

ESTERIFICATION OF 1-PROPANOL AND 1-BUTANOL WITH SOME ORGANIC ACIDS USING INORGANIC ION-EXCHANGE RESIN (ZIRCONIUM TUNGSTATE) AS A CATALYST

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Studies have been investigated on the esterification of 1-propanol and 1-butanol with different organic acids in presence of inorganic cation exchanger zirconium tungstate (H⁺-form). The influence of molecular weight, structure of acids and alcohols and temperature on the fractional conversion have been studied. The effect of metal-amine form of zirconium tungstate as a catalyst especially in the esterification of propionic acid with methanol and ethanol separately have been investigated. It was found that the rate of esterification decreases with decreasing the exchange capacity of the resin depending on the metal-amine forms, whereas the activation energy of reaction increased. It was important found that the zirconium tungstate in H⁺-form a good catalyst for such esterification. In both cases the experimental data was found to fit a second order bimolecular kinetic equation. The rate constant (k_r) for seven acids have been calculated and found to bear a linear relationship with the reciprocal of temperature.

Key words: Esterification, Ion-exchange resin, Acid.

Introduction

Heterogenous catalytical esterification of alcohols with organic acids, in the presence of organic cation exchanger in the hydrogen form have been reported [1-7]. Some workers have carried out investigations regarding the use of inorganic cation exchange resins in the esterification reactions of organic acids with alcohols [8]. However, no data is available on the effect of organic acids with alcohols.

The aim of the present study is to evaluate the mono-chloro-esterification reaction of seven acids, viz., formic, acetic, monochloro and dichloro-acetic, propionic, butyric and valeric acids with 1-propanol and 1-butanol separately in the presence of zirconium tungstate inorganic cation exchanger (H⁺-form) as a catalyst. Kinetic equations have been applied to calculate the value of reaction velocity constant (K_r) for each reaction. The influences of metal amine forms of zirconium tungstate on the rate of esterification reaction and on the fractional conversion have been investigated.

Experimental

The chemicals used in the present study were either BDH-Analar, Prolabo, Koch-light or E-Merck (GR) grade. The catalyst used was zirconium tungstate, prepared as per the procedure described elsewhere [9]. Determination of exchange capacity of the resin was carried out according to the reported method [10].

Calculation. Before soaking (M XI = V X 0.01 by (X) - and after soaking is also simplified by (Y). The number of gm moles of the metal ion taken up by the exchanger is calculated using:

$$\frac{\text{Number of gm moles of the metal ion taken up} \times 10 \times 1000}{5 \times 2 \times 1000 \times \text{equiv. Wt of the metal ion}}$$

Thermal treatment. The different forms of zirconium tungstate in H (I), Zn (II) Cu(II) and Ni (II) were subjected to a process of thermal heating at different temperatures. The sample was kept in a muffle furnace for 3 hrs at 80°, 120°, 240°, 300°, 480°, 600°, 780°, and 900° respectively. The weight loss for hydrogen ranges from 0.009-17.11, Zn (II) from 0.008-16.17 Cu (II) from 0.008 - 16.0 and Cd (II) from 0.007 - 15.7 and 0.006 - 15.5.

X-ray analysis was carried out in Cairo Electric Company (Central Chemical Laboratory), Philips (1373). It can be concluded that all of the used samples are amorphous.

The esterification reaction was carried out in three necked one litre flask placed in a constant temperature bath. The acid and the portion of alcohol were charged into the flask. The contents were kept thoroughly agitated for a few minutes and finally the catalyst was taken out at regular intervals for analysis using 0.1 N NaOH solution.

Results and Discussion

The results obtained for the fractional conversion of formic, acetic, mono and dichloroacetic, propionic, butyric and valeric acids to their esters with propanol and 1-butanol as a function of reaction temperature are given in Tables 1 and 2. The rate of esterification reaction under the experimental conditions studied was found to be markedly influenced with the reaction temperature. In the case of esterification of the two alcohols with formic acid (Fig 1-6A) the values of specific rate constant (K_r) are found to be very high when compared with the values obtained in the case of other acids, indicating higher rates of conversion in case of formic acid. Further, it is observed that the values of activation energy in case of dichloroacetic acid (DCA) are higher as compared with the

TABLE 1. REACTION VELOCITY CONSTANTS, ENERGIES OF ACTIVATION AND THERMODYNAMIC ACTIVATION PARAMETERS FOR THE CATALYZED ESTERIFICATION OF PROPANOL WITH VARIOUS CARBOXYLIC ACIDS.

Acid	Molecular weight	Temp. °C	X _{Ae}	K X 10 ⁻⁴ Experimental	K X 10 ⁻⁴ Theoretical	E _a , Cal. mol ⁻¹	ΔE* (Cal. mol ⁻¹)	-Δ ₁ S* Cal. deg mol ⁻¹	ΔG,* Cal. mol ⁻¹
Formic	46.026	75	0.88	46.156	45.9375	5949.1017	4566.1497	54.429366	23507.569
		70	0.86	40.0644	40.5238		4586.0197	54.43269	23256.432
		64	0.83	34.9934	34.6916		4609.8637	54.357761	22928.429
Monochloro acetic	94.50	75	0.83	9.42944	9.40334	7046.0992	5663.1472	54.433335	24605.947
		70	0.81	8.04254	8.10593		5683.0172	54.425591	24350.994
		64	0.74	6.59566	6.74338		5706.8612	54.41893	24046.04
Dichloro acetic	128.94	75	0.78	5.32398	5.52286	7414.1791	6031.227	54.511624	25001.266
		70	0.74	4.57986	4.72384		6051.097	54.471491	24734.818
		64	0.69	3.76721	3.8922		6074.941	54.439764	24421.142
Acetic	60.05	75	0.70	2.9992	2.79614	7884.9205	6501.9685	54.2994	25398.159
		70	0.64	2.48862	2.368		6521.8385	54.31122	25150.586
		64	0.60	2.00575	1.92726		6564.6825	54.295553	24843.283
Propionic	74.08	75	0.62	2.56998	2.55239	7948.00	6565.048	54.425075	25504.979
		70	0.60	2.18723	2.1587		6584.918	54.383864	25238.583
		64	0.56	1.76846	1.75403		6608.762	54.358597	24927.609
Butyric	88.11	75	0.43	1.36417	1.50396	8313.8075	6930.8555	54.632584	25942.994
		70	0.38	1.14402	1.26221		6950.7255	54.605335	25680.355
		64	0.33	0.949449	1.01588		6974.5695	54.5092	25344.169
Valeric	102.13	75	0.35	0.961258	0.890076	8676.8558	7293.9038	54.30959	26193.641
		70	0.32	0.792202	0.741024		7313.7738	54.231902	25915.316
		64	0.28	0.636141	0.624989		7337.6178	54.227755	25612.371

TABLE 2. REACTION VELOCITY CONSTANTS, ENERGIES OF ACTIVATION AND THERMODYNAMIC ACTIVATION PARAMETERS FOR THE CATALYZED ESTERIFICATION OF BUTANOL WITH VARIOUS CARBOXYLIC ACIDS.

Acid	Molecular weight	Temp. °C	X _{Ae}	K X 10 ⁻⁴ Experimental	K X 10 ⁻⁴ Theoretical	E _a , Cal. mol ⁻¹	ΔH* (Cal. mol ⁻¹)	-Δ ₁ S* Cal. deg mol ⁻¹	ΔG,* Cal. mol ⁻¹
Formic	46.026	75	0.87	43.5873	42.4921	6003.0211	4620.0691	54.388222	23547.17
		70	0.86	38.325	37.4419		4639.9391	54.3637	23286.688
		64	0.85	33.0341	32.0048		4663.7831	54.312271	22967.018
Monochloro acetic	94.50	75	0.82	8.75433	8.74375	7096.4285	5713.4765	54.436356	24657.324
		70	0.80	7.63695	7.52901		5733.3465	54.381696	24386.268
		64	0.73	6.24589	6.2552		5757.1905	54.377871	24082.532
Dichloro acetic	128.94	75	0.74	5.08955	5.19947	7455.9099	6072.9579	54.481201	25032.415
		70	0.70	4.31063	4.4333		6092.8279	54.470228	24776.116
		64	0.61	3.45192	3.65708		6116.6719	54.489634	24479.678
Acetic	60.05	75	0.70	3.38821	2.73348	7900.5964	6517.6444	54.011987	25313.815
		70	0.64	2.85356	2.31395		6537.5144	54.99374	25057.31
		64	0.58	2.26121	1.88268		6561.3534	54.010792	24762.995
Propionic	74.08	75	0.55	2.02524	2.01879	8110.204	6727.252	54.432374	25669.718
		70	0.50	1.72701	1.70157		6747.122	54.380462	25399.62
		64	0.45	1.39071	1.37675		6770.966	54.354824	25088.541
Butyric	88.11	75	0.40	1.34033	1.42988	8348.7394	6965.7874	54.567243	25955.187
		70	0.37	1.12739	1.19916		6985.6574	54.532594	25690.337
		64	0.35	0.91662	0.964222		7009.5014	54.475476	25367.736
Valeric	102.13	75	0.33	0.680591	0.691899	8850.7795	7467.8275	54.471432	26923.885
		70	0.30	0.58185	0.574148		7487.6975	54.383436	26141.216
		64	0.27	0.483314	0.455646		7511.5415	54.257688	25769.382

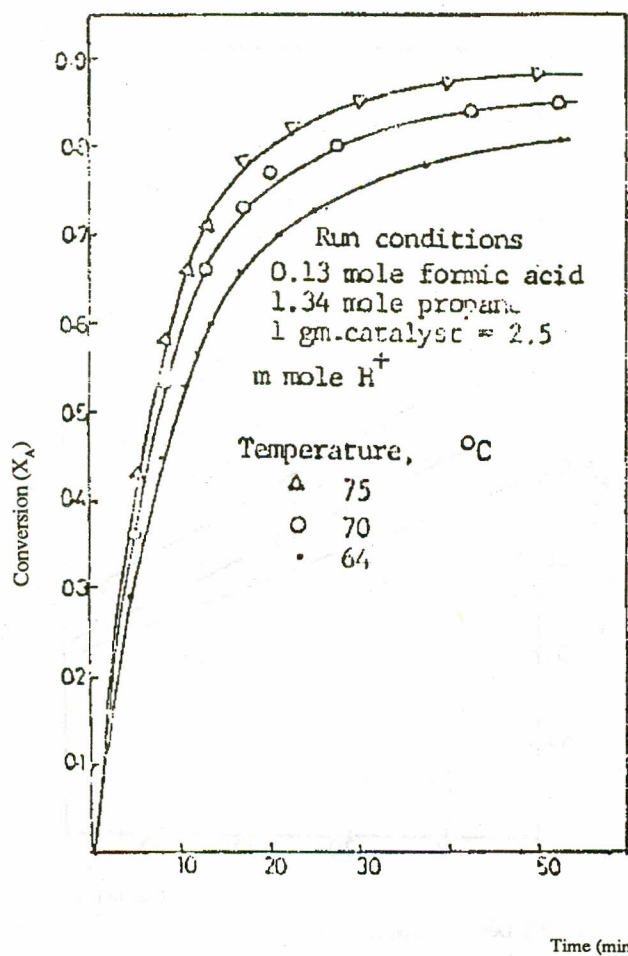


Fig. (1A). Effect of reaction temperature on the conversion of formic acid.

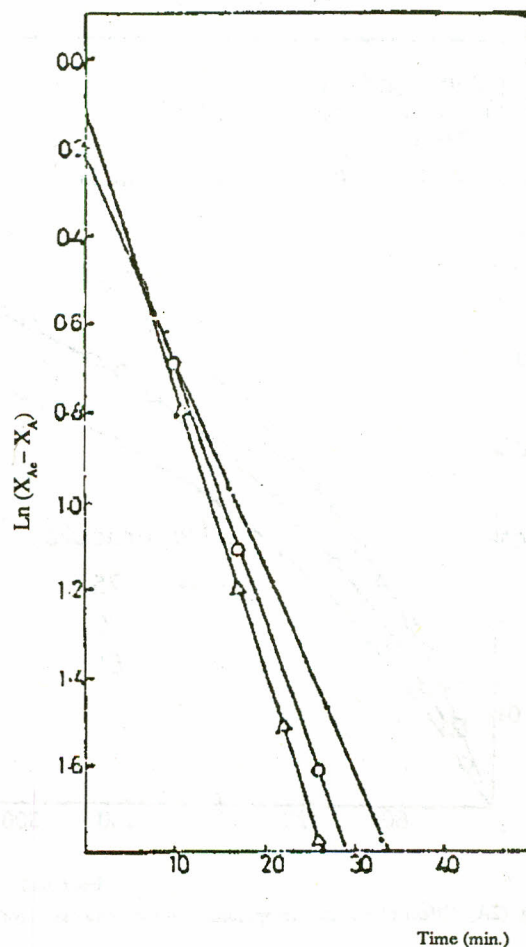


Fig. (1C). Determination of X_{Ae}.

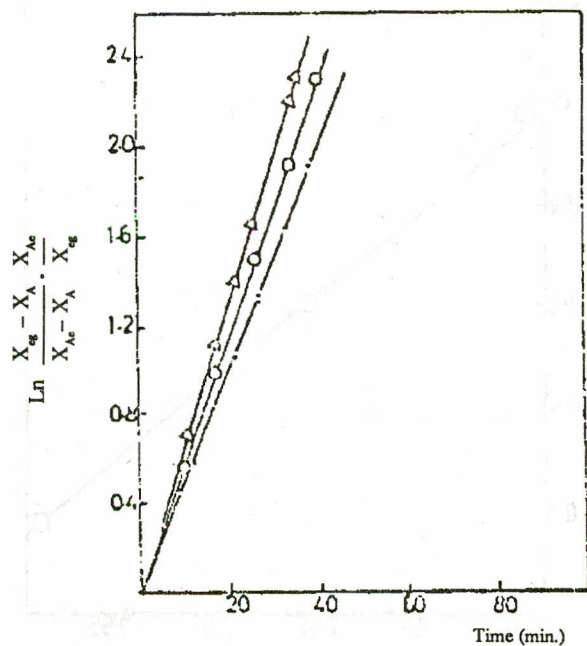


Fig. (1B). Linear transformation.

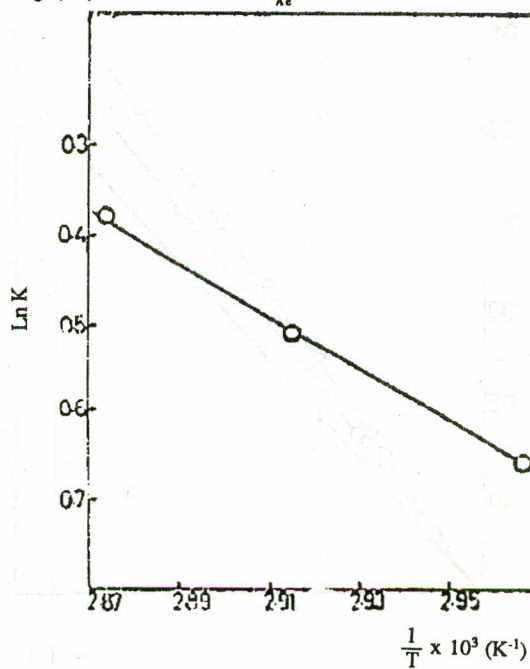


Fig. (1D). Effect of temperature on reaction rate constant.

Fig. 1. Esterification of formic acid with propanol.

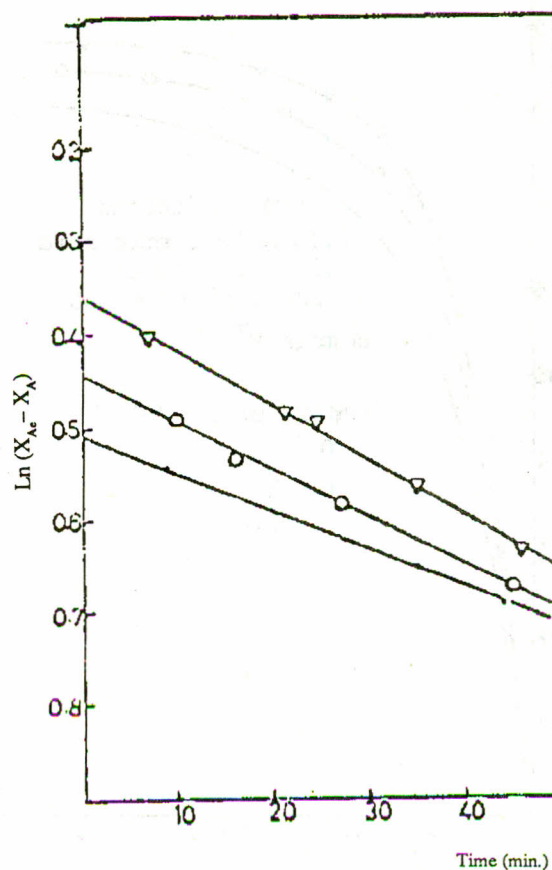
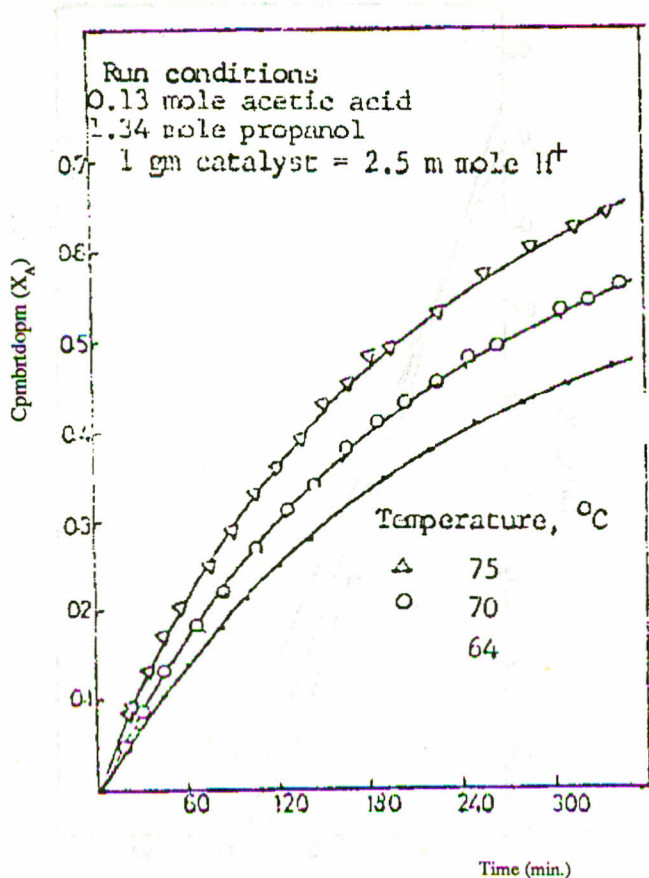


Fig. (2A). Effect of reaction temperature on the conversion of acetic acid.

Fig. (2C). Determination X_{Ae} .

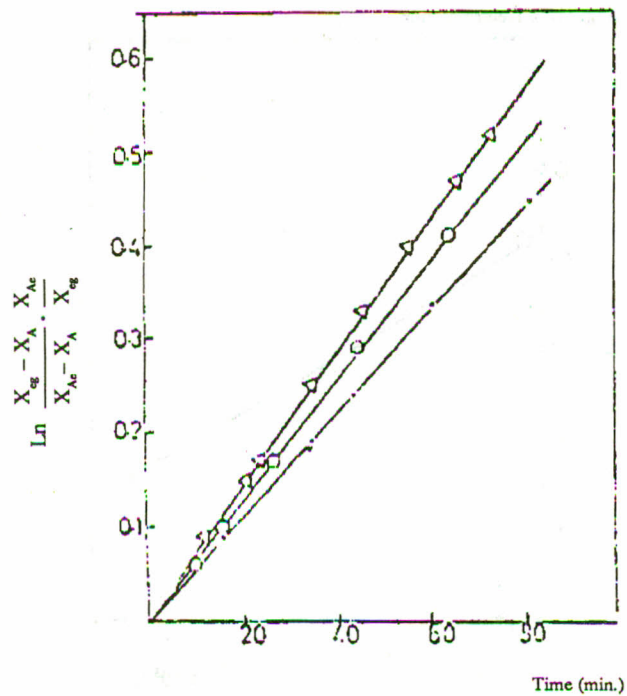


Fig. (2B). Linear transformation.

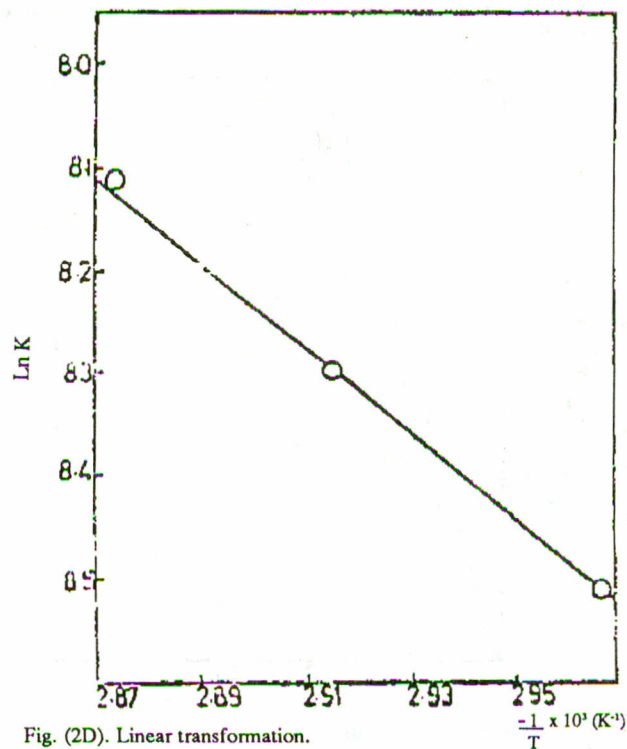


Fig. (2D). Linear transformation.

Fig. 2. Esterification of acetic acid with propanol.

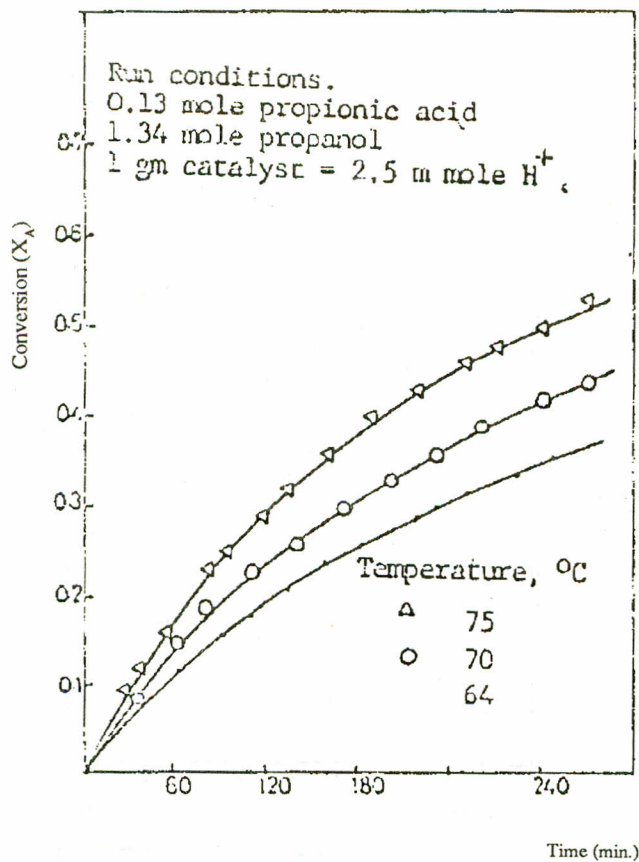


Fig. (3A). Effect of reaction temperature on the conversion of propionic acid.

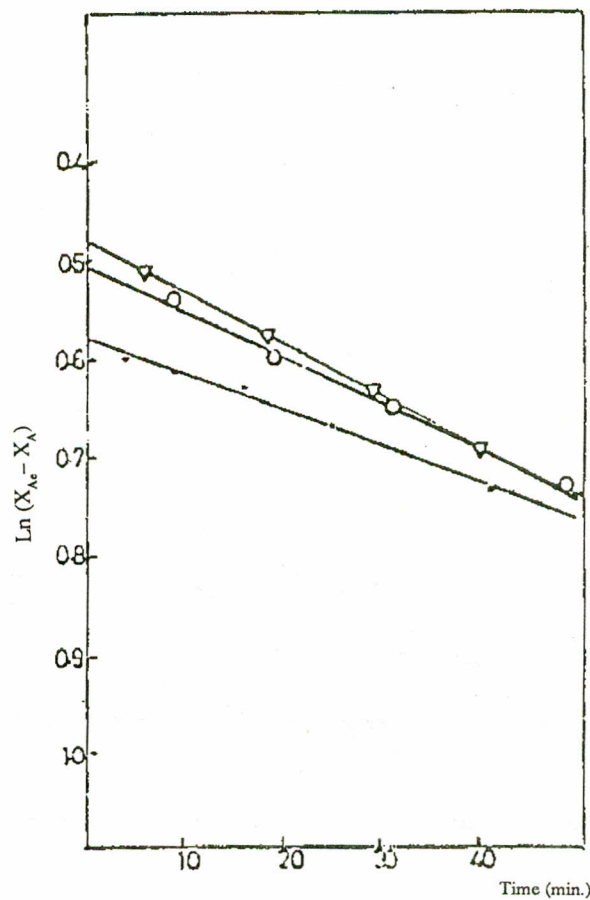


Fig. (3C). Determination of X_{Ae}.

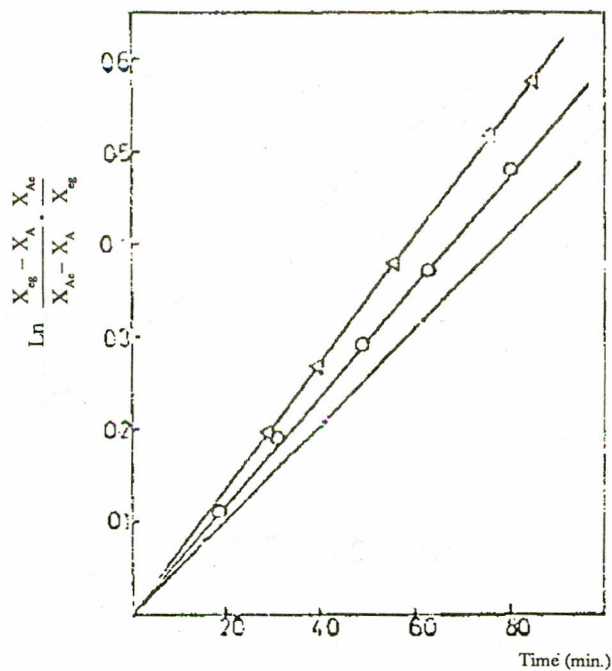


Fig. (3B). Linear transformation.

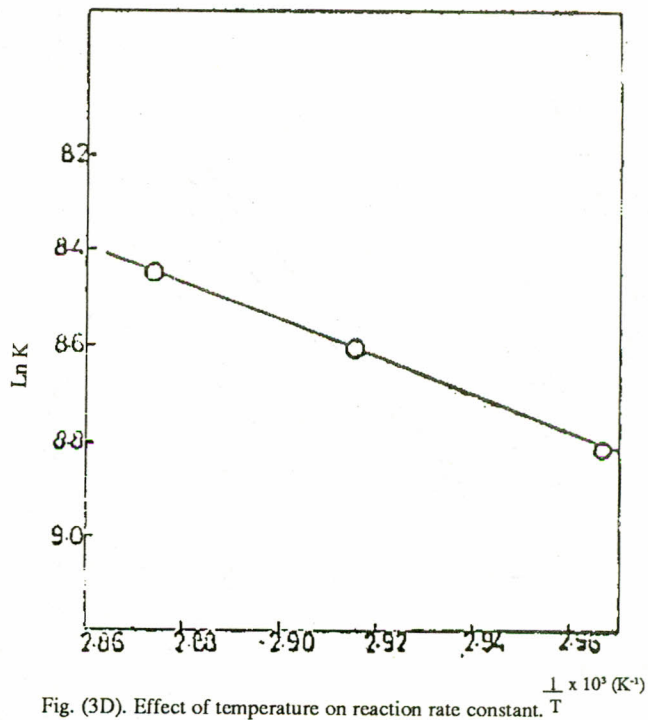


Fig. (3D). Effect of temperature on reaction rate constant.

Fig. 3. Esterification of propionic acid with propanol.

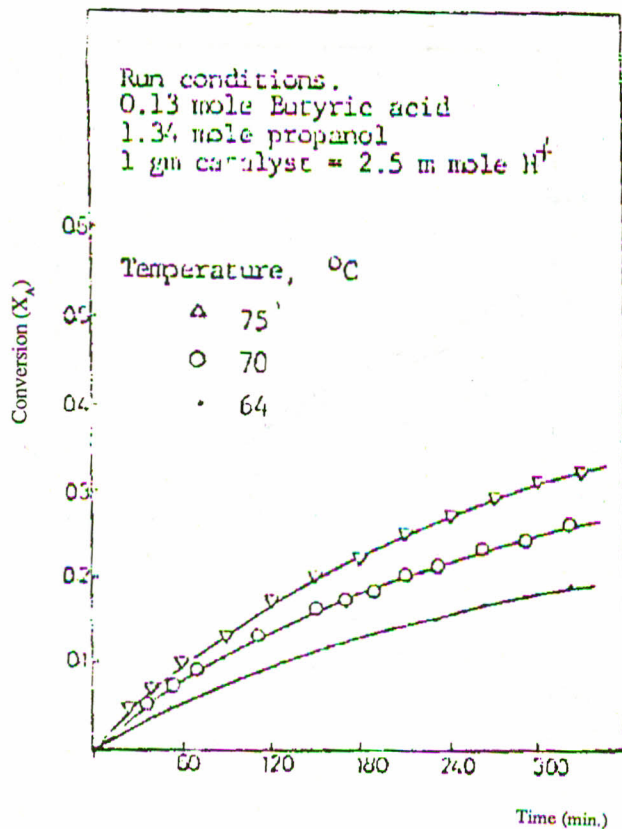


Fig. (4A). Effect of reaction temperature on the conversion of valeric acid.

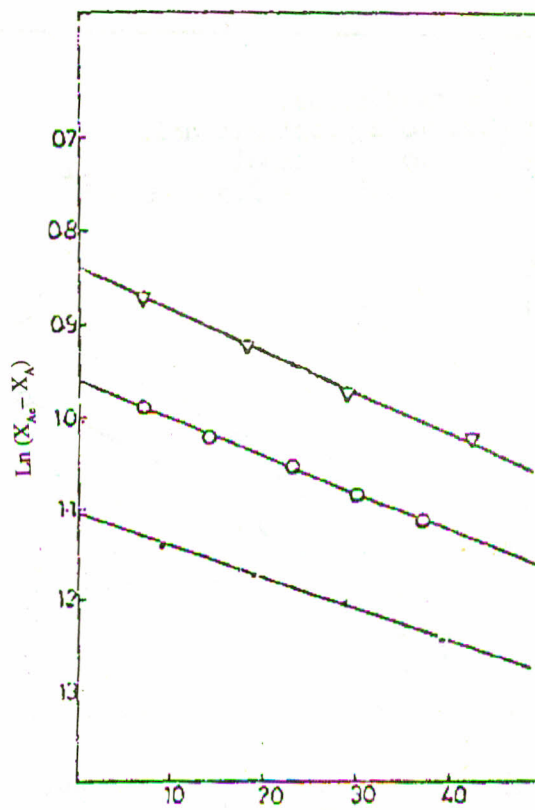


Fig. (4C). Determination of X_{Ae} .

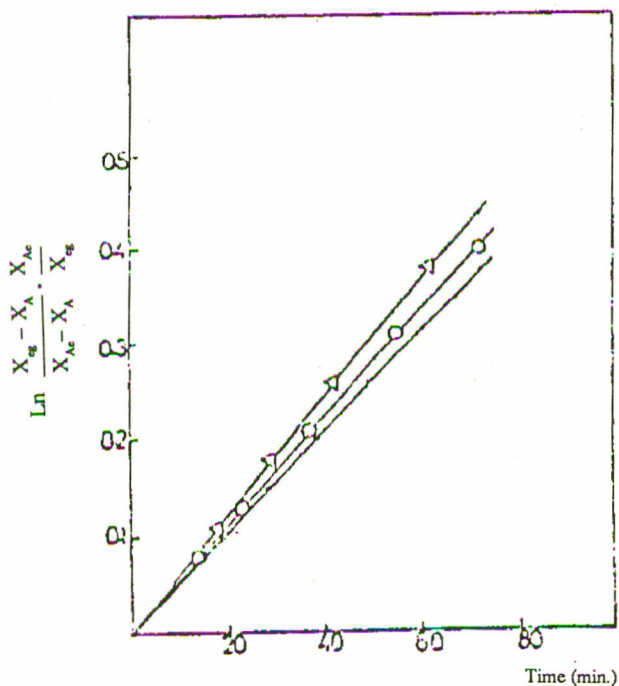


Fig. (4B). Linear transformation.

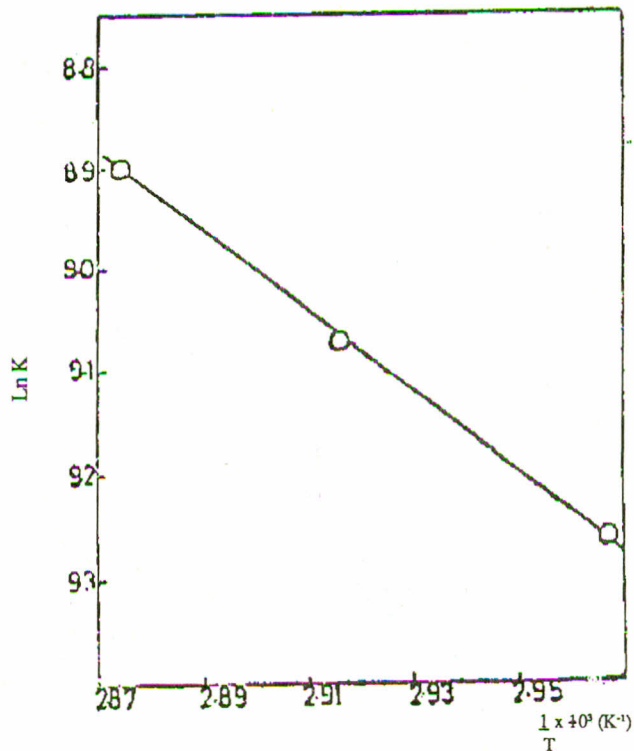


Fig. (4D). Effect of temperature on reaction rate constant.

Fig. 4. Esterification of butyric acid with propanol.

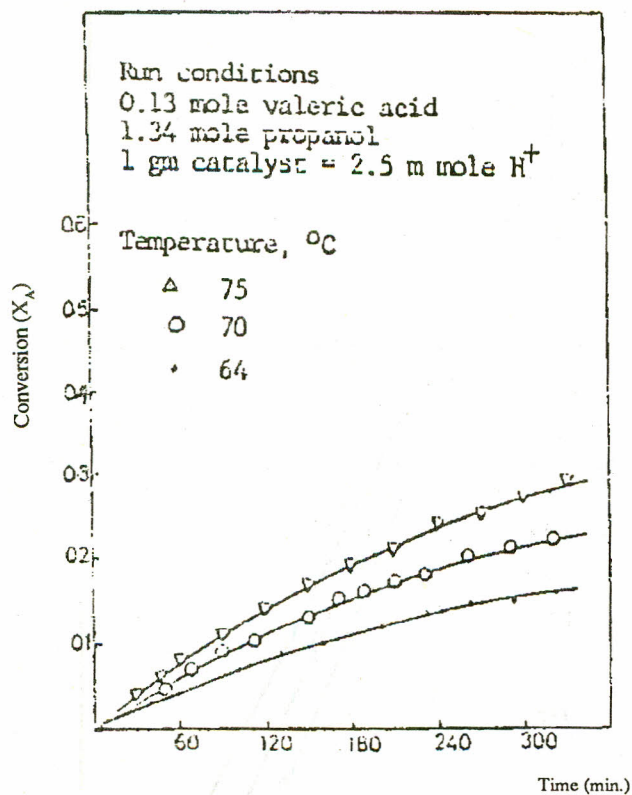


Fig. (5A). Effect of reaction temperature on the conversion of butyric acid.

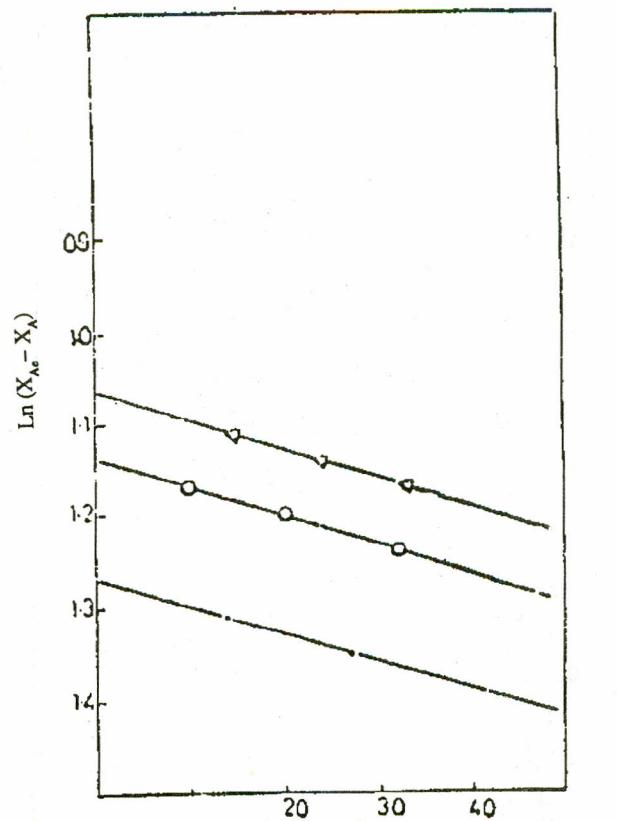


Fig. (5C). Determination of X_{Ae}.

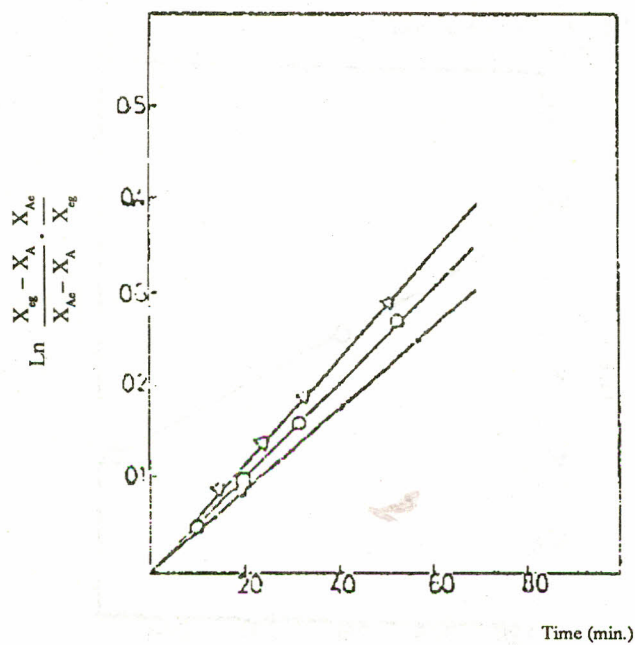


Fig. (5B). Linear transformation.

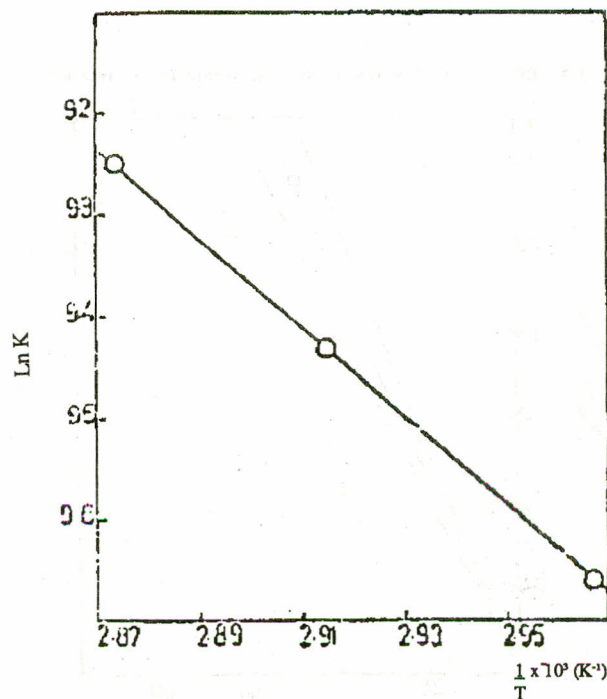


Fig. (5D). Effect of temperature on reaction rate constant.

Fig. 5. Esterification of valeric acid with propanol.

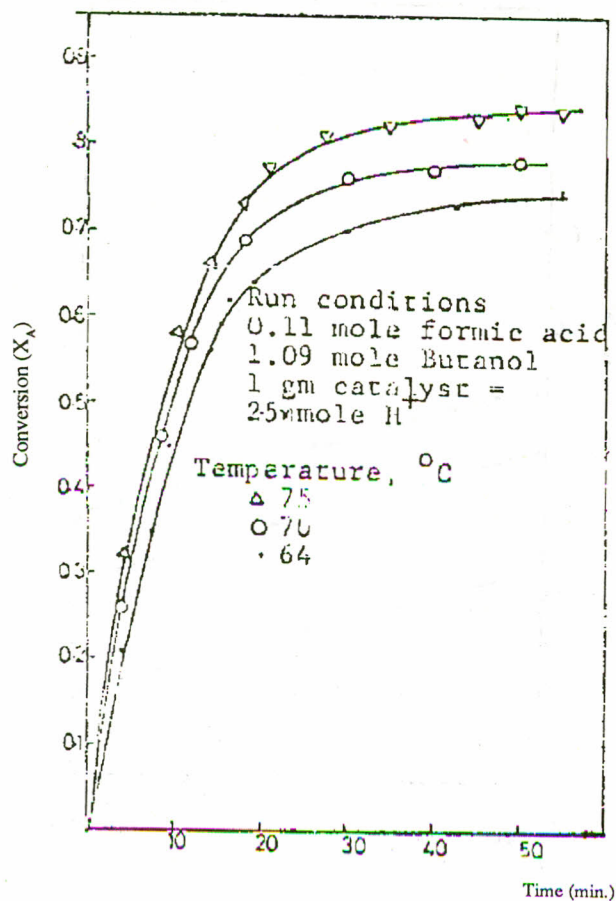


Fig. (6A). Effect of reaction temperature on formic acid conversion.

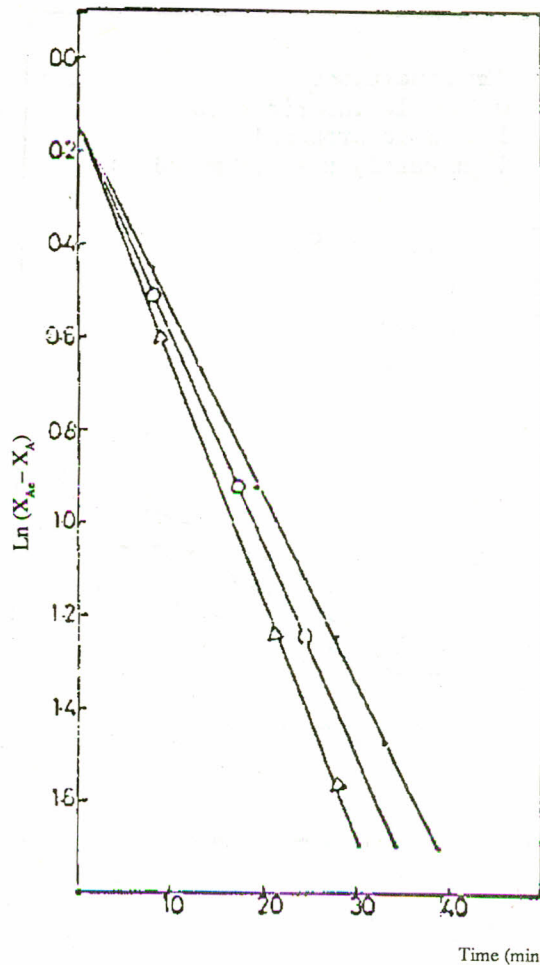


Fig. (6C). Determination of X_{Ae} .

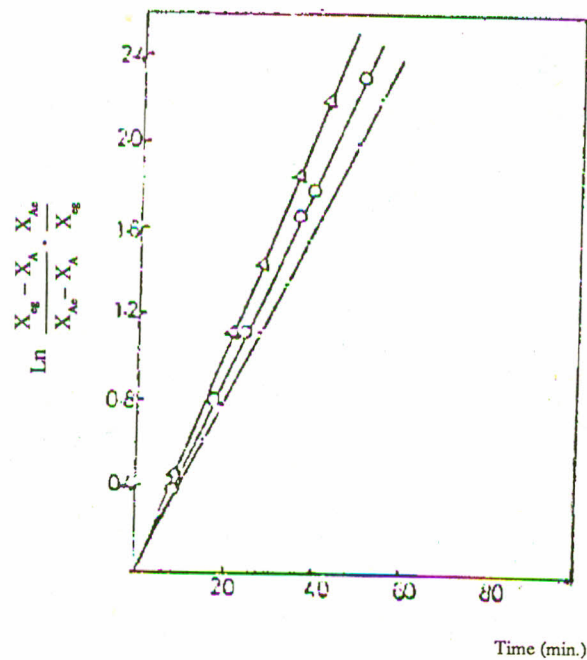


Fig. (6B). Linear transformation.

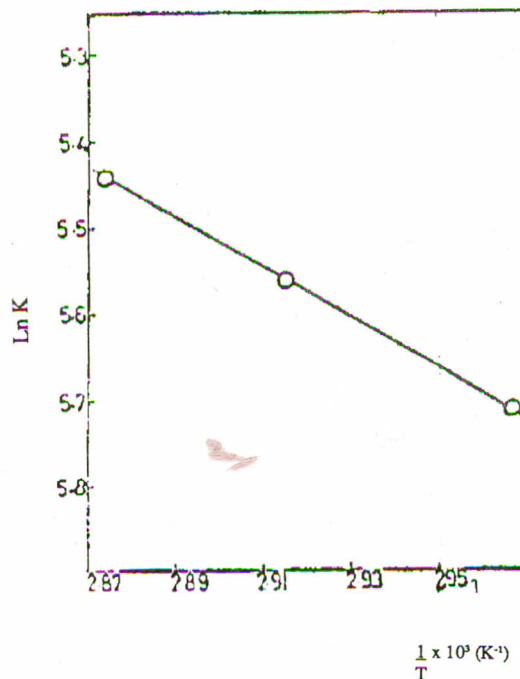


Fig. (6D). Effect of temperature on reaction rate constant.

Fig. 6. Esterification of formic acid with butanol.

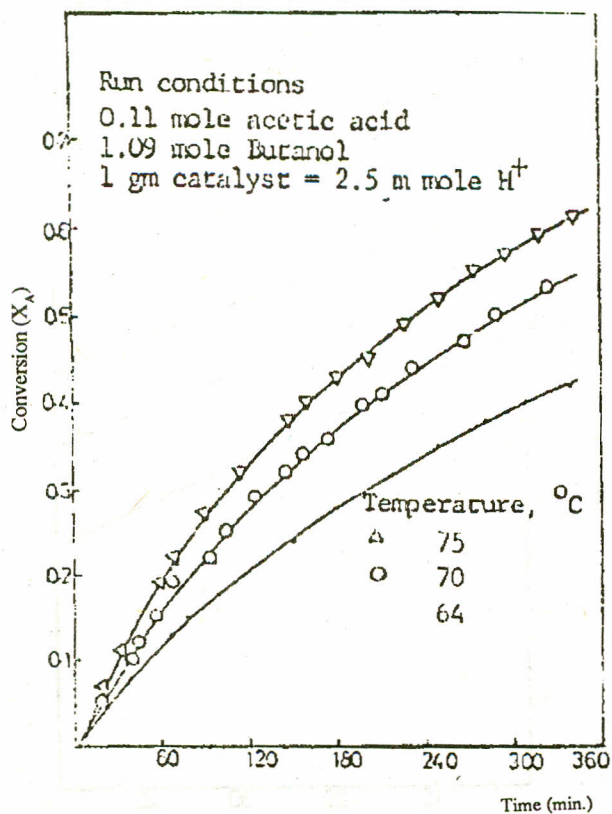


Fig. (7A). Effect of reaction temperature on the conversion of acetic acid.

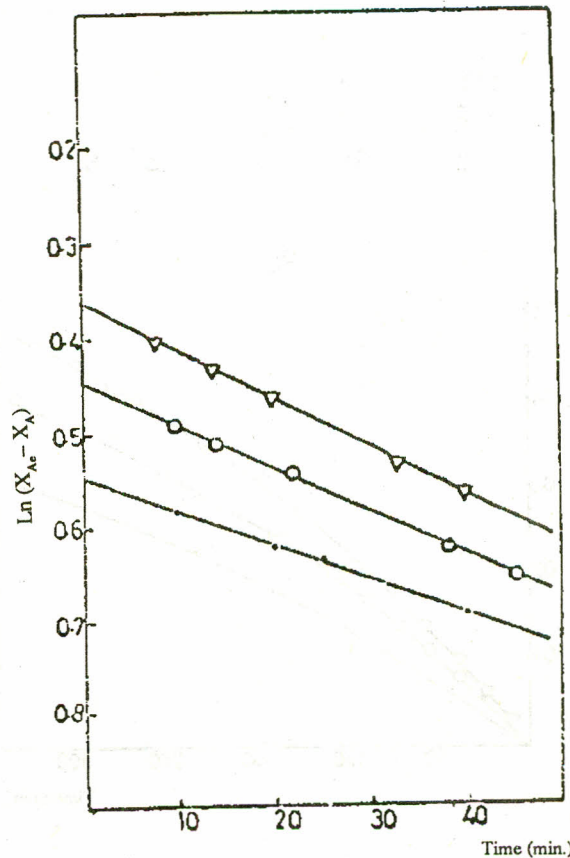


Fig. (7C). Determination of X_{Ae}.

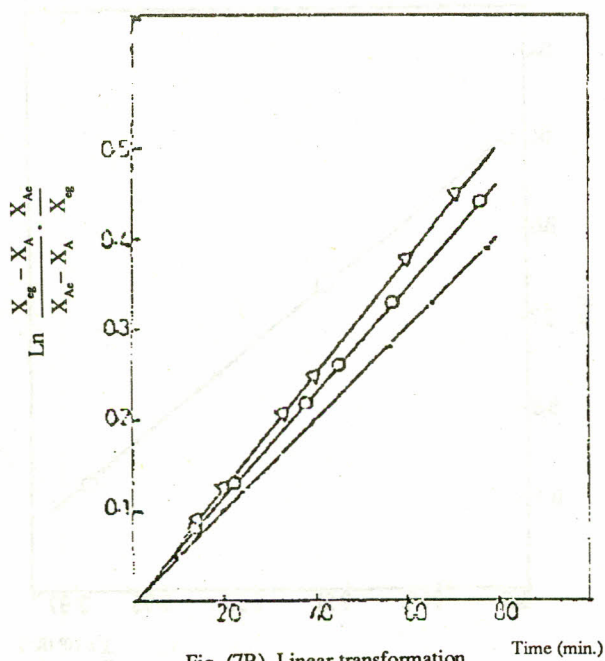


Fig. (7B). Linear transformation.

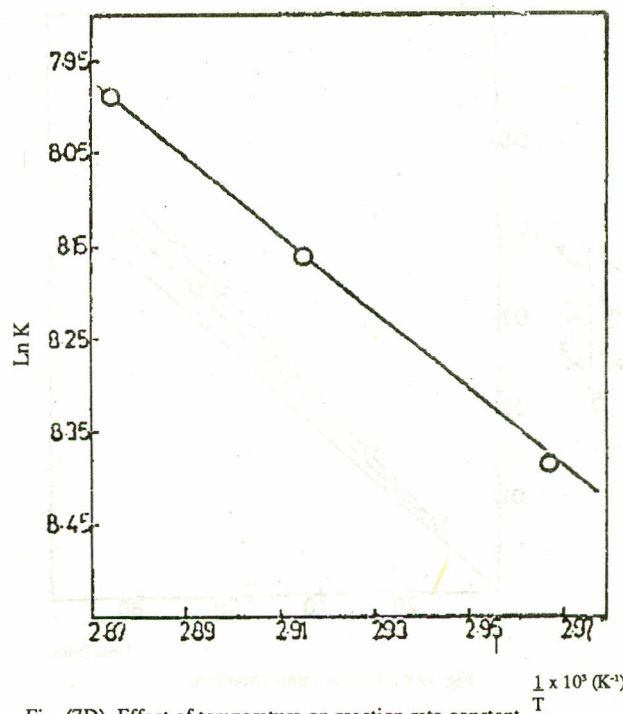


Fig. (7D). Effect of temperature on reaction rate constant.

Fig. 7. Esterification of acetic acid with butanol.

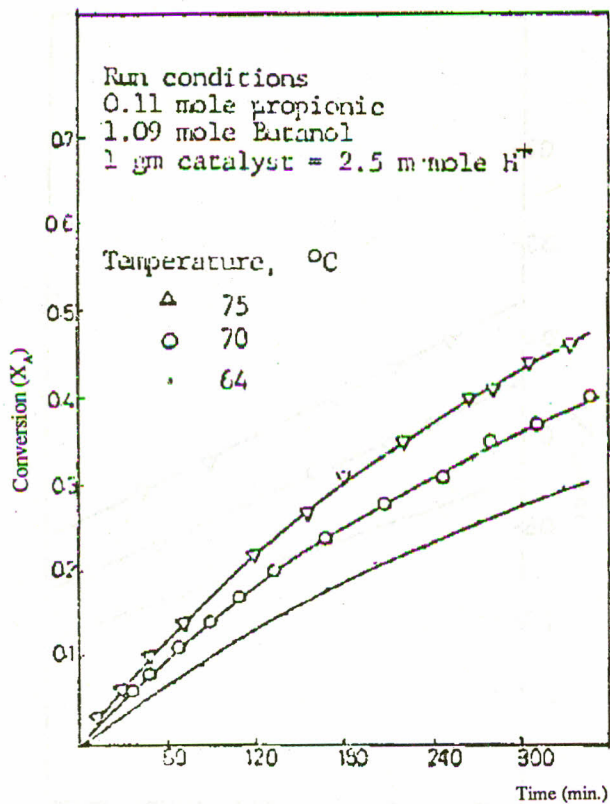


Fig. (8A). Effect of reaction temperature on the conversion of propionic acid.

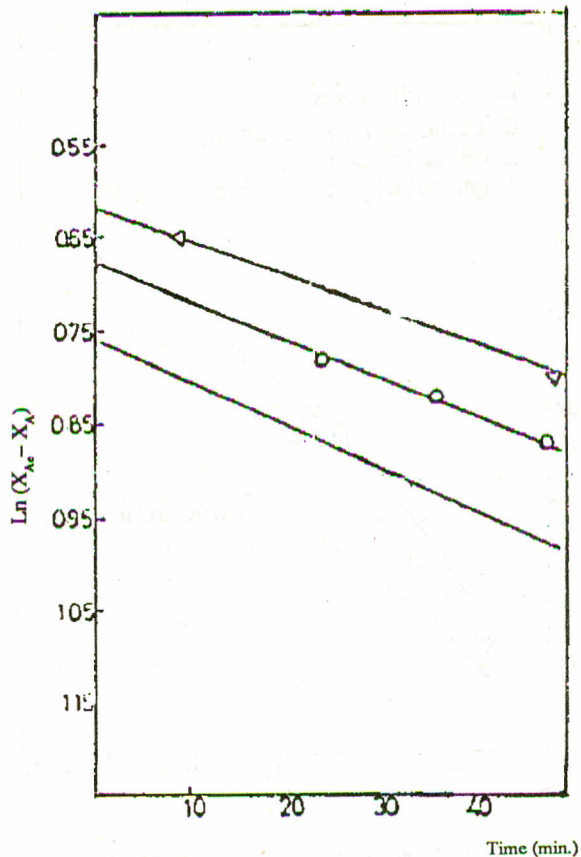


Fig. (8C). Determination of X_{Ae}.

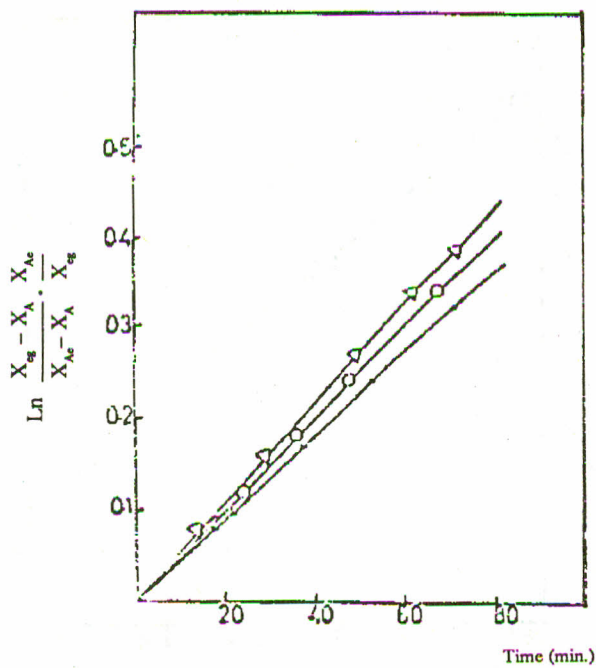


Fig. (8B). Linear transformation.

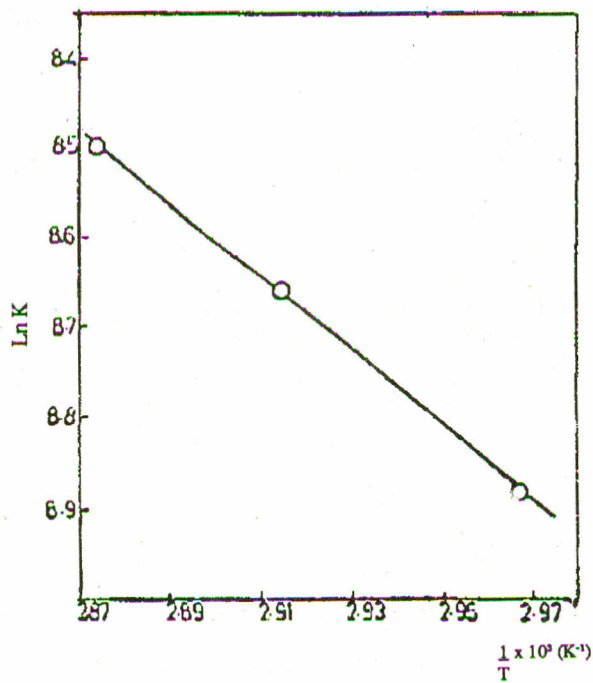


Fig. (8D). Effect of temperature on reaction rate constant.

Fig. 8. Esterification of propionic acid with butanol.

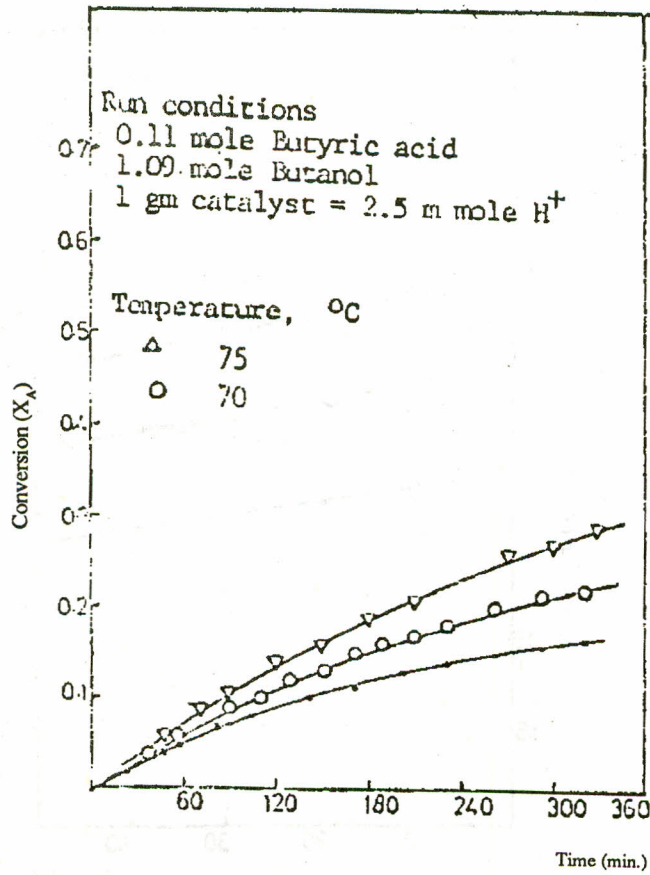


Fig. (9A). Effect of reaction temperature on the conversion of butyric acid.

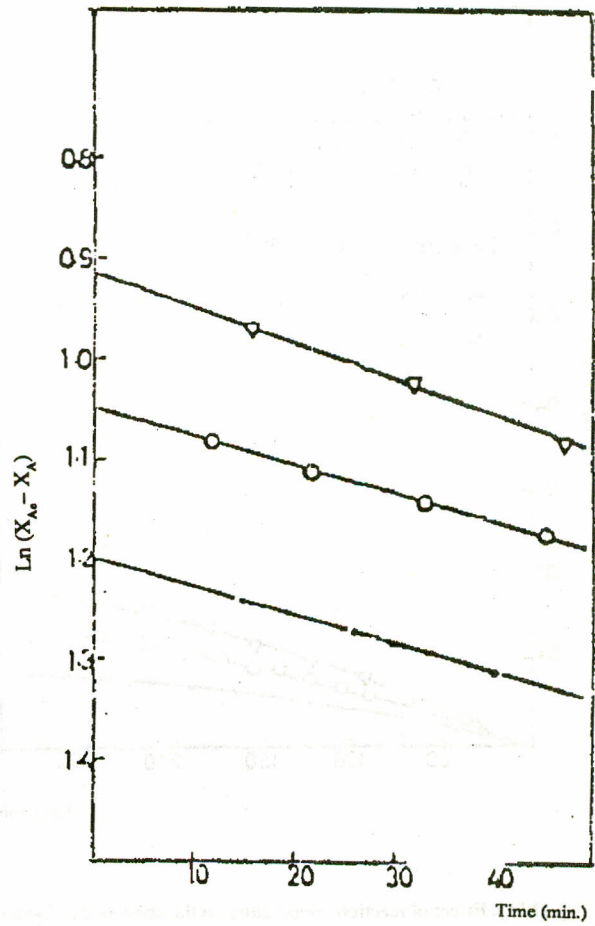


Fig. (9C). Determination of X_{Ae} .

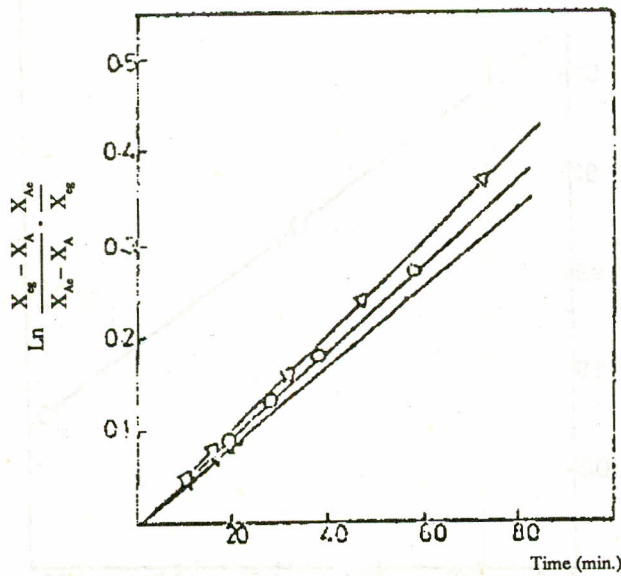


Fig. (9B). Linear transformation.

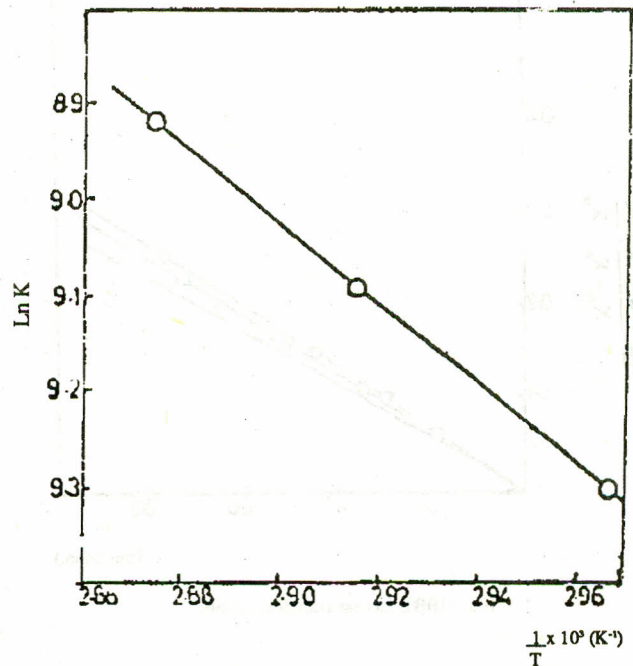


Fig. (9D). Effect of temperature on reaction rate constant.

Fig. 9. Esterification of butyric acid with butanol.

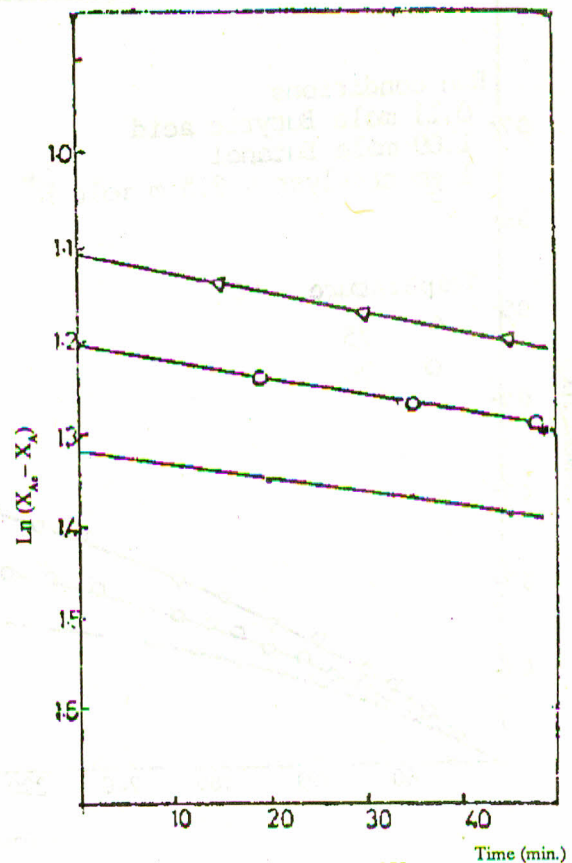
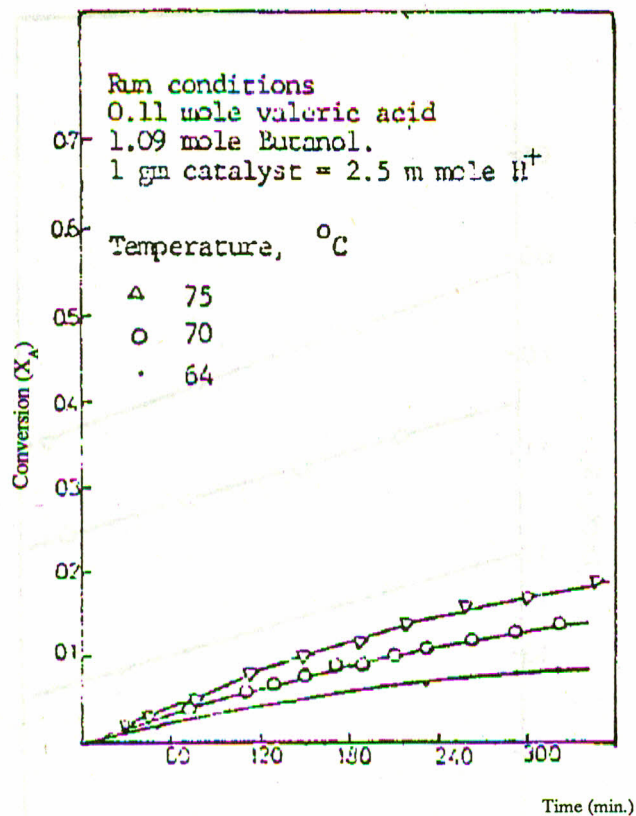


Fig. (10C). Determination of X_{Ae}.

Fig. (10A). Effect of reaction temperature on the conversion of valeric acid.

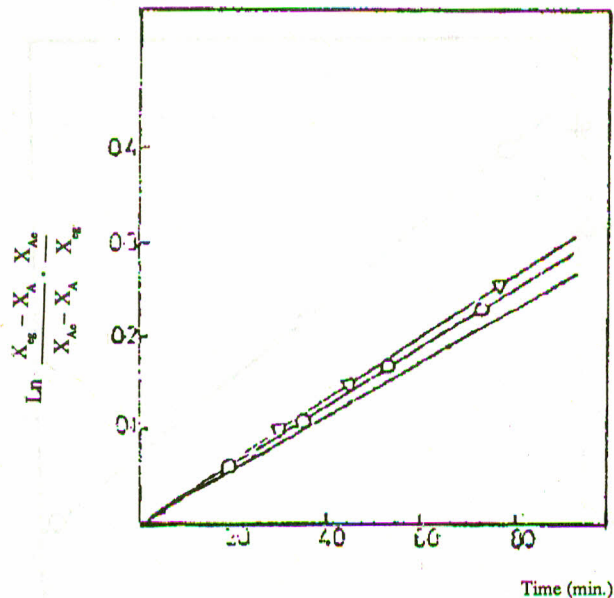


Fig. (10B). Linear transformation.

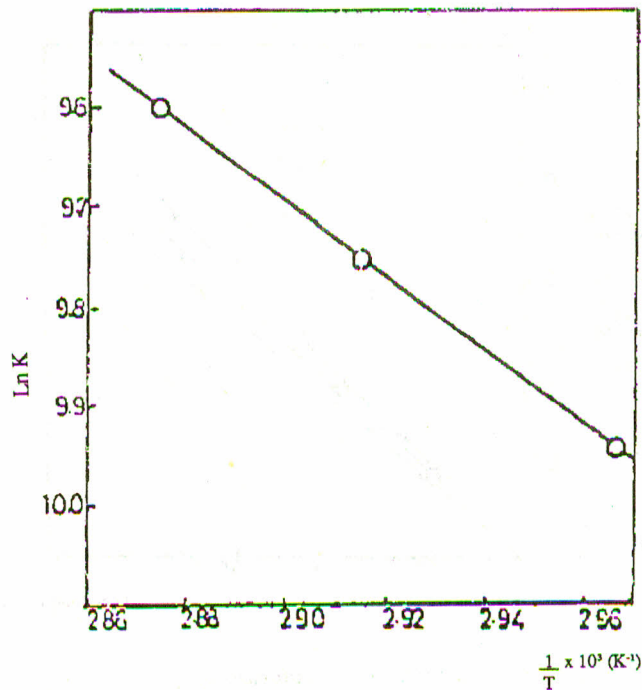


Fig. (10D). Effect of temperature on reaction rate constant.

Fig. 10. Esterification of valeric acid with butanol.

value of activation energy of monochloroacetic acid (MCA). This means that MCA is more reactive than DCA, although it has a low dissociation constant. It is probable that MCA may produce HCl during the esterification reaction and causes a promoting effect on the catalyst process [5,8].

The plots of $\log Kr$ versus $1/T$ for the esterification of two alcohols with various carboxylic acids, (Figs 1-10/D) show that a linear relationship is obtained, indicating that the data follow Arrhenius plots. It is evident that E_a increases with increasing molecular weight of the acids and alcohols.

The activation energy (E_a) obtained by the data obtained on the kinetics of esterification of propionic acid with methanol and ethanol are presented in Table 3. It can be noticed from Table 3 all the studied alcohols were controlled by the chemical reaction inside the particle size of the catalyst. This means that the sorption equilibrium of the reacting species between the catalyst and solution phases is rapidly established and is maintained throughout the process. If the reactant molecules are of larger molecular weight, slow inter particle diffusion may reduce the over all rate and consequently have a slow mobility in the matrix.

It is noticed from Table 3 that the esterification of propionic acid with methanol or ethanol are identical for catalyst forms of five metal amines. It can be concluded that the most active form of the catalyst is the one giving higher acid conversion i.e., the hydrogen form catalyst, indicating that it has the greatest density of acid sites. (Ni (II) amine form gives the lowest rate of conversion. Other amines follow the order Zn (II) amine, Cu (II), amine and Cd (II) amine. This sequence correlates well with the order of decreasing their sorption capacities in various ionic forms.

TABLE 3. REACTION VELOCITY CONSTANTS FOR THE ESTERIFICATION OF METHANOL AND ETHANOL WITH PROPIONIC ACID USING CATALYST IN DIFFERENT IONIC FORMS (1 gm) AND MOLAR RATIO OF ALCOHOL : ACID, 10 : 1.

Esterification reaction	X_{Ac}	T, °C	Catalyst in different ionic forms	$K \times 10^{-4}$ (dm ⁻³ mol ⁻¹ S ⁻¹)
Propionic acid with methanol	0.75	62	H ⁺	4.01573
	0.74	62	Zn (II) -amine	3.62768
	0.72	62	Cu (II) -amine	3.42615
	0.70	62	Cd(II) -amine	3.08353
	0.69	62	Ni (II) -amine	2.80321
Propionic acid with ethanol	0.72	75	H ⁺	2.93338
	0.70	75	Zn (II) -amine	2.64004
	0.68	75	Cu (II) -amine	2.47504
	0.66	75	Cd (II) -amine	2.20003
	0.64	75	Ni (II) -amine	1.98003

Calculation of activation parameters. The activation energy E_a was determined from Arrhenius plot. The change of enthalpy of activation ΔH^* was evaluated from the relation [11].

$$\Delta H^* = \frac{d \ln Kr}{dT} = -RT \quad \text{or} \quad \Delta H^* = E_a - 2RT$$

The change of free energy of activation ΔG^* was given from Eyring's equation [14].

$$\Delta G^* = -RT \ln k^{**} \quad \text{where} \quad k^{**} = hKr/TK$$

where Kr is the constant, K is Boltzmann constant, h is plank's constant. The change of entropy of activation ΔS^* is calculated using the relation.

$$Kr = K T/h e^{\Delta S^*/R}, \quad -e^{-E_a/RT}$$

The values of E_a for the catalyzed esterification of acids with alcohols is found to be in the range of 5-10 Kcal/mol [12].

The value of ΔG^* ranged between 23 and 26 K cal/mol which is very common in connection with the catalyzed reaction in solutions in the presence of a catalyst. It is also noticed that ΔH^* changes in accordance with the variation of ΔS^* .

Evaluation of the rate data. Sharma *et al.* [1] deduced the following relation:

$$\ln \frac{X_{cg} - X_A}{X_{Ac} - X_A} \frac{X_{Ac}}{X_{cg}} = \frac{2B - (B+1) X_{Ac} C_{Ao} X Kr t}{X_{Ac}}$$

where X_{cg} is a constant given by

$$X_{cg} = \frac{B \times X_{Ac}}{(B+1) X_{Ac}} - B$$

The values of Kr are obtained by plotting

$$\ln \frac{X_{cg} - X_A}{X_{Ac} - X_A} \frac{X_{Ac}}{X_{cg}}$$

versus time t Figs (1-10/B)

The values of X_{Ac} (fractional conversion at equilibrium) is obtained either experimentally when equilibrium is attained or by fitting the experimental data in the equation.

$$X_A = X_{Ac} (1 - e^{kt})$$

The value of X_{Ac} is assumed and then $\log (X_{Ac} - X_A)$ is plotted against time t , where a linear transformation is obtained. The correct value of X_{Ac} (Figs. 1-10/C) is obtained when the assumed value agrees with that obtained experimentally. Kr values were calculated theoretically according to the relation

$$Kr = B/W \text{ m. equiv. } e^{-E_a/RT}$$

assuming that W and B have no effect on the activation energy [1,7].

Nomenclature:

- B = Initial molar ratio of alcohol to acid,
 C_A = concentration of acids in bulk, gm mol/L
 k, K^* = reaction velocity constant litre gm/mole sec.,
 t = time, sec.,
 T = temperature, °K,
 W = gm catalyst/100 gm reactants.
 X_A = fractional conversion of acid,
 X_{Ac} = fractional conversion of acid at equilibrium,
 X_{eg} = constant,
 H^* = enthalpy change, cal/gm mole,
 G^* = free energy change, cal/gm mole,
 S^* = entropy change, cal/gm mole,

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