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RESEARCH ARTICLE

KINETICS AND MECHANISM OF HYDROLYSIS OF UREA AND N, N′-DIACETYL UREA IN PRESENCE OF COBALT(II), COPPER(II), ZINC(II)-SCHIFF BASE COMPLEXES.

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Abstract

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Solid aquo Co^{II}, Cu^{II} and Zn^{II} complexes of Schiff bases derived from amino acids and salicylaldehyde had been prepared, characterized and used as model enzymes of Urease. Using a pH-stat method, the kinetics of acid hydrolysis of urea and its derivative N,N′-diacetyl urea in the presence of the complexes had been studied in pH range of 4.91–6.19 at 30^0C and $I = 0.10$ mol dm^{-3} (KNO_3). It was found that the hydrolytic reactions followed first order kinetics (pseudo-unimolecular) with respect to urea or N,N′-diacetyl urea concentration. The complexes enhanced the rate of hydrolysis markedly; the values of the second-order rate constants (k_H) being 10^6 times greater than those found in the absence of the catalysts. Comparison showed that the complexes acted as better catalysts for urea [$k_H = (0.79–2.34)\times10^2$ dm^3 mol^{-1} s^{-1}] than N,N′-diacetyl urea [$k_H = (0.36–1.19)\times10^2$ dm^3 mol^{-1} s^{-1}] towards the hydrolysis reactions. The catalytic performance of the complexes was 30-100% greater in urea than in N,N′-diacetyl urea. The proposed mechanism involved the formation of mixed ligand chelate complex by replacement of two coordinated labile water molecules by NHR′ (R′= H or $COCH_3$) and carbonyl group of urea or N,N′-diacetyl urea followed by nucleophilic and electrohilic attacks by H_2O and H^+ respectively. The average half-life period ($t_{½}$) ranges for urea and N,N′-diacetyl urea hydrolysis were 450–676 and 529–807 seconds respectively. $[Co^{II}(Gly)(Sal)(H_2O)_3]$ was found as the most efficient catalyst towards urea hydrolysis reactions. This investigation would establish the potential catalytic role of the complexes in hydrolyzing urea and its derivative, and thereby would throw more light on hydrolytic mechanism of urease enzyme.

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Introduction:-

Schiff bases derived from heterocyclic aldehydes has special centre of attraction in many areas like biological, medicinal, analytical and pharmacological fields [1]. Schiff bases (secondary ketimines or aldimines) are important type of polydentate ligands in coordination chemistry. It was reported that Schiff bases of amino acids formed stable complexes with transition metal ions of different geometries and could play a significant role in the kinetics of hydrolytic reactions [2-4]. The carboxylate, amine, amido-nitrogen, imidazole, thiol, methylthiol and hydroxyl (phenolic) groups of amino acids are important metal binding sites in biological systems [5]. It was therefore

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thought that the coordination environment of the metal atom in Schiff base complexes might be similar to that in the active site of certain enzymes such as urease.

Urease (EC 3.5.1.5) is a nickel-containing hydrolase enzyme that catalyses the hydrolysis of urea into ammonia and carbon dioxide through formation of intermediate carbamate ion ($H_2N.CO.NH_2 + H_2O \rightarrow H_2N.COO^- + NH_4^+$)[6]. It was reported that urease, having six sub-units (each of molecular weight 83,000 g mol^{-1}) [3:3 (alpha:beta) stoichiometry with a 2-fold symmetric structure] and α_6 structure, might possess 3-4 active sites per molecule [7]. Such complex structural features account for superior specificity and tremendous efficiency of urease. Since the actual three dimensional structure of urease and its catalytic mechanisms for various hydrolytic reactions are not yet very well-established, we performed model studies on urease towards the hydrolysis of urea and its derivative N,N′-diacetyl urea.

Many studies were performed on kinetics of urea-urease systems [6,8-9]. But limited studies were made on metal ion catalyzed hydrolysis of urea and its derivative. Blakeley et al. [10] studied the ethanolysis and hydrolysis of N-(2-pyridylmethyl) urea in presence of Ni(II), Co(II) and Mn(II). They found Ni(II) as the best catalyst that enhanced the rate of hydrolytic reaction about 10^4 times. Banu [11] studied the catalytic activities of Zn(II), Co(II), Ni(II), Cu(II), Ru(II), Pd(II) and Mn(II) ions towards the hydrolysis of urea at pH range 6.01-7.60 and found that the reactions were of first order with respect to H^+ or urea. This study aimed to study the catalytic effects of Co(II), Cu(II), Zn(II)-Schiff base aquo-complexes towards the hydrolysis of urea and N,N′-diacetyl urea. To our knowledge, this is the first paper that reports the kinetics and mechanism of the mentioned hydrolytic reactions by pH-stat method in acidic pH range.

Materials and Methods:-

2.1 Materials

The chemicals used in this investigation were of high purity analytical grade. Ultrapure water (18.2 M Ω.cm), prepared by purifying distilled de-ionized water with a Milli-Q A10 (Millipore Corporation, USA) system, was used throughout. Glycine (Fluka), L-Leucine (Fluka), L-Proline (Fluka) and salicylaldehyde (BDH) were used as supplied. The other reagents were from Merck (Germany), Fluka (Switzerland) or Aldrich (USA) and were used without further purification, except for ethanol. Super dry ethanol (99.9%) was prepared by Lund and Bjerrum method [12] with Mg turnings and iodine. NIST certified reference Buffer solutions (Sigma-Aldrich, USA) of pH 7.00±0.01 (25^0C) and 4.00±0.01 (25^0C) were employed to calibrate the pH-meter.

2.2 Preparation of Transition Metal-Schiff Base Complexes

Schiff bases were prepared by condensation reactions according to the standard reported procedure [13-14, 19]. To a solution containing 0.005 mole of salicylaldehyde (0.611 g) in 20.0 cm^3 of 99% C_2H_5OH, 0.005 mole of the amino acid (Glycine, L-Leucine or L-Proline) in 10.0 cm^3 of ultrapure water was added dropwise with constant stirring. The mixture was kept at 55^0C in a water bath for about 4 h. Generally a reddish yellow colored Schiff base solution was formed. A filtered solution containing 0.005 mole of copper (II), cobalt (II) or Zinc (II) acetate in 10.0 cm^3 of ultrapure water was added to the Schiff base solution dropwise with constant stirring. The mixture was again kept at 55^0C for about 6 h and allowed to stand at room temperature for 2-3 h. The complexes were precipitated by the addition of a small amount of petroleum ether. They were then removed by filtration, washed several times with 99% EtOH followed by Et_2O and finally dried in a vacuum desiccator over P_4O_{10}.

2.3 Characterization of Schiff Base Complexes

For characterization purposes, elemental analyses, FT-IR spectra analyses and conductivity measurements were made with the prepared Schiff base complexes. Elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer (Perkin-Elmer Corp., USA). IR spectra were recorded on a Pye-Unicam SP3-300 FT-IR Spectrometer (Pye-Unicam Ltd., UK) as KBr pellets in the region 4000-600 cm^{-1} and Nujol mulls sandwich between CsI plates in the region 600-200 cm^{-1}. Conductivity measurements were made with 1.0×10^{-3} mol dm^{-3} solution of the complexes in Dimethyl sulfoxide (DMSO) using HANNA HI 216 multi-range EC/Resistivity meter (HANNA Equipments, China) having automatic temperature compensation (ACT) mode. The data are summarized in Table 1.

2.4 Kinetic Study

The pH-stat method [15] was followed for monitoring the kinetics of the hydrolysis of urea and N,N´- diacetyl urea in the presence of the complexes. The procedure consisted in mixing a definite volume of thermally equilibrated aqueous solutions of urea or N,N´- diacetyl urea and the Schif base complex to which H_2SO_4 solution was added so that the final reactant solution was about 50 cm^3 at 30^0C with pH in the range 4.91–6.19. A calculated amount of KNO_3 was added to maintain a constant ionic strength of 0.1 mol dm^{-3}. In order to maintain a constant pH, H_2SO_4 was added from a microburette (accuracy ±0.01 cm^3). A microprocessor controlled pH meter (Jenway, England, model 3030), having ATC mode and capable of reading upto three decimal places with an accuracy of ± 0.002 unit, was used to check the pH value at different times. The pH was maintained constant to within 0.01–0.02 unit. The typical conditions employed for kinetic measurements were: 1.0×10^{-4} mol dm^{-3} transition metal-Schiff base complex and 1.0×10^{-4} mol dm^{-3} urea or N,N´- diacetyl urea. Values of hydrogen ion concentration were obtained from the pH, using K_w = 13.997 and an activity coefficient of 0.688 at 30^0C.

2.5 Statistical Analysis

The hydrolysis data of the kinetic measurements were verified statistically for both urea and N,N′-diacetyl urea. The datasets obtained were treated separately for analyzing basic statistical parameters and for making cross-tabulations and cross-plots. The SPSS (release 20.0), STATGRAPHICS Centurion (release 18.1.01) and Microsoft Excel (release 12.0) were employed for the purpose. Mathematical models were established based on simple and multiple regression analyses. The models were cross-checked by analyzing ANOVA, *P* value, *r* value (Pearson correlation coefficient) and Durbin–Watson statistics. For these, Curve Expert (release 1.40) and STATGRAPHICS Centurion software were employed. The Box-Whisker plot was constructed using SPSS.

Results and Discussion:-

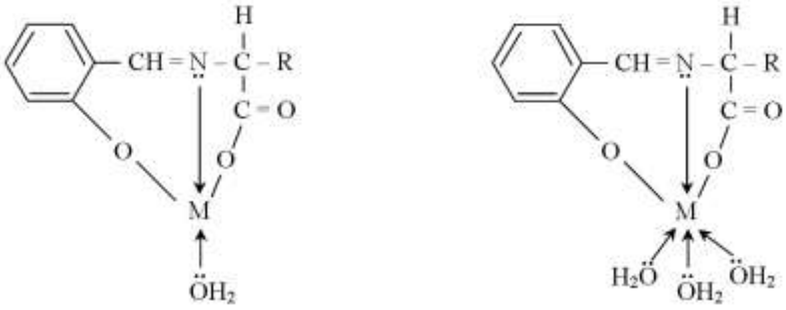
3.1 Structure of the Schiff base complexes

The IR spectra of the Schiff bases (not shown here) and the complexes (Table 1) provide information about the metal-ligand bonding. In the IR spectra of the Schiff bases complexes, the C=N stretching frequency, $\nu_{C=N}$, shifted from 1620-1660 cm^{-1} to lower frequency region 1600-1630 cm^{-1} indicating that azomethane (C=N) nitrogen is coordinated to the metal. The symmetric stretching frequency of COO group, ν_{COO}, shifted from 1400-1450 cm^{-1} to the region 1390-1340 cm^{-1} indicating that COO oxygen is coordinated to the metal. The O-H stretching frequency, ν_{O-H}, appears at 3300-3420 cm^{-1}. All these indicate the coordination of the Schiff base and water molecule(s) with the metal. In the lower frequency region, strong bands are observed at 400-440 cm^{-1} and 290-350 cm^{-1} in the spectra of all the complexes that have been assigned to ν_{M-O} and ν_{M-N} vibrations respectively, thus leading further support to the proposed coordination in the complexes. The analyses of IR spectra are in accordance with namy authors [22-23]. The presence of coordinated water is indicated by the broad absorption band centered around 3300-3420 cm^{-1}. The bands at 870-900 cm^{-1} and 730-750 cm^{-1} may be attributed to the rocking and wagging modes of the coordinated water respectively. The agreement between the experimental and calculated data of elemental analysis (Table 1) was very satisfactory. The conductivity studies, indicating that the complexes were of non-eletrolytic in nature, supported our proposed structure of the complexes. The analyses of experimental data suggested the general structure of the transition metal – Schiff base complexes as represented by Fig 1.

Table 1:- Analytical and spectroscopic data for the transition metal-Schiff base complexes.

Complex^a	**Color**	**Calculated (found) (%)**					**FT-IR (band maxima in cm**$^{-1}$**)**						**Λ_m**^{b}
		C	**H**	**N**	**Metal**		**$\nu_{C=N}$**	**ν_{COO}**	**ν_{O-H}**	**ν_{M-O}**	**ν_{M-N}**		**(S cm^2 mol^{-1})**
$[Cu^{II}(Gly)(Sal)(H_2O)]$	Green	41.5 (41.3)	3.5 (3.5)	5.4 (5.3)	23.4 (23.6)		1620	1360	3400	408	308		0.00
$[Zn^{II}(Gly)(Sal)(H_2O)]$	Pale yellow	41.2 (41.1)	3.5 (3.4)	5.3 (5.5)	24.9 (24.9)		1628	1358	3300	405	290		0.00
$[Zn^{II}$(L-Leu)(Sal)$(H_2O)]$	White	49.0 (48.9)	5.4 (5.3)	4.4 (4.4)	20.5 (20.3)		1625	1365	3300	420	308		0.00
$[Co^{II}(Gly)(Sal)(H_2O)_3]$	Brown	37.0 (36.9)	3.1 (3.1)	4.8 (5.0)	21.8 (21.7)		1616	1360	3410	406	295		0.00
$[Co^{II}$(L-Pro)(Sal)$(H_2O)_3]$	Brown	43.4 (43.4)	3.9 (3.8)	4.2 (4.0)	17.7 (17.7)		1605	1348	3415	410	325		0.00

^{a} Gly, L-Leu, L-Pro and Sal stand for Glycine ($C_2H_5NO_2$), L-Leucine ($C_6H_{13}NO_2$), L-Proline ($C_5H_9NO_2$) and Salicylaldehyde (C_6H_4(OH).CHO) respectively; ^{b} Λ_m stands for molar conductance.



[M = Cu(II) or Zn(II)] [M = Co(II)]

Fig 1:- Structure of the transition metal-Schiff base complexes.

3.2 Kinetics of the Hydrolytic Reactions

If the hydrolysis reactions obeyed first order kinetics, it should follow the following equation:

$$\ln (V_\infty - V_t) = -k_{obs}\, t + \ln V_\infty \qquad (1)$$

The values of $\ln (V_\infty - V_t)$, where V_∞ is the volume of acid consumed (in cm^3) at the end of the reaction and V_t is the volume consumed (in cm^3) at time t (in minute), were calculated from experimental data (provided to SI). Plots of $\ln (V_\infty - V_t)$ versus time were all linear with Pearson correlation coefficients of 0.985 or better. Hence the hydrolysis reactions obeyed first order kinetics with respect to urea or N,N′-diacetyl urea. A representative plot of urea hydrolysis by $[Cu^{II}(Gly)(Sal)(H_2O)]$ is shown in Figure 2. The observed first order rate constants (k_{obs},), obtained from the slopes of the linear plots, are summarized in Table 2.

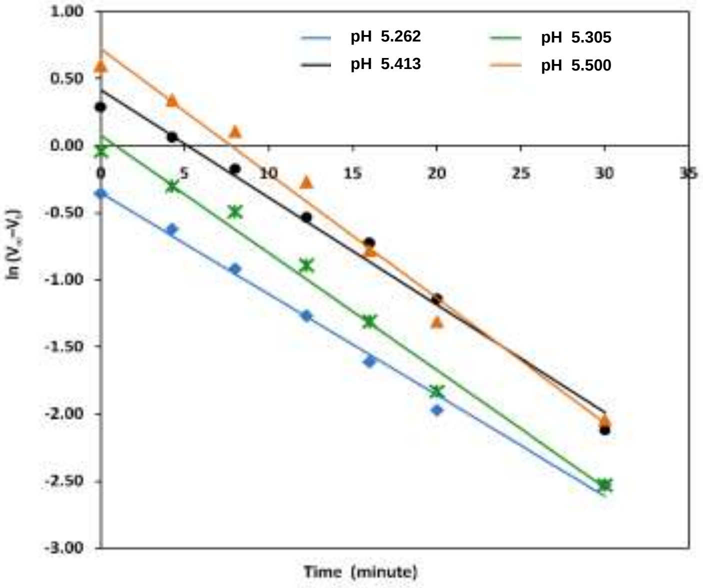


Fig 2:- Experimental data for hydrolysis of urea in presence of $Cu^{II}(Gly)(Sal)(H_2O)]$ at 30^0C and $I = 0.10$ mol dm^{-3} [$C_{urea} = C_{complex} = 1.00 \times 10^{-4}$ mol dm^{-3}].

Since the *P* values in the ANOVA Tables were less than 0.01, the relationships (y = - mx + c) were statistically significant at 99% confidence level. The *r* values of 0.995 or better indicated a fairly strong relationship amongst the variables. Since the Durbin-Watson values were greater than 1.4, there were no serious autocorrelation in the residuals. These strongly validated our regression equation based models.

In order to understand the dependence of k_{obs} on hydrogen ion concentration, k_{obs} were plotted against $[H^+]$. In all cases, the relations found were linear with positive intercepts (Figure 3). The rate expression for these reactions can therefore be written in the form:

$$k_{obs} = k_H [H^+] + k_o \qquad (2)$$

where the k_o term arises due to water attack on the intermediate complex and is expressed by the relation $k_{H_2O} = k_o / 55.5$. The k_{H_2O} value can be obtained in each case from the intercept, while the k_H value is derived from the slope of the respective plot. The k_H and k_{H_2O} values thus obtained are presented in Table 3. The kinetic scheme for the hydrolysis of urea and N,N´-diacetyl urea in the presence of the Schiff base aquo-complexes may be presented as:

$$[ML(H_2O)_x] + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ML(H_2O)_{x-2}S] \qquad (3)$$

$$[ML(H_2O)_{x-2}S] + H^+ \xrightarrow{k_H} [ML(H_2O)_{x-2}A] + NH_2R' \qquad (4)$$

$$[ML(H_2O)_{x-2}S] + H_2O \xrightarrow{k_{H_2O}} [ML(H_2O)_{x-2}A] + NH_2R' + OH^- \qquad (5)$$

where L = Schiff base ligand, S = urea or N,N´-diacetyl urea, A = cyanic acid or acetyl cyanic acid anion, R′ = hydrogen or acetyl group.

Reaction (3) is assumed to be fast, while reactions (4) and (5) are assumed to be slow since these involve breaking of C-N bond of urea [4] or N,N´-diacetyl urea. Confining attention to acid hydrolysis only, the rate expression can be written as: $v = k_2\ [ML(H_2O)_{x-2}S]\ [H^+]$. Using the value of $[ML(H_2O)_{x-2}S]$ from equilibrium reaction (3) gives:

$$v = k_2\, k_1\, [S]\, [ML(H_2O)_x]\, [H^+] / k_{-1} = k_{obs}\, [S] \qquad (6)$$

Equation (6) explains the order of with respect to both urea or N,N´-diacetyl urea and $[H^+]$, and also shows that at a particular pH, k_{obs} should depend on the concentration of the complex.

Table 2:- The experimental k_{obs} and $t_{½}$ (half-life period) range for the hydrolytic reactions.

Substrate	**Complex / Ion**	**pH range**[a]	**$10^3\ k_{obs}$ / s^{-1}**	**$t_{½}$ / s**
Urea	$[Cu^{II}(Gly)(Sal)(H_2O)]$	5.262 – 5.500	1.16 – 1.47	597 – 471
	$[Zn^{II}(Gly)(Sal)(H_2O)]$	4.910 – 5.602	0.97 – 1.34	714 – 517
	$[Zn^{II}(L\text{-}Leu)(Sal)(H_2O)]$	5.085 – 5.596	1.13 – 1.72	613 – 403
	$[Co^{II}(Gly)(Sal)(H_2O)_3]$	5.295 – 6.185	0.87 – 1.85	797 – 375
	$[Co^{II}(L\text{-}Pro)(Sal)(H_2O)_3]$	5.050 – 5.402	1.05 – 1.43	660 – 485
N,N´-diacetyl urea	$[Cu^{II}(Gly)(Sal)(H_2O)]$	5.351 – 5.950	0.86 – 1.41	806 – 491
	$[Zn^{II}(Gly)(Sal)(H_2O)]$	5.240 – 5.890	0.87 – 1.10	797 – 630
	$[Zn^{II}(L\text{-}Leu)(Sal)(H_2O)]$	5.200 – 5.828	0.96 – 1.51	722 – 459
	$[Co^{II}(Gly)(Sal)(H_2O)_3]$	5.295 – 5.840	0.73 – 1.35	949 – 513
	$[Co^{II}(L\text{-}Pro)(Sal)(H_2O)_3]$	5.170 – 6.140	0.91 – 1.26	762 – 550

[a] a particular hydrolytic reaction was monitored at a particular pH within the mentioned range.

Table 3:- Hydrolysis data (k / $dm^3\ mol^{-1}\ s^{-1}$) at 30°C; $I = 0.1\ mol\ dm^{-3}$ (KNO_3).

Substrate	**Complex / Ion**	**$10^{-2}\ k_H$**	**$10^5\ k_{H_2O}$**
Urea	$[Cu^{II}(Gly)(Sal)(H_2O)]$	1.15	1.09
	$[Zn^{II}(Gly)(Sal)(H_2O)]$	0.79	1.27
	$[Zn^{II}(L\text{-}Leu)(Sal)(H_2O)]$	1.00	0.97
	$[Co^{II}(Gly)(Sal)(H_2O)_3]$	2.34	1.09
	$[Co^{II}(L\text{-}Pro)(Sal)(H_2O)_3]$	1.00	0.79
N,N´-diacetyl urea	$[Cu^{II}(Gly)(Sal)(H_2O)]$	1.06	1.15
	$[Zn^{II}(Gly)(Sal)(H_2O)]$	0.37	1.42
	$[Zn^{II}(L\text{-}Leu)(Sal)(H_2O)]$	0.79	1.39
	$[Co^{II}(Gly)(Sal)(H_2O)_3]$	1.19	0.89
	$[Co^{II}(L\text{-}Pro)(Sal)(H_2O)_3]$	0.36	1.61

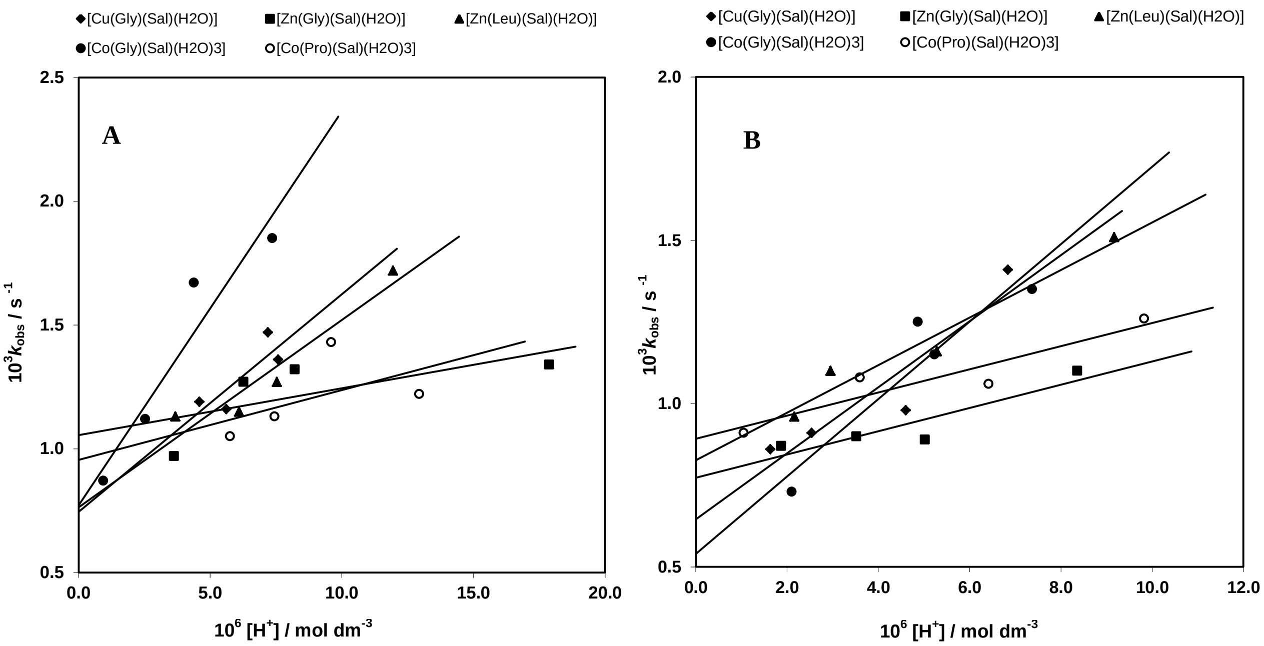


Fig 3:- Plot of k_{obs} versus [H^+] for hydrolysis of urea in presence of different Schiff base complexesat 30°C; $I = 0.1$ mol dm^{-3} (KNO_3) [A: Urea, B: N,N$'$-diacetyl urea].

3.3 Comparison of Efficiencies of Transition Metal-Schiff Base as Catalysts

Urea is very resistant to spontaneous hydrolysis. The pseudo-first order rate constant of non-enzymatic degradation of urea in aqueous medium was reported as 6.1×10^{-9} s^{-1} [10] and the enzyme urease increased the rate to 10^{14} folds. In our investigation, we found that the rate constant k_H for urea hydrolysis in the presence of the complexes were within the range of $(0.79–2.34)\times10^2$ dm^3 mol^{-1} s^{-1}, implying that the complexes acted as better catalysts for the hydrolytic reactions. The hydrolysis reactions in absence of the complexes or metal ions could not be followed by pH-stat procedure. Comparison of the values with the rate constants for non-enzymatic degradation of urea from the works of Laidler [16] revealed that our results corresponded to a rate enhancement by the order of 10^6. The k_H values for N,N$'$-diacetyl urea hydrolysis by the complexes were $(0.36–1.19)\times10^2$ dm^3 mol^{-1} s^{-1}. The lower reactivity of N,N$'$-diacetyl urea relative to urea (decreased by 30-100%) may be attributed to (i) inductive effect of the acetyl carbonyl group and (ii) steric hindrance of the bulky acetyl group, the combined effect of which decreased the coordinating power of the lone pair electrons on the ($NHCOCH_3$) nitrogen atom to the metal [17-18]. This decreased the possibility of formation of mixed ligand chelate complex resulting in lower rate constant k_H for hydrolysis of the urea derivative. It is noted that cobalt(II) complex of the Schiff base derived from glycine and salicylaldehyde was found to be the most efficient catalyst used in the investigation.

3.4 Half-life Period ($t_{½}$) of the Hydrolytic Reactions

The half-life period ($t_{½}$) of the hydrolysis reactions of urea and N,N′-diacetyl urea catalyzed by the complexes were estimated based upon the equation ($t_{½} = \ln 2 / k_{obs}$) and represented in Box-and-Whisker plots (Figure 4). The average half-life period ($t_{½}$) ranges for urea and N,N$'$-diacetyl urea hydrolysis were 450–676 and 529–807 seconds (7.50–11.27 and 8.82–13.45 min) respectively. The minimum $t_{½}$ values of 6.25 and 7.62 min for urea and N,N′-diacetyl urea hydrolysis corresponded to catalysis of [$Co^{II}(Gly)(Sal)(H_2O)_3$] and [$Zn^{II}$(L-Leu))(Sal)($H_2O$)] respectively. This implies that [$Co^{II}(Gly)(Sal)(H_2O)_3$] acted as better catalyst for urea hydrolysis, whereas [Zn^{II}(L-Leu))(Sal)(H_2O)] for N,N′-diacetyl urea. It is to be noted that the $t_{½}$ for uncatalyzed hydrolysis of urea was reported as 8.15 days [24].

3.5 Probable Mechanism of the Hydrolytic Reactions

The general proposed reaction mechanism for the hydrolysis of urea and N,N$'$-diacetyl urea by the transition metal-Schiff bases complexes is depicted in Fig 5. The primary step probably involves the formation of the mixed ligand chelate complex by the replacement of two coordinated water molecules by NHR$'$ and the carbonyl groups of urea or N,N$'$-diacetyl urea. This species undergoes acid hydrolysis to form [ML $(H_2O)_{x-2}$A] and NH_2R' in a secondary step. For the complexes having only one water molecule in the coordination sphere, it was assumed that these complexes expanded their coordination number to five in order to accommodate both the NHR$'$ and the carbonyl groups, and followed similar kinetic path. The expansion of coordination number was in good agreement with nany authors [20-21]. The present data are in accordance with the mechanism proposed for urea or N,N′-diacetyl urea hydrolysis, whereby transient coordination of the carbonyl group to the metal atom caused substantial activation towards the electrophilic attack by hydrogen ion to the amino or acetyl amino nitrogen.

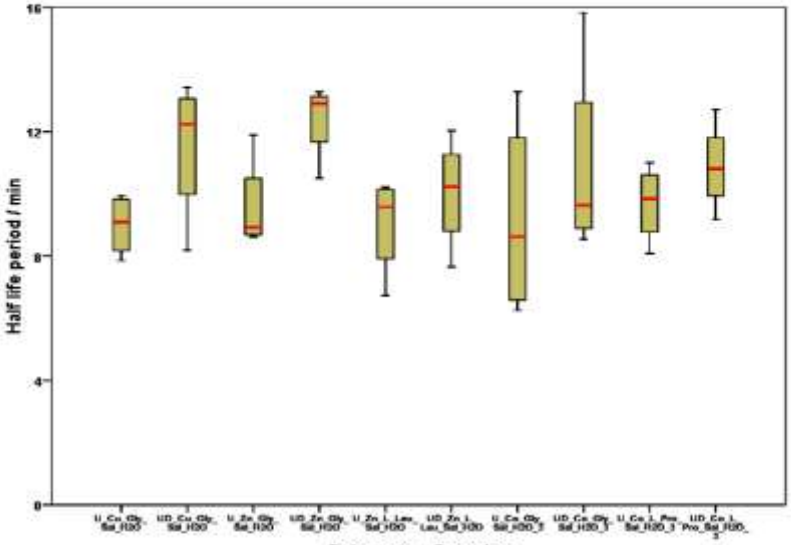


Fig 4:- Box-and-Whisker plots for half-life periods of the hydrolysis reactions. [(▬) indicates median; lower and upper box boundaries 25th and 75th percentiles of each distribution; Whiskers as vertical lines ending in horizontal lines at the largest and smallest observed values; (*) indicates outside value and (O) far outside value.]

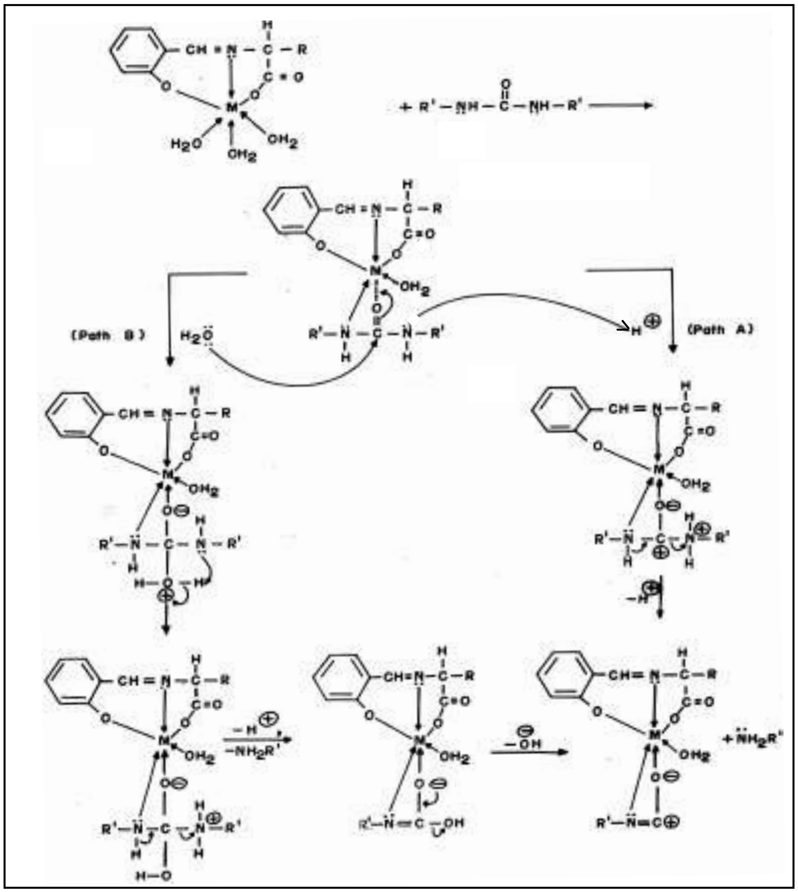


Fig 5:- General proposed reaction mechanism for the hydrolysis of urea and N,N′-diacetyl urea by the complexes.

Conclusions:-

Solid aquo Co^{II}, Cu^{II} and Zn^{II} complexes of Schiff bases derived from amino acids and salicylaldehyde had been prepared, characterized and used as model enzymes of Urease. Using a pH-stat method, the kinetics of acid hydrolysis of urea and its derivative N,N$^{\prime}$-diacetyl urea in the presence of the complexes had been studied in pH range of 4.91–6.19 at 30^0C. It was found that the hydrolytic reactions followed first order kinetics (pseudo-unimolecular) with respect to both urea or N,N$^{\prime}$-diacetyl urea and [H^+]. The complexes enhanced the rate of hydrolysis markedly, as the values of the second-order rate constants being 10^6 times greater than those of uncatalyzed reaction. The complexes acted as better catalysts for urea than N,N$^{\prime}$-diacetyl urea towards the hydrolysis reactions. The complexes catalyzed urea hydrolysis 30-100% more than N,N$^{\prime}$-diacetyl urea hydrolysis. The proposed mechanism involved the formation of mixed ligand chelate complex by replacement of two coordinated labile water molecules by NHR′ (R′= H or $COCH_3$) and carbonyl group of urea or N,N$^{\prime}$-diacetyl urea followed by acid hydrolysis. The average $t_{½}$ ranges were 450–676 and 529–807 seconds for urea and N,N$^{\prime}$-diacetyl urea hydrolysis respectively. The complex [Co^{II}(Gly)(Sal)(H_2O)$_3$] acted as better catalyst for urea hydrolysis, whereas [Zn^{II}(L-Leu))(Sal)(H_2O)] for N,N′-diacetyl urea towards the hydrolysis reaction.

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