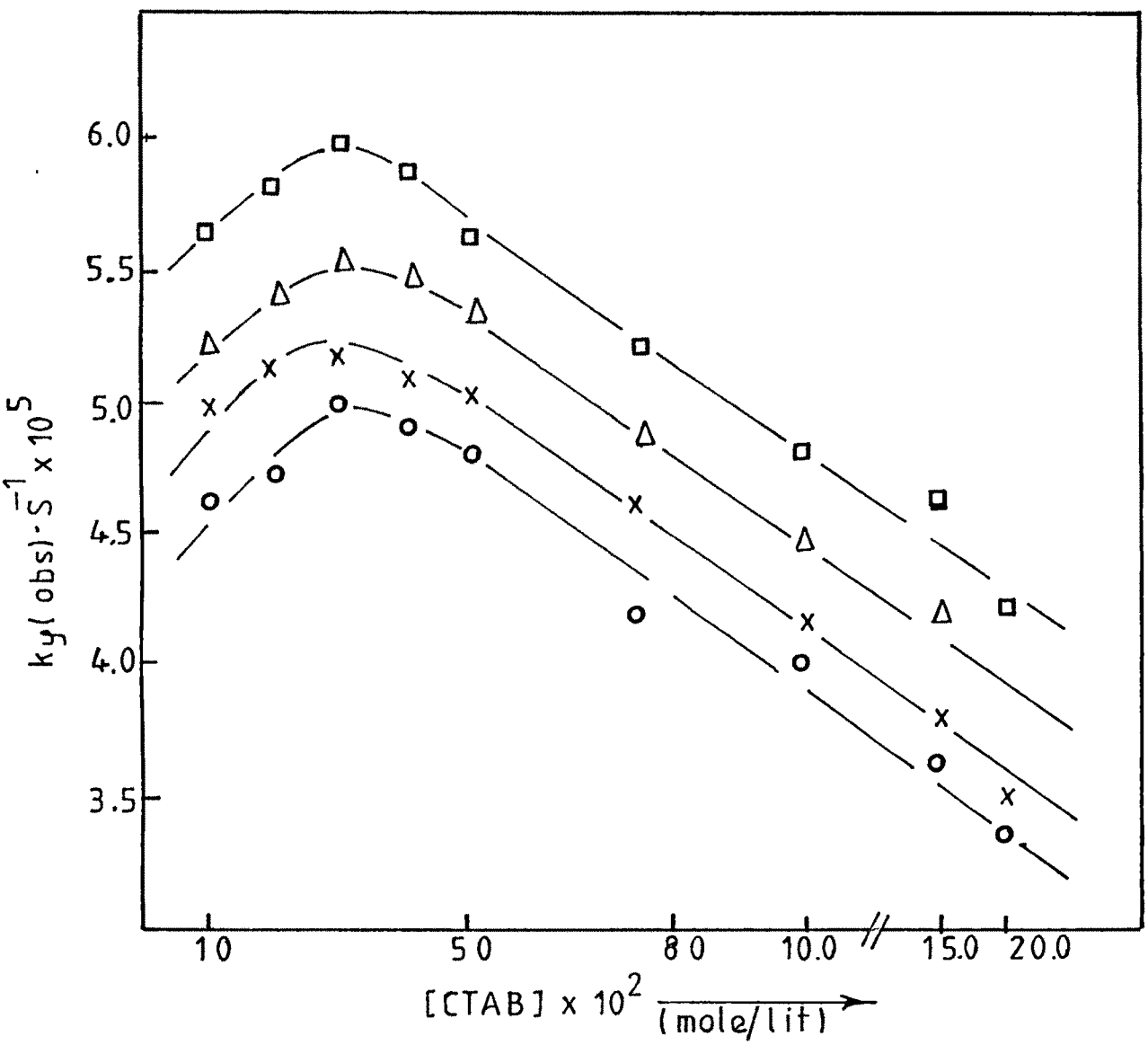


Fig. 62 Effect of temperature on the hydrolysis of EtGly in presence of Cu^{2+} · O -30°C, X - 35°C, Δ - 40°C, □ - 45°C

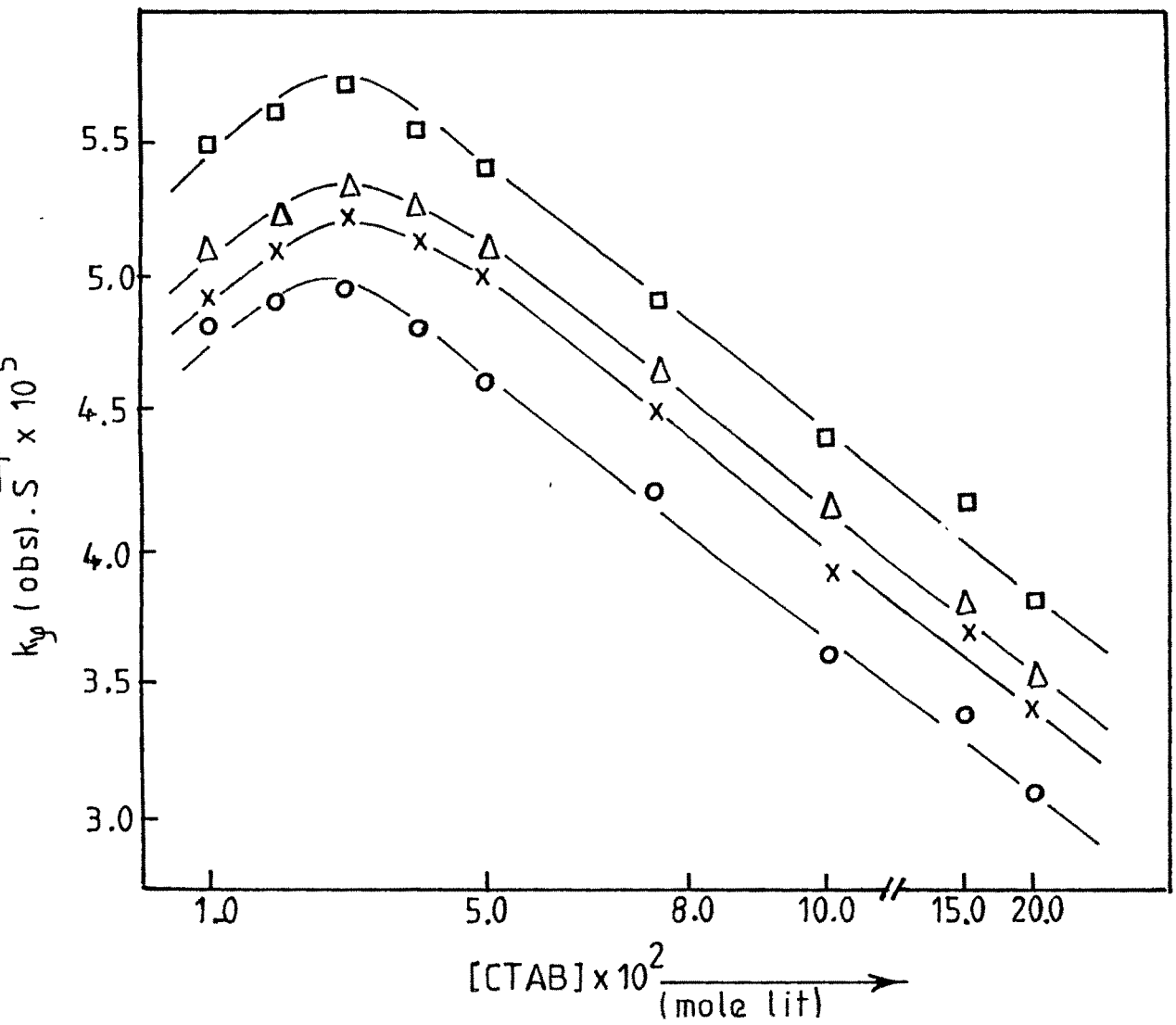


Fig. 63 Effect of temperature on the hydrolysis of EtGly in presence of Cu-DET O -30°C, X - 35°C, Δ - 40°C, □ - 45°C

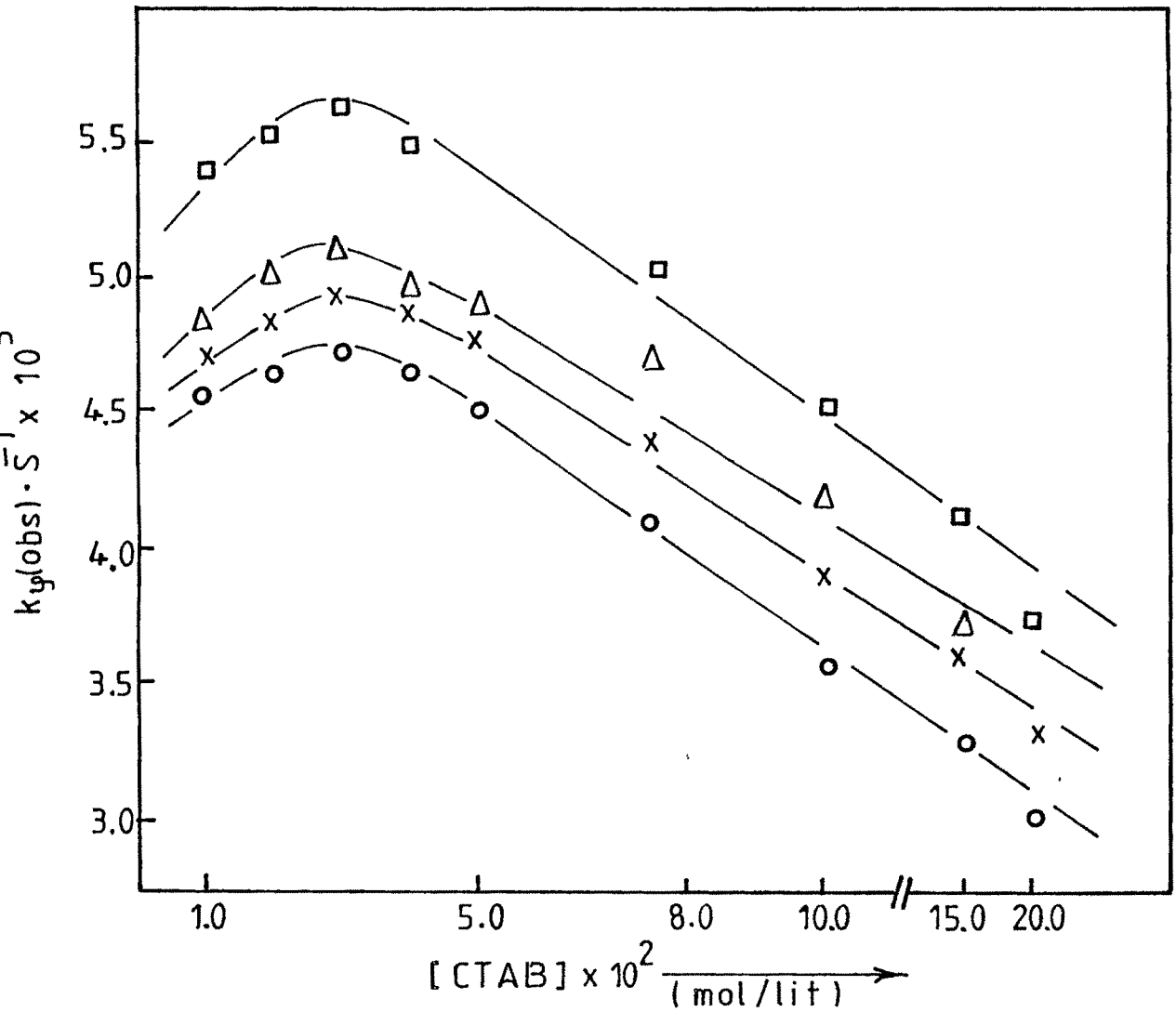


Fig 64 Effect of temperature on the hydrolysis of EtGly in presence of Cu^{2+} - O-phen · O -30°C, X - 35°C, Δ - 40°C, □ - 45°C

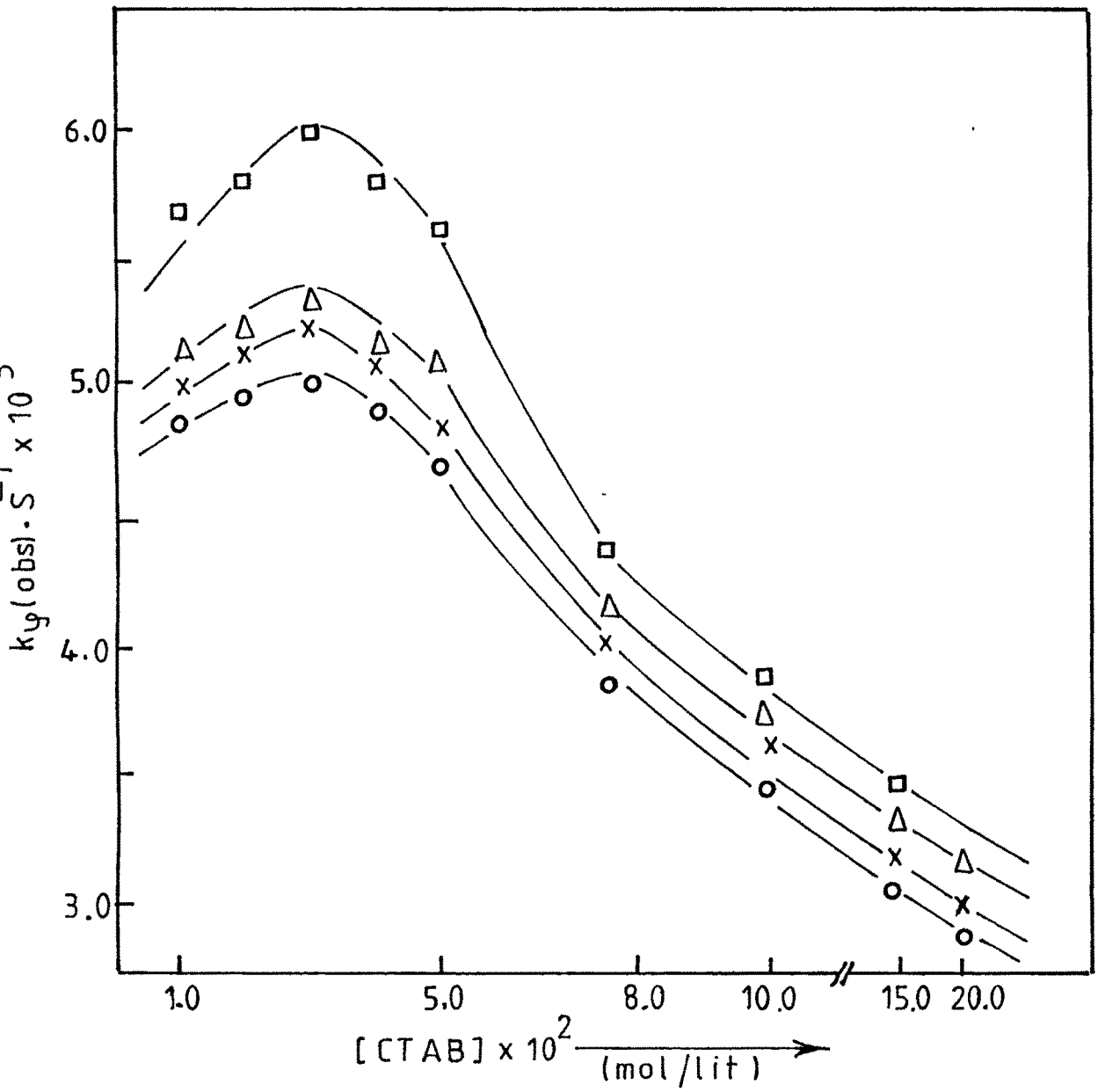


Fig 65 Effect of temperature on the hydrolysis of EtGly in presence of Cu^{2+}- bipyl · O -30°C, X - 35°C, Δ - 40°C, □ - 45°C

3.3 Mixed Surfactants

In most practical applications well chosen mixtures of surfactants can be made to perform better than single surfactants. Optimisation of performance are achieved by trial and error formulations of mixtures. Many a mixtures of surfactants are capable of performance unobtainable by single and pure surfactants. They have been used for stable emulsion, household detergent, oil recovery from oil field and in many more areas. In all these cases mixtures out-perform single component systems and this syngergism between components is at the very heart of most well-formulated surfactant systems. Although a lot of work has been done in the field of mixed surfactants,the behaviour of mixed surfactants are not yet well understood. A large number of surfactants have been used as catalysts for good number of reactions, as mentioned earlier, however, no citation is there in literature showing use of mixed surfactants as catalyst Therefore, it is desirable to make use of the special properties of mixed surfactants in the field of catalysis also. This section of the chapter focusses on some kinetic study of the hydrolysis of amino acid esters in the mixed surfactant environment.

In order to carryout the experiments in mixed surfactant, cationic (CTAB) and non-ionic (Brij 35) surfactants were chosen in equimolar quantities. The rate constant for hydrolysis of MeGly, EtGly, diMeGly & PhGly were determined using different concentrations of mixed surfactants at pH 6.8 and pH 11.

pH 6.8

Table (34) presents the rate constants at pH 6.8 and also shows the concentration effect (Fig. 66) of the mixed surfactants on the rate of hydrolysis. The rate constants at pH 6.8 were quite low due to low concentration of H^+ as well as OH^- ions. The presence of surfactant has an effect on the rate constant. When studied the rate constants using different concentration of mixed surfactants ($2x10^{-4}$ to $1x10^{-4}$ M) (Fig 66). It is observed that in almost all cases there is a gradual increase in rate constant till 0.001M of mixed surfactant and then there is a decrease. This trend is similar to what was observed in case of single surfactant medium at pH 6.8 although the rate enhanacment values are different in the two

Table 34 Effect of Concentration of Mixed Surfactant 1 1 (CTAB/BRIJ-35) on Glycine ester hydrolysis at 40oC and at pH 6 8

CTAB / Brij 35	CTAB+Brij35	EtGly				MeGly				diMeGly				PhGly			
(mole/lit)	Mix Surf Con (mole/lit)	k_{CTAB} x 10^6	k_{Brij} x 10^6	k_{x+y} x 10^6	k_{Mix} x 10^6	k_{CTAB} x 10^6	k_{Brij} x 10^6	k_{x+y} x 10^6	k_{Mix} x 10^6	k_{CTAB} x10^6	k_{Brij} x10^6	k_{x+y} x 10^6	k_{Min} x 10^6	k_{CTAB} x 10^6	k_{Brij} x 10^6	k_{x+y} x 10^6	k_{Min} x 10^6
		x	y			x	y			x	y			x	x		
-		1 82				2 44				0 894				0 88			
0 0001	0 0002	1 86	1 41	3 27	2 54	2 77	1 94	4 71	2 71	0 914	0 897	1 81	1 64	0 90	0 89	1 79	0 91
0 00025	0 0005	1 86	1 48	3 34	3 86	2 79	1 94	4 73	4 78	1 340	0 897	2 24	4 71	0 92	0 91	1 83	1 97
0 00035	0 00075	1 89	1 51	3 40	3 89	2 84	1 97	4 81	4 90	1 370	0 890	2 26	5 79	0 97	0 92	1 89	3 77
0 0005	0 001	2 31	1 53	3 84	3 87	3 01	2.01	5 02	5 09	1 410	0 900	2 31	4 81	-	0 89	-	3 79
0 001	0 002	2 81	1 74	4 55	3 85	3 65	2 12	5 77	5 69	1 470	0 907	2.38	4 60	1 01	0 90	1 91	3 60
0 0025	0 005	2 82	1 77	4 64	1 63	3 71	2 40	6 11	5 64	2.890	0 204	4 75	3 74	1 32	1.02	2 34	2.38
0 005	0 01	2 87	1 77	4 64	1 63	3 71	2 40	6 11	5 64	2 890	0 204	4 75	3 74	1 32	1 02	2.34	2 38

cases When compared the rate enhanacement duc to 0.001M mixed surfactants and that due to individual surfactants separately it is observed that in all the esters except MeGly the enhancement in mixed surfactant is much more than that due to 0.001 CTAB or Brij 35 It was also more than the additive value of k in these surfactants. Of all the esters dimethyl glycinate hydrolysis catalysis in mixed surfactant was the highest (6 5 times)

pH 11

Presence of OH^- in high concentration results into the rate constant of glycine esters of the order of 10^{-4} S^{-1} (Table 35) The presence of surfactants has an enhancement effect When compared with the rate at pH 6.8 the rate enhanacment at pH 11 by mixed surfactant is much larger It is almost 64 times for diMeGly in ≈0.001 M of mixed surfactant. In all the cases of estes studied the rate constant in presence of mixed surfactant is much more than the additive value of the individual surfactants.

All the results indicate that it is not the additive effect of constituent surfactants in the mixture, instead there is synergism This observed synergism could be due to

1) The CMC of the mixed surfactant is much lower ≈ $4.5x10^{-1}$ M (S T method) as compared to CMC of CTAB $1x\ 10^{-3}$ M Thus aggregation number should be high (The Aggregation number determined by fluorescence spectra was not satisfactory as it was not reproducible) and thus the size of micelle could be big This provides large surface area Thus more quantity of the reactants could be at the surface of the micelle i e. local concentration of the reactants increases which make the reactions to be faster.

2) In mixed surfactant CTAB, cationic surfactant and Brij 35, non-ionic surfactant are present. Considering these surfactants individually CTAB at pH 11 can have a high concentration of OH^- at its surface due to electrostatic interaction and can enhance the rate of hydrolysis but it cannot have large concentration of glycine ester bound to it and enhancement is not very large. Brij 35 having high adsorbability of water due to polar head group can retain water at its surface, and thus can have high concentration of substrates dissolved in water but as it has no charge, it cannot attract the attacking OH- to its surface and hence the rate enhancement in Brij 35 is very low or almost no enhancement is

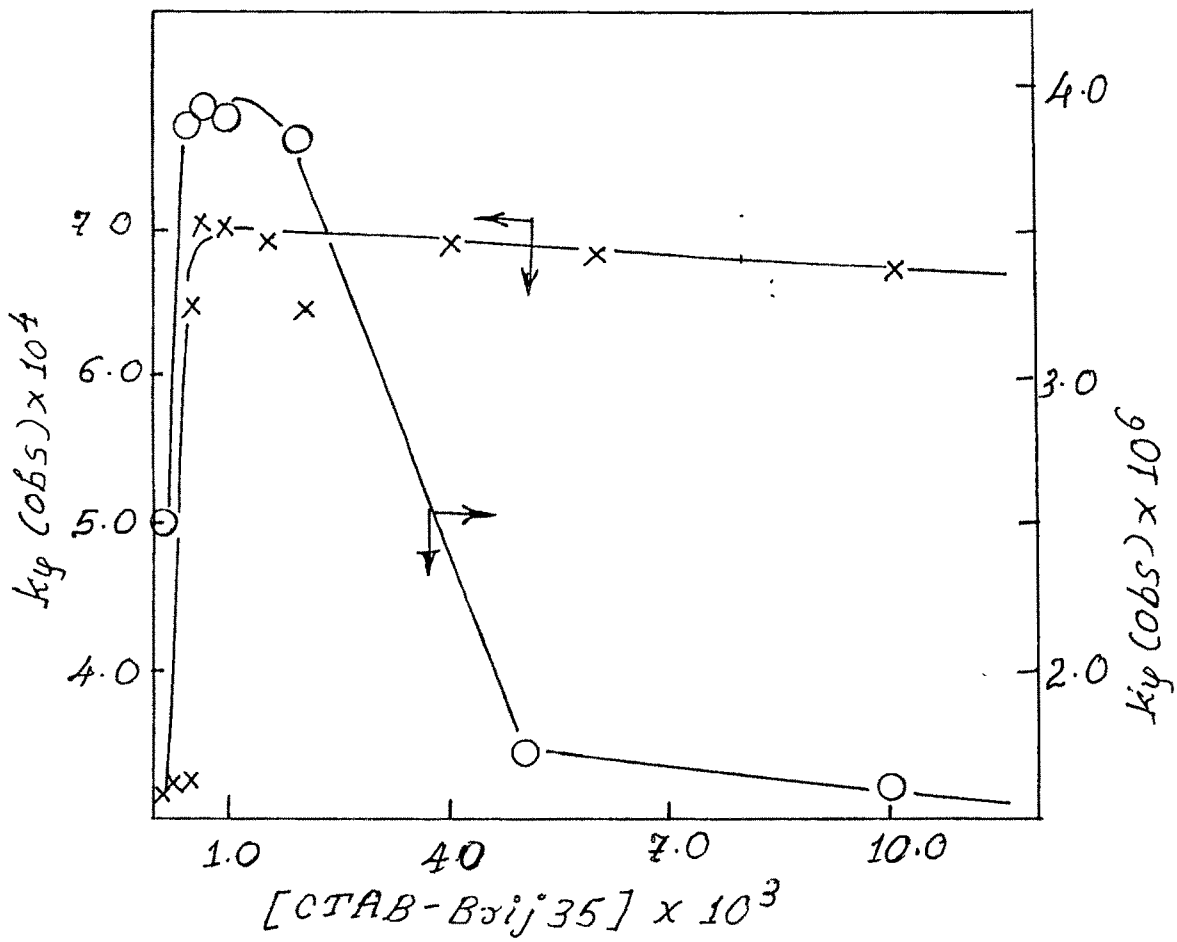


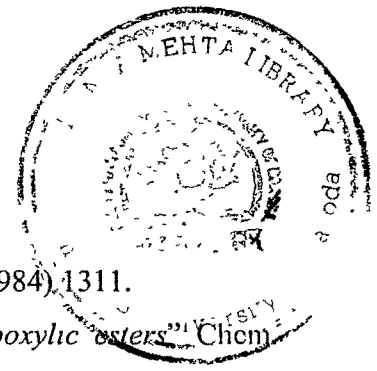
Fig 66 Variation of rate constant of hydrolysis of EtGly with concentration of mixed surfactant (CTAB & Brij 35) at 40°C : O - pH 6 8, X - pH 11,

Table 35 Effect of Concentration of 1.1 mixed surfactant (CTAB/Brij 35) on Glycine ester hydrolysis at 40°C and at pH 11

CTAB / Brij 35	CTAB+Brij35	EtGly				MeGly				diMeGly				PhGly			
(mole/lit)	Mix Surf Con (mole/lit)	k_{CTAB} x 10^4	k_{Brij} x 10^4	k_{x+y} x 10^4	k_{Mix} x 10^4	k_{CTAB} x 10^3	k_{Brij} x 10^3	k_{x+y} x 10^3	k_{Mix} x 10^3	k_{CTAB} x10^4	k_{Brij} x10^4	k_{x+y} x 10^4	k_{Min} x 10^3	k_{CTAB} x 10^4	k_{Brij} x 10^4	k_{x+y} x 10^4	k_{Min} x 10^3
		x	y			x	y			x	y			x	x		
-	-	1 12				0 97				0 62				0 58			
0 0001	0 0002	1 11	1 10	2 21	3 27	0 99	0 98	1 97	1 91	0 67	0 61	1 28	0 164	0 81	0.78	1 59	-
0 0002	0 0004	1 14	1 14	2 28	3 40	1 04	0 99	2 03	2 01	0 67	0 63	1 30	0 170	0 84	0 74	1 58	-
0 00025	0 0005	1 18	1 16	2 34	6 46	1 08	0 99	2 07	4 07	0 68	0 63	1 31	3 90	0 86	0 79	1 65	1 32
0 0003	0 0006	1 24	1 16	2 40	7 12	1 10	1 01	2 11	4 10	0 71	-	-	3 96	0 91	0 79	1 70	-
0 0005	0 001	1 52	1 18	2 70	7 01	1 21	1 04	2 25	3 95	0 74	0 65	1 39	3 90	1 04	0 80	1 88	1 14
0 00075	0 0015	1 98	1 21	3 19	6 87	1 28	1 09	2 37	3 91	0 77	0 67	1.44	3 91	1 07	0 80	1 87	-
0 001	0 002	2 17	1 14	3 31	6 41	1 34	1 10	2 44	-	0 82	0 68	1 50	3 67	1 10	0 89	1 99	1 07
0 002	0 004	2 31	1 19	3 50	6 81	1 39	1 17	2.46		0 84	-	-	-	1 10	-	-	-
0 003	0 006	2 39	1 11	3 50	6 57	1 42	1 09	2 51		0 84	0 69	1 53	-	1 14	0 83	1 97	-
0 005	0 01	2 51	1 18	3 69		1 47	1 11	2 58		0 87	0 71	1 48	-	1 17	0 77	1 94	-

observed. However, in the mixed surfactant of CTAB & Brij35 the properties of the two are combined and there is synergism. Thus the enhanacment in the rate of hydrolysis in mixed surfactant medium may be due to (1) or (2) or may be a combined effect of both.

Hydrophobicity of the substrate also plays a role. diMeGly, has been found to have maximum enhanacment in the rate as its hydrophobicity is the highest amongst the ester studied When Mixed surfactant is used at much lower concentration but above its CMC, the rate enhanacement is observed. Thus one can observe that using much smaller quantities of surfactants in mixture the catalysis of glycine esters takes place to a greater extent than what was observed with single surfactants at higher concentrations.



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