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Solvent Effects on the Catalytic Hydrolysis of Acetamide by Co-Mo-Oxide Catalyst

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Solvent effect on the catalytic hydrolysis of acetamide by Co-Mo-oxide catalyst were investigated in glycerol, ethylene glycol and ethanol-water. The used percentages of organic solvent are: 25, 45 and 65% v/v, at 60°C. The results shown that the reaction follows a second order kinetics in all cases which illustrates that solvents alter the reaction rate without influencing the mechanism. The used polar organic solvents in presence of $CoO-MoO_3$ catalyst probably leads to a certain type of bond with water molecule. The formation of this bond increases with the polarity of the organic solvent which may led to a decreases in the water activity with increasing the per cent of organic solvent. Aslo it was found that the medium of higher dielectric constant D is characterized by higher reaction rate.

INTRODUCTION

Catalytic hydrolysis of amide has been studied and discussed in two reviews[1,2]. Studies of the acid and alkaline hydrolysis of acetamide were carried out over a wide range of water-dioxane mixtures in order to clarify specific solvent effects on the reaction rate[3]. The rate of acidic and alkaline hydrolysis of acetamide was measured in different *iso*propanol-water mixtures[4]. The calculated velocity constants, *iso*-composition and *iso*-dielectric energies of activation were discussed in terms of solvation effects and were confirmed by thermodynamic data. Structure medium and temperature dependence of acid-catalysed amide hydrolysis were discussed by Smith and Yates[5].

The kinetic acidity dependence and medium dependence of the activation parameters have been analysed[6]. The rate constants of the hydrolysis of protonated acetamide in dioxane-water mixtures were calculated from kinetic data and known acid constants of the amide[7]. The acidic and alkaline hydrolysis of amides has also been studied in acetone-water and ethanol-water mixtures[8,9].

The effects of solvent on the acidic and alkaline hydrolysis of acetamide in various *tert* butanol-water mixtures were studied in the temperature ranges 25°–50°C. In the acidic hydrolysis, the velocity constant decreased noticeably with successive addition of the organic solvent whereas the *iso*-composition activation energy increased in the same direction[10].

A few investigation of catalytic hydrolysis of acetamide concerning the effect of mixed oxide catalysts on the rate of the hydrolysis has been published[11,12]. In the present. work, we have studied the solvent effects on the kinetics and mechanism of acetamide hydrolysis in glycerol, ethylene glycol and ethanol-water solutions of different composition.

EXPERIMENTAL

The acetamide used was a product of (BDH) and was further purified by successive crystallization from ethyl alcohol and benzene. Conductivity water was used in the preparation of the solvent mixtures. Methanol and ethylene glycol of the pure "Merck" quality were further purified by distillation. "Merck" bidistilled glycerol was used as received.

Preparation of the catalyst: The catalyst used in this study is composed of oxide of cobalt and molybdenum with atomic ratio is 1 : 1. The mixed oxide catalyst $CoO-MoO_3$ is prepared from aqueous solutions of ammonium molybdate and cobalt nitrate were used as starting materials. The precipitation was carried out at 60°C in a vessel containing ammonium molybdate solution and the temperature was kept constant by means of thermometer dipped in the solution. The cobalt nitrate solution was added slowly and the solution was continuously stirred during the addition. The pH of solution was maintained constant 6.8. After complete precipitation the solution was immediatly filtered and the precipitate washed several times with bidistilled water and dried at 120°C for 2 hrs. Finally, the solid catalyst obtained were calcined in air at 500°C for 3 hrs. where they transformed into mixed oxides of cobalt and molybdenum. The cobalt and molybdenum content in catalyst were determined gravimetrically as described by Vogel[13]. The results of analysis were found to be in accordance with the theoretical composition of the prepared $CoO-MoO_3$ catalyst.

Rate of hydrolysis: 25 ml of 0.4 M acetamide solution, containing the appropriate amount of the alcohol, were intoduced in 250 ml flask and the weight of catalyst was added. The flask was stirred unformly by a magnetic stirrer which was immersed in a thermostated water at ± 0.05°C. The rate of the reaction was followed with drawing 5 ml samples (using a certified pipette) of the reaction mixture at different time intervals and analysed by titration against NaOH. The amount of alkali consumed is a measure of the amide decomposed.

RESULTS AND DISCUSSION

The catalytic hydrolysis of acetamide in presence of mixed oxide ($CoO-MoO_3$) as catalyst with the per cent of added organic solvent is investigated. The used percentages of organic solvent are: 25, 45 and 65% v/v for glycerol, ethylene glycol and ethanol. The reaction was carried out as a batch equilibrium with constant stirring at 60°C. A constant weight of catalyst (1.0 gm) was added to the reaction. The rate constant was determined through evaluating the formed acetic acid against standard sodium hydroxide solution using phenolphthalein as indicator. The effect of solvent on the per cent of hydrolysis and the rate constant for the catalytic hydrolysis of acetamide in presence of CoO–MoO_3 as catalyst is shown in Table-1 and Figs. 1–3; this result shows that the reaction follows a second order kinetics in all cases which illustrates that such solvents alter the reaction rate without influencing the mechanism.

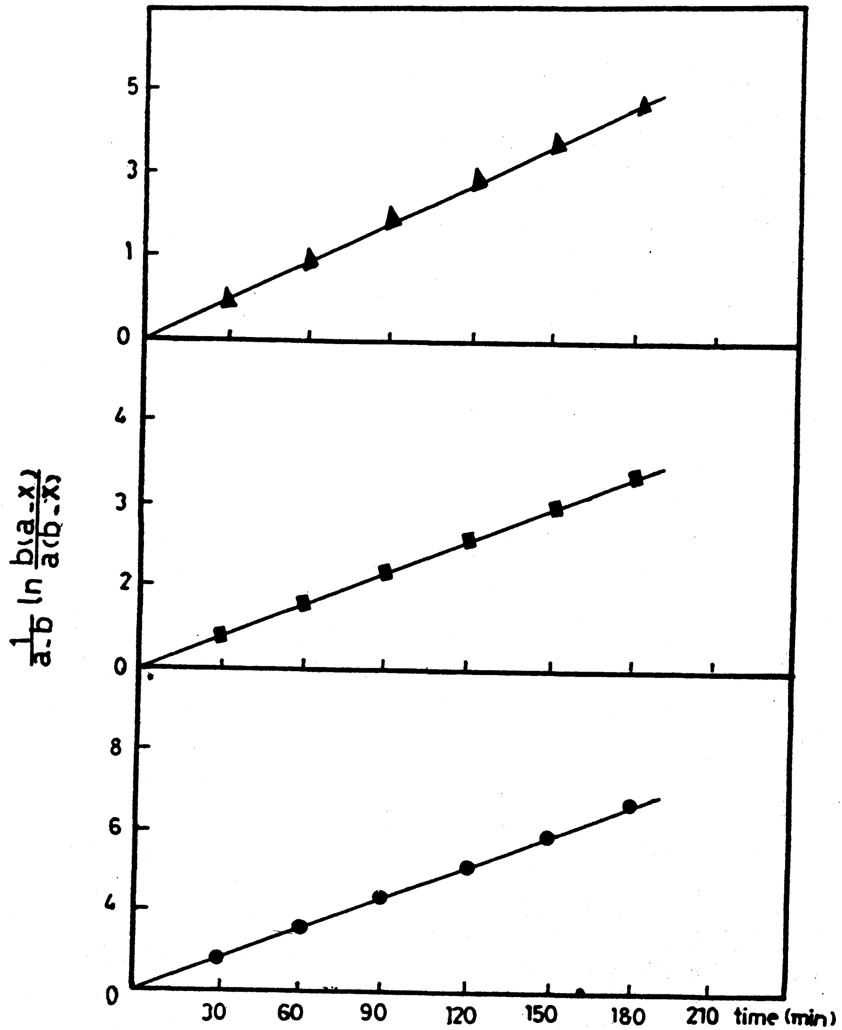

Fig. 1 Ethanol-Water ●25%, ■45%, ▲65%.

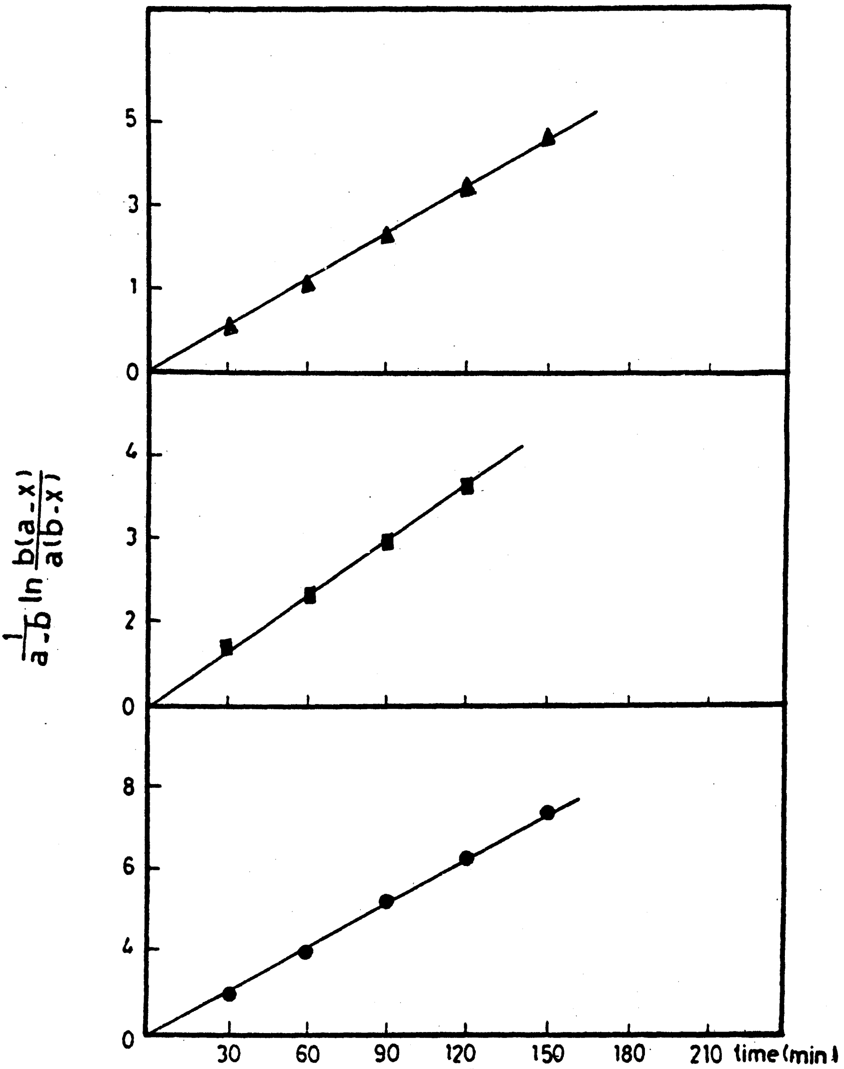

Fig. 2 Ethanol glycol-Water ●25%, ■45%, ▲65%.

TABLE 1
SOLVENT EFFECT ON THE PER CENT OF HYDROLYSIS AND RATE CONSTANT

Solvent per cent	Glycerol		Ethylene-glycol		Ethanol	
	% of hydrolysis	$K \times 10^4$ (min^{-1})	% of hydrolysis	$K \times 10^4$ (min^{-1})	% of hydrolysis	$K \times 10^4$ (min^{-1})
25%	89.4	3.94	85	3.52	80.5	3.15
45%	72.5	2.83	85	2.43	60.5	1.51
65%	57.9	1.84	85	1.46	51.4	1.01

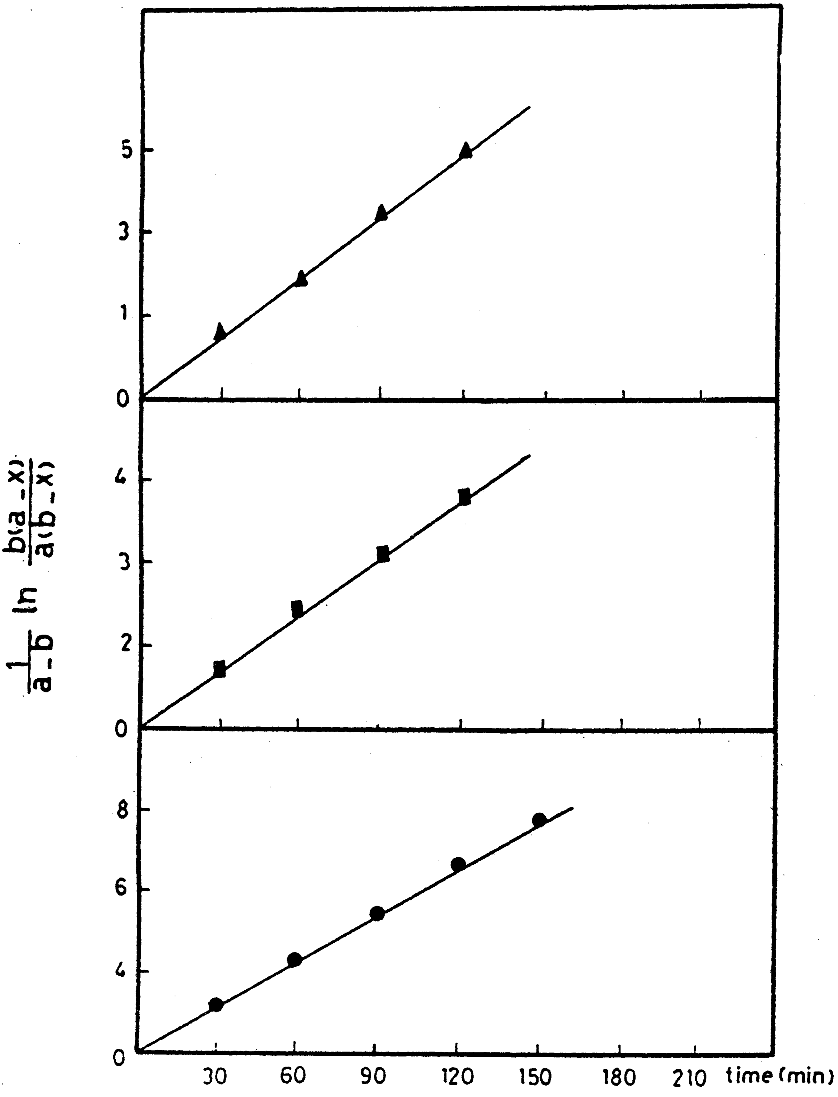

Fig. 3 Glycerol-Water ●25%, ■45%, ▲65%.

It is mentioned[14] that the acidity is apparently reduced by the first addition of dioxane. Moreover the rate constant decreases slightly in successive addition of dioxane, then increases passing through a minimum in case of the acid hydrolysis at about 50% wt. of dioxane. To account for such behaviour it is suggested that the tetrahedral structure of water has been largly broken by successive addition of dioxane and so the proportion of free water molecule increases as water activity decrease. In the present study, the used polar organic solvents in presence of $CoO-MoO_3$ catalyst probably leads to a certain type of bond with water molecule.

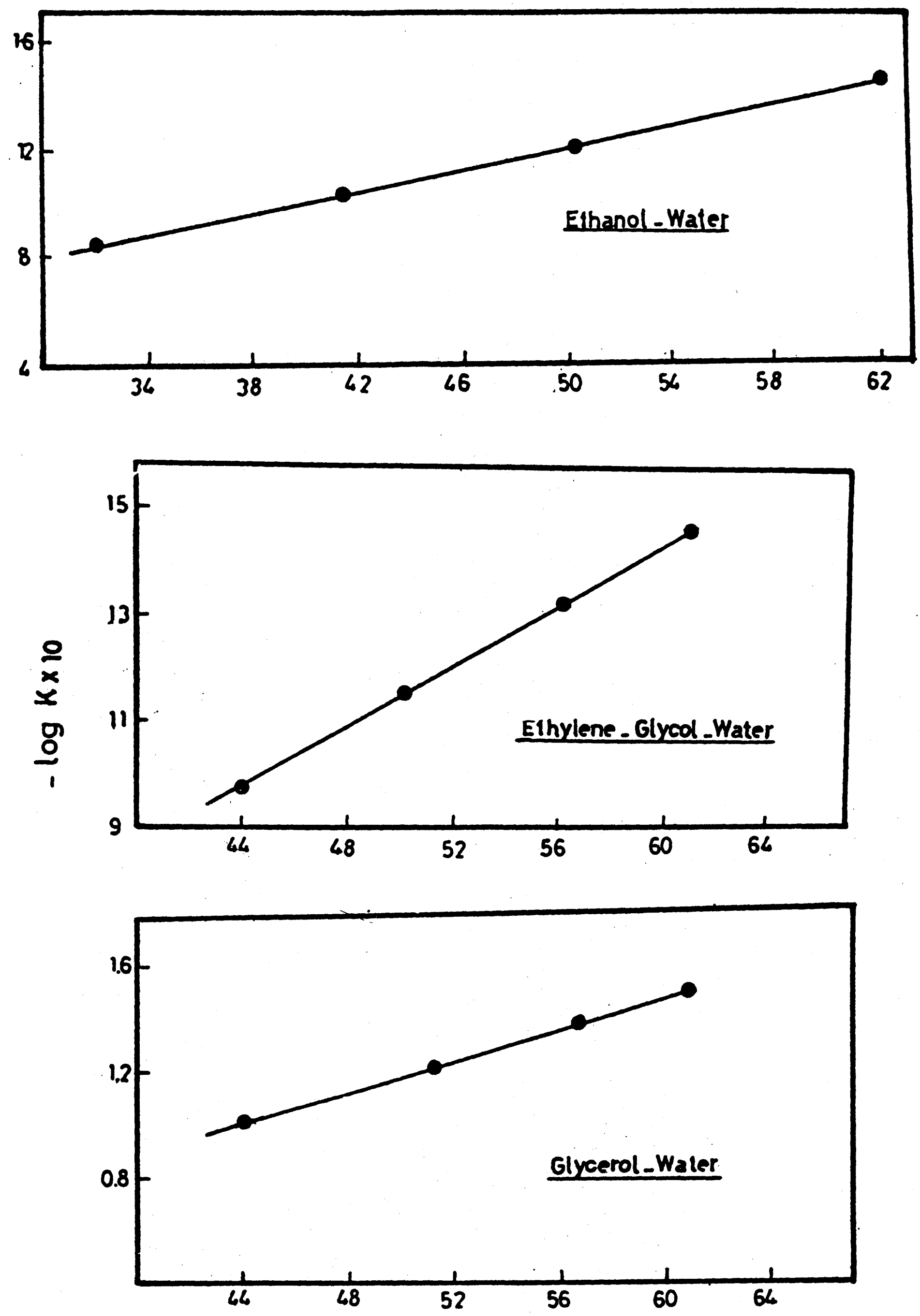

Fig. 4 Relation between log k and dielectric constant(D).

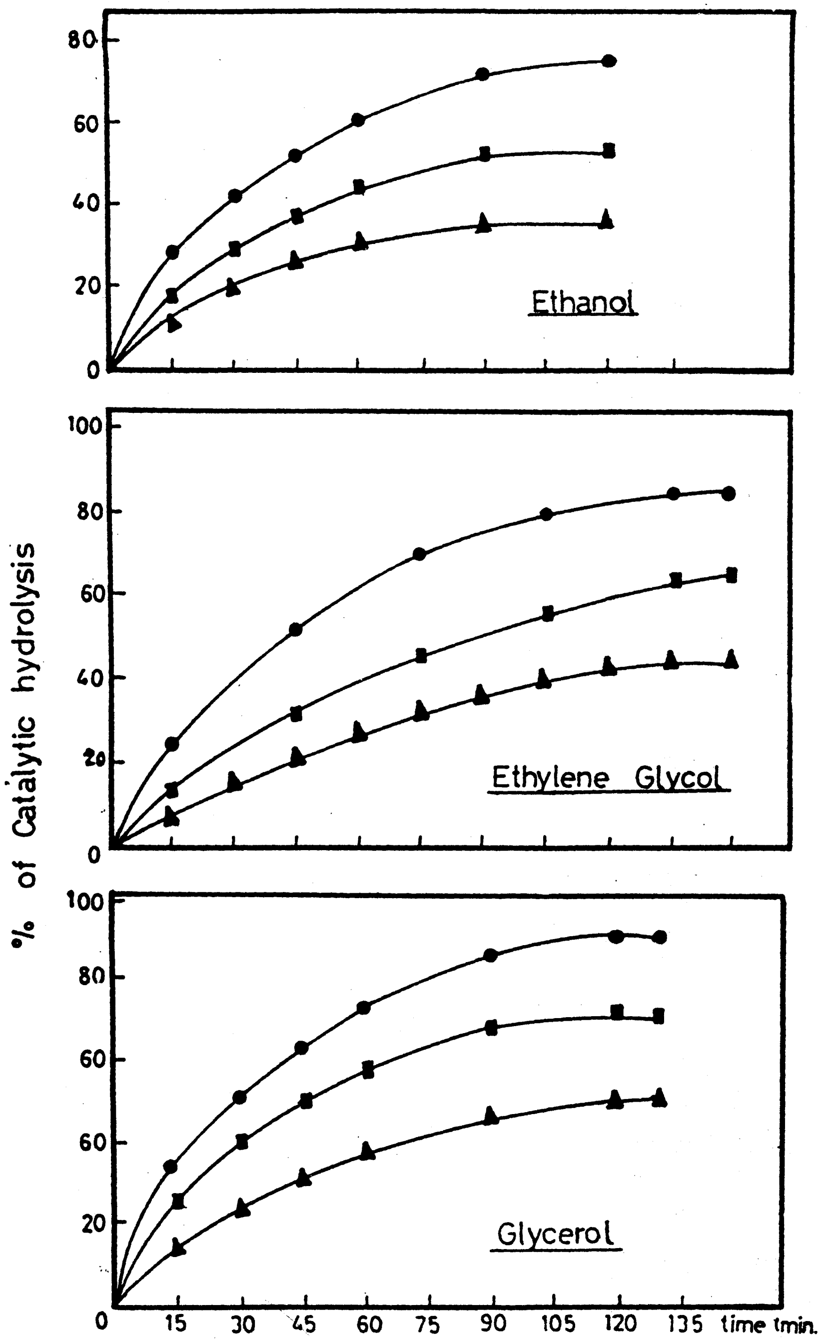

Fig. 5 Relation between different per cent of solvents and per cent of catalytic hydrolysis: ●25%, ■45%, ▲65%.

The formation of this bond increases with the polarity of the organic solvent which may lead to a decrease in the water activity with increasing the per cent of organic solvent.

Data in Table 2 illustrate the value of dielectric constant at different ratios of the used organic solvent. It is found that the medium of higher dielectric constant, is characterized by higher reaction rate. Increasing the quantity of organic solvent is known to decrease the dielectric constant of the medium as compared with water. Hence increasing the quantity of organic solvent is accompanied by a decrease in the rate of hydrolysis. At the same per cent of organic solvent it is found that the rate of hydrolysis is higher in presence of the solvent of highest dielectric constant. The value of log k plotted against the dielectric constant D for the various water organic solvent (Fig. 4). It shown that the rate of catalytic hydrolysis of acetamide in presence of CoO–MoO$_3$ as catalyst, decrease linearly with the decrease in the dielectric constant of the solvent. No increase in the rate of hydrolysis with further increase in the ratio of organic solvent, is observed and consequently no minimum is reached in the rate constant for such heterogeneous catalytic reaction. The values of rate constant at the respective similar ratio of organic solvent proceeds according the following sequence:

Glycerol > Ethylene glycol > Ethanol.

TABLE 2
RELATION BETWEEN VALUES OF DIELECTRIC CONSTANT (D) AND VALUES OF RATE CONSTANT

Organic solvent	25%		45%		65%	
	$K \times 10^4$	D	$K \times 10^4$	D	$K \times 10^4$	D
Glycerol	3.94	56.01	2.83	51.17	1.84	45.39
Ethylene glycol	3.52	55.38	2.43	49.81	1.46	43.68
Ethanol	3.15	50.81	1.51	40.93	1.01	31.62

Plots of per cent of catalytic hydrolysis of acetamide in presence of CoO–MoO$_3$ as catalyst against time (min) show relative decrease in the rate of hydrolysis, rate constant and per cent of the hydrolysis with the ratio of organic solvent as shown in Fig.-5. To examine the possible esterification reaction of the used organic solvent (as alcohol) with the liberated acid, some experiments were carried out, by different quantity of acetic acid, the theoretically calculated that liberates from acetamide and the experimentally with the respective alcohol were used in the hydrolysis of acetamide in presence of glycerol, ethylene glycol and ethanol in quantity of 65% of the whole solution. The same quantities of CoO–MoO$_3$ catalyst, organic solvent were used and the reaction was conducted in each run at the same temperature and for the same time which was used in presence of acetamide. The results show that at such reaction conditions, the consumed quantity of the liberated acid in the process of estrification is very small 0.95% for ethanol, 1.43% for ethylene glycol and 1.89% for glycerol, such small quantities could be considered to have negligable effect on the attained results of the rate constant, and per cent of the hydrolysis of acetamide in presence of CoO–MoO_3 as catalyst.

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