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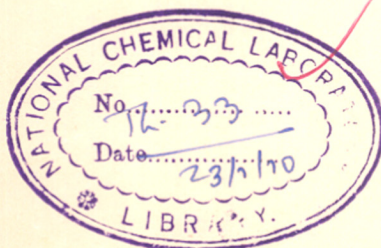
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CATALYSIS BY ION EXCHANGE RESINS

COMPUTERISED

A thesis submitted to
University of Bombay

for the degree of
DOCTOR OF PHILOSOPHY

in
Physical Chemistry



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by
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May 1969

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S.H.BAKSHI

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May 1969

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CHAPTER - I

INTRODUCTION

INTRODUCTION

Ion-Exchange Materials

Ion-exchange materials consisting of a crosslinked polymeric skeleton, are insoluble in water and all organic solvents. This polymer skeleton serves as a carrier for ion-exchange groups and the activity of the resins depends upon the number of exchange groups per structural unit.

These polymeric materials carry an electrostatic charge which is exactly nullified by the charges on the labile ions. These ions are cations in cation-exchange resins and anions in anion-exchange resins.

Presence of carboxylic, phenolic, sulfonic, phosphonic groups result in cation-exchange resins, while amino, substituted amino, quaternary ammonium groups result in anion-exchange resins.

Ion-exchange materials are mainly of two types : inorganic and organic. Inorganic ion-exchange materials comprise mainly of natural products and some synthetic ones. Organic exchangers are essentially synthetic resins.

Inorganic exchangers:

Way^{1,2} and Thompson³ reported the phenomenon of cation-exchange in soil nearly 100 years ago and they

established that the exchange of cations in the soil was due to aluminium silicates. In general, the mineral substances were of no practical value as ion exchangers but the substance named as glauconite having the empirical formula $K(Fe,Al)Si_2O_6$ was used in large quantities for many years for water softening. Minerals like ultramarine, apophyllite natrolite, beidellite, montmorillonite, prophyllite also exhibit cation-exchange properties. However, one mineral, spatite, a calcium phosphate of the formula $3Ca_3(PO_4)_2Ca(F,Cl)_2$ has the property of exchanging anions.

In 1907, Gens⁴ succeeded in synthesizing an inorganic ion exchanger by fusing alumina, quartz and soda ash. This product had a low ion-exchange value but it was insoluble in water. But this fusion process was later superseded by the precipitation^{5,6} and gelation methods.⁷⁻¹¹ By this method sodium aluminium silicate was prepared by mixing sodium silicate and aluminium sulphate or sodium aluminate in order to obtain it in a gel form or as a precipitate. The product obtained was further processed to get the desired particle size. Composition of this synthetic ion exchanger viz. Na_2O , Al_2O_3 , $6SiO_2 \cdot 6H_2O$ resembled closely that of the natural zeolites.

Organic ion exchangers:

In 1934, it was discovered¹²⁻¹⁷ that certain coals exhibit cation-exchange properties after treatment with hot sulphuric acid or with sulphur trioxide and fuming sulphuric acid. These substances were quite stable with acids and

alkalies. Cation-exchange properties of these substances were mainly due to sulfonic groups, but these exchangers also exhibited the exchange properties due to carboxylic groups at high pH values.

Later Adams and Holmes¹⁸ tried to synthesize insoluble organic cation and an ion exchanger by condensing polyhydric phenols with formaldehyde and by condensing polyamines and formaldehyde respectively. The cation and anion-exchange resins thus obtained had low exchange capacities and were active only at particular pH values.

Cation-exchange resins¹⁹ of higher capacity were later synthesized by condensing phenol sulfonic acid or phenol methylene sulfonic acid with formaldehyde and these resins were found to be more stable than sulphonated coal.

Anion-exchange resins obtained either from aromatic or aliphatic amines were only effective during their contact with strong acids.

A cation-exchange resin²⁰ containing carboxyl groups was then prepared by condensing 1 : 3 : 5 resorcylic acid, phenol and resorcinol with formaldehyde.

But the capacities of the cation-exchange resins obtained by the condensation of phenolic derivatives and formaldehyde were limited by the fact that a proportion of unsubstituted phenol must be included to yield the crosslinks. Attempts

were later made to synthesize the resin with higher capacities by condensing benzaldehyde disulfonic acid with resorcinol and conversion of this product to resin by reaction with formaldehyde. This was the basis of German Wofatit KS & K resins.^{20,21}

In all these resins it can be easily seen that the exchange group was already present in one of the substances taking part in the reaction and the process was only conversion of that substance to a solid resin by condensation with formaldehyde. But the resins thus prepared had a limited chemical stability.

These types of resins²² are now prepared by first condensing phenols with formaldehyde to get a crosslinked resin, which are further sulfonated to get the desired product.

A notable advance in the manufacture of ion-exchange resins occurred in 1942 when D'Alelio^{23,24} prepared a cross-linked polystyrene resin and then attached sulfonic groups to the skeleton by treating it with fuming sulfuric acid or chlorosulfonic acid. The crosslinking agent used was divinyl benzene and the product possessed a higher concentration of sulfonic groups, and hence a higher ion-exchange capacity than any resin made hitherto. This cation-exchange resin contains one sulfonic group per benzene ring, and the exchange capacity was found to be 4.7 to 5.0 meqs/gm of dry resin. The best of the phenol sulfonic acid resin contains approximately five sulfonic groups in every twelve benzene

rings and the capacity is about 2.5 meq/gm. These styrene divinyl benzene based unfunctional resins contain only sulfonic groups and due to absence of phenolic hydroxyl group they are very stable to high temperatures and to higher concentrations of acids and alkalis. The styrene divinyl benzene copolymer is prepared by suspension polymerization and these resins are available in bead form.

A unfunctional carboxylic resin²⁵ was prepared by copolymerising methacrylic acid with a crosslinking agent like divinyl benzene. Styrene divinyl benzene resins containing $-PO(OH)_2$ and $-CH_2PO(OH)_2$ groups are also available.

D'Alelio later proposed the synthesis of anion-exchange resin^{27,28} by nitration of styrene divinyl benzene copolymer and then reduction of nitro groups to amino groups. But now the basic groups have been successfully introduced in the styrene divinyl benzene copolymer by first chloromethylating²⁹⁻³¹ it and then treating with tertiary amines resulting in strongly basic resins.^{32,33} Treatment of primary and secondary amines to the chloromethylated styrene divinyl benzene copolymer results in a weakly basic resin.^{34,35} Development in ion-exchange resins was later followed by the synthesis of selective or specific resins,³⁶⁻⁴⁰ redox resins,⁴¹⁻⁵⁰ resins for the separation of optical isomers⁵¹⁻⁵³ and resins for catalytic purposes.⁵⁴⁻⁵⁷

Applications

Natural and synthetic alumino silicates were first used for softening of water in the beginning of twentieth century

and it was only a short time later that these materials were found to be good catalysts. Catalytic activity of these silicate exchangers resulted from their acidic nature and also due to the presence in them of manganese, iron, chromium and tin.

Zeolites⁵⁸⁻⁶¹ have been used in the oxidation of sulphur dioxide, benzene, toluene, phenol, naphthalene, anthracene, alcohols, also for synthesis of ammonia and reduction of nitrobenzene to aniline. It is also reported that many organic compounds like naphthalene can be hydrogenated by catalysts consisting of a metal such as copper, nickel, platinum on a zeolite carrier. Seldon Company⁶² succeeded in the reduction of carbonyl compounds using 'inorganic zeolite exchangers'. In the thermal cracking of hydrocarbons over alumina-silica zeolites, a hydrogen ion associated with the tetrahedral aluminium in the catalyst was found to be responsible for the catalytic activity.⁶³⁻⁶⁶

Sachanen and O'Kelly⁶⁷ reported that benzene or toluene can be successfully alkylated using activated clays. Activated clays have also been found to be the best catalysts for alkylation of phenols and naphthalene with alcohols, ethers or olefins.⁶⁸ Synthesis of hexamethyl benzene from phenol and methanol using activated alumina catalyst is also reported.⁶⁹

Ion-exchange resins are used as catalysts for many organic or inorganic chemical reactions. This is true of gases, liquids and solutes. Reactions of liquids and solutes catalysed by ion-exchange resins are dependent on catalytic

activity of the counter ions and hence catalysis by ion-exchange resins⁷⁰ is considered to be analogous to homogeneous phase catalysis by dissolved electrolytes. Ion-exchange properties therefore influence to a large extent the catalytic activity of the ion-exchange resin.

In the heterogeneous catalysis of the reactions of gases with ion exchangers, the reaction occurs at the external and the internal surface of the catalyst and the reactants get activated by adsorption.⁷⁰ Reactions such as cracking of hydrocarbons and hydration of olefins have been accomplished over zeolite resin. The reaction mechanism suggested by different workers involves the formation of carbonium ions as reaction intermediates.^{63,71} Stepwise reaction mechanism for cracking of isobutylene over zeolites⁶³ is reported as follows:-

The chain termination is effected by

Regeneration of the catalyst occurs with step No.4.

The reaction mechanism for the hydration of olefins⁷¹ is explained as follows

Both the mechanisms mentioned above involve proton transfer from the catalyst, which should be acidic to the reactants.

Larger surface of the catalyst always helps to increase the rate of reaction. Crystalline zeolite exchangers are therefore used as catalysts for gas reactions due to their porous structure. But the conventional gel type ion-exchange resins cannot be used since the polymeric matrix contracts and closes the pores if they are not in contact with the solvent. However the latest macroreticular resins are porous and hence can be utilised.

Catalytically active species in large number of reactions of liquids and solutes are H^+ and OH^- ions. It has been found that an ion-exchange material which contains the catalytically active ion as the counter ion can replace dissolved electrolytes. The reaction occurs in the pores of the ion-exchange resin where the active species are available. The pores of ion exchangers which are in contact with the reaction mixture contain solvent, solutes and counter ions. Like homogeneous solutions, the counter ions are mobile and solvated. Hence the counter ions which are catalytically active in homogeneous solutions are equally active in the pores of the resin. Hence the mechanism of heterogeneous catalysis by the resins is similar to that of homogeneous catalysis by dissolved electrolytes.⁷⁰ This is also confirmed from the same values of order of reactions and activation energies obtained in both the cases. Catalysis of liquid phase reaction by ion-exchange resins is therefore considered to be a homogeneous catalysis in the pore liquid.

The use of solid ion exchangers has the following advantages over homogeneous catalysis by dissolved electrolytes:-

- 1) a continuous process in columns is possible
- 2) in batch operations the catalyst can be readily removed from the reaction products either by decantation or filtration.
- 3) it is possible to isolate the reaction intermediates which cannot be obtained in homogeneous catalysis
- 4) ion-exchange resins can discriminate between small, and large molecules. The greater selectivity of the ion exchanger catalyst will be advantageous.
- 5) purity of the products is superior since side reactions can be completely eliminated or are less significant.

Organic ion-exchange resins are preferred to inorganic ion exchangers as catalysts for liquid phase reactions. The resins are superior to the inorganic ion exchangers because of the higher mobilities of the reactants and products in the pores of the catalysts. So also the organic ion-exchange resins are more stable towards acids. However inorganic exchangers can withstand higher temperatures of operation while organic exchangers will be affected at higher temperatures.

The following table summarises some of the numerous reactions studied using organic ion-exchange resins.

Reactions catalysed by cation-exchange resins

Reaction type	Reactants	Resin form	Reference
Ester hydrolysis	Methyl acetate	- SO ₃ H	72, 73
	Butyl acetate	- SO ₃ H	72
	Ethyl acetate	- SO ₃ H	72-75
	Ethyl n-butyrate	- SO ₃ H	75
	Ethyl n-caproate	- SO ₃ H	75
Hydrolysis	Cellulose	- SO ₃ H	76
	Amides	- SO ₃ H	77, 78
	Dinitrophenyl gelatine	- SO ₃ H	79
	Proteins	- SO ₃ H	80-82
	Carbohydrates	- SO ₃ H	83
Inversion	Sucrose	- SO ₃ H	84-89, 97
Acetal formation	n-butyl alcohol and paraformaldehyde	- SO ₃ H	90
	Glycerol and paraformaldehyde	- SO ₃ H	90
	Methyl alcohol and methyl acrolein	- SO ₃ H	92
	Benzaldehyde and n-butyl-, n-hexyl-, and n-heptyl alcohols	- SO ₃ H	92
	Ethylene glycol and paraformaldehyde	- SO ₃ H	93

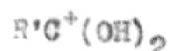
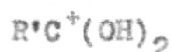
Reaction type	Reactants	Resin form	Reference
Acetal formation (Contd)	Furfural and n-heptyl alcohol	- SO ₃ H	94
	Pentaerythritol and carbonyl compounds	- SO ₃ H	95
Condensation	Phenol and allyl alcohol and propionaldehyde	- SO ₃ H	96
Polymerization	Styrene and other unsaturated hydrocarbons	- SO ₃ H	98, 104
Dehydration	Alcohols (Cyclic)	- SO ₃ H	99, 100
	Chlorotetracycline	- SO ₃ H	101
Hydration	Isoolefins	- SO ₃ H	102, 103
	Tertiary amylenes	- SO ₃ H	105
	Acetylenes	- SO ₃ H	106, 108
Rearrangements	Hydrazobenzene	- SO ₃ H	107
Epoxidation	Olefinic compounds	- SO ₃ H	109
Alkylation	Phenol ethers	- SO ₃ H	110
	Phenol	- SO ₃ H	111-113
	Alkyl benzenes	- SO ₃ H	114
	Para-cresol	- SO ₃ H	115
Decomposition	Cumene hydroperoxide	- SO ₃ H	116
Bisphenol A synthesis	Phenol and acetone	- SO ₃ H	117

Reaction catalysed by anion-exchange resins

Reaction type	Reactants	Resin form	Reference
Hydrolysis	Ethyl acetate	Weak base	118
Aldol condensation	Ketones and aldehydes	Weak base and strong base	119, 120
Knoevenagel	Various aldehydes and ketone	Strong and weak base	119, 121
Condensation cyanoethylation	Various alcohols) and acrylonitrile)	Strong base	122-124
Preparation of ethylene	1-2 dibromoethane) and 1-2 dichloro-) ethane)	Strong base	125

Esterification with ion-exchange resins:

Esterification reactions catalysed by ion-exchange resins have received a great deal of attention. Esters are generally prepared by the action of an alcohol on an organic acid, in presence of a strong mineral acid. But hydrogen form cation ion-exchange resins are found to be equally efficient catalysts as compared to the mineral acids. The reaction mechanism for the esterification reactions catalysed with ion-exchange resins can be explained as follows:

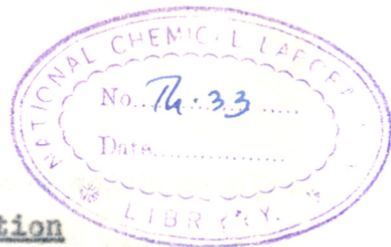


Literature survey shows that various investigators have studied different esterification reactions in presence of different catalysts. A list of esterification reactions catalysed by ion-exchange resins is given below.

Esterification reactions catalysed by ion-exchange resins

Reaction	Resin used	Reference
1. Ethyl alcohol and acetic acid	Sulphonated styrene - divinyl benzene copolymer	126-129, 141
2. Butyl alcohol and acetic acid	Sulphonated phenolic (Dowex 30)	133
	Polymeric carboxylic, phosphonic	131
	Silicone based WoFatit SiAs 20	134
	Sulphonated coal	130
	Sulphonated styrene - divinyl benzene copolymer	131-133
3. Butyl alcohol and oleic acid	Sulphonated coal, sulphonated phenolic resin	135, 136
	Sulphonated styrene - divinyl benzene copolymer	137
4. Ethyl alcohol and cyanoacetic acid	Sulphonated phenolic resin	100
5. Lauric acid and diethylene glycol	Sulphonated polystyrene resin	138
6. (Ethyl laurate) from coconut oil and ethyl alcohol.	Sulphonated polystyrene resin	139
7. 2-butane and acetic acid	Phenol-formaldehyde resin with a methylene sulfonic group	140
	Sulphonated styrene-divinyl benzene copolymer with macroreticular structure	148

Reaction	Resin used	Reference
8. Maleic anhydride with various glycols	Sulphonated styrene - divinyl benzene copolymer	142
9. Ethyl alcohol and chloroacetic acid	Zeokarb H (Sulphonated coal)	135
10. Allyl alcohol and phthalic anhydride	Sulfonated phenolic resin	143
11. Butyl alcohol and phthalic anhydride	Amberlite IR 120, Dowex 30, sulfonated coal.	133, 144
12. Adipic acid with n-butyl, n-hexyl and n-octyl alcohol	Amberlite IR 120, Dowex 30 Sulfocarbon N.S. Sulfocarbon L	133
13. Phthalic anhydride and ethyl alcohol	Amberlite IR 120, Dowex 30 Sulfonated coal	133
14. Allyl alcohol with acetic acid	Amberlite IR 120	145
15. Pentaerythritol and 5-9 fatty acid	KU 2 sulfonated styrene DVB copolymer	146
16. Disproportionated rosin, prehydrogenated rosin, dihydro-abietic acid and lauric acid with pentaerythritol and lauryl alcohol.	Metallic resinates	147
17. Methyl and ethyl alcohol with chloroacetic, tartaric, adipic, maleic acid.	Sulphonated phenolic resin	151
18. Methyl alcohol with salicylic acid	Sulphonated resin	149
19. Adipic acid with ethylene glycol.	Amberlite IR 120, IRC 50 Tulsion 14, Zeokarb 215	150



Scope of the present investigation

In the present investigation, detailed study of the efficacy of four cation-exchange resins as catalysts has been carried out. Though they are all cation exchangers, these resins have different physico chemical characteristics. The esterification reactions studied were

1. Butanol-oleic acid.
2. 2-Ethyl hexanol-phthalic anhydride
3. Adipic acid with ethylene, diethylene and propylene glycol
4. Sebacic acid with ethylene, diethylene and propylene glycol

Esterification reactions Nos. 1 and 2 are usually carried out in the presence of strong mineral acid. Esters formed in reactions No.1 and 2 are butyl oleate and di-octyl phthalate which are used as plasticizers for various elastomers. Hence for this use the plasticizer should be completely free of mineral acidity. For this reason, during the esterification of butanol-oleic acid and 2 ethyl hexanol-phthalic anhydride, the final product formed has to be washed free of acid. This washing process is time consuming and involves use of large volumes of wash water.

Reactions Nos. 3 and 4 are usually carried out above 200°C and that too under reduced pressure to remove the

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water formed during the reaction. Substances which catalyse simple esterifications (reactions Nos. 1 & 2) catalyse polyesterification reactions as well.

In general, acidic substances are used in most large scale operations. Para toluene sulphonic acid¹⁵² seems to be the most popular catalyst in the manufacture of polyesters.

Other compounds¹⁵³ which have found favour as catalysts for polyesterification are hydroquinone, gaseous hydrochloric acid, tannic acid, pyrogallol, sodium hydrogen sulphate and aromatic amines such as aniline and phenylene diamine. Alkali metal silicates¹⁵⁴ are also suggested as catalysts for polyesterification.

With catalysts like sulphuric acid, sodium hydrogen sulphate and zinc chloride, the reaction between unsaturated acids and unsaturated alcohols becomes too violent.

An important consideration in the choice of catalyst for polyesterification reaction is the ease of its removal. If the catalyst is not removed properly, its presence has adverse effects on the properties of the polyester. Gaseous and highly volatile compounds are preferred as catalysts since they can be easily topped off. Thermally unstable catalysts are destroyed by heating.

In this laboratory, investigations were carried out to prepare polyesters needed for the synthesis of polyurethane foams by using ion-exchange resins as catalysts.¹⁵⁰ Polyesters

used for making flexible foams were free from acidity, which was the additional advantage in using ion-exchange resin catalysts. In the above communication¹⁵⁰ the author claims that although ion-exchange resins are costlier than the mineral acids, their use will be quite economical for the polyester preparation due to following reasons.

1. Resins can be easily separated from the polyester.
2. Resins can be reused.
3. Polyesterification can be achieved at low temperatures in shorter time and at atmospheric pressure.

Taking into consideration all these advantages, it was planned to study the reactions listed earlier with different types of cation exchangers and assess their suitability.

The resins studied for their catalytic effect in these reactions were Amberlyst 15, Amberlite IR 120, Zeocarb 215 and Tulsion 14.

Literature data reveals that Amberlite IR 120^{133, 144, 150} has been used as a catalyst for different esterification reactions but Amberlyst 15, a newly marketed product has not been utilised for esterification reaction.

Tulsion 14, an indigenously available resin has been compared with Zeocarb 215 of similar exchange capacity in the esterification reactions. Preliminary data showed its usefulness.¹³⁷

Effects of catalyst concentration, particle size, temperature and ratio of reactants have been fully investigated and reported. Results obtained have been discussed to reveal the utility of these ion-exchange resins for the catalysis of esterification reactions.

CHAPTER - I

INTRODUCTION

1.1

CHAPTER - II

MATERIALS AND METHODS

2.1

MATERIALS AND METHODS

1. Butanol oleic acid reaction

Raw materials:

Butanol - This was purified by drying over anhydrous sodium sulphate and was then distilled.

Boiling point - 117°C

Oleic acid - Oleic acid was purified by distilling it under reduced pressure.

Boiling range - 282°C at 100 mm.

Cation-exchange resins:

1. Amberlyst 15
2. Amberlite IR 120
3. Zeokarb 215
4. Tulsion 14.

2. 2-Ethyl Hexanol-phthalic anhydride reaction

Raw materials:

2 Ethyl hexanol - Chemically pure 2 Ethyl-hexanol was purified further by distilling at 181°C .

Phthalic anhydride - Analar grade phthalic anhydride m.p. 131°C was used without any treatment

- Benzene - Benzene was washed free of thiophene, dried over calcium chloride and distilled.
- Toluene - It was washed free of thiophene, dried over calcium chloride and distilled.
- Xylene - It was washed free of thiophene, dried over calcium chloride and distilled.

Cation-exchange resins:

Amberlyst 15.

Amberlite IR 120

Zeokarb 215

Tulsion 14.

3. Adipic acid - ethylene, propylene and diethylene glycol reaction.
4. Sebacic acid - ethylene, propylene and diethylene glycol reaction

Raw materials

Adipic acid - This was analytical grade product M.P. 151°C

Sebacic acid - This was analytical grade product
M.P. 134.5°C.

Ethylene glycol - B.D.H. Grade was distilled at 197°C
under dry condition and used.

Diethylene glycol - Chemically pure product - was
distilled under dry condition at 245°C
and used.

Propylene glycol - Chemically pure product, was distilled under dry condition at 188°C and used.

Solvents - Benzene, toluene, xylene. All the solvents were washed free of thiophene, dried thoroughly over calcium chloride and then distilled.

Cation-exchange resin catalysts:

1. Amberlyst 15
2. Amberlite IR 120
3. Zeokarb 215
4. Tulsion 14.

Ion-exchange resin catalysts:

1. Amberlyst 15 : (a sulphonated styrene divinyl benzene copolymer)

Amberlyst 15 is a strongly acidic resin and is in bead form. This resin has been particularly developed for heterogeneous catalysis in nonaqueous media. It has also been reported to be more effective for catalysis in non polar media. This resin has been used for the removal of certain impurities in non-aqueous systems. This resin is reported to have some special advantages over the conventional sulphonic acid cation-exchange resins for catalysis in non-aqueous media. It possesses a porous structure sometimes referred to as a

macroreticular structure. Due to this structure, the resin particles possess a high degree of porosity which gives rise to a larger surface area and high catalytic activity. The pores in the resin particles are very rigid and are fixed within the resin beads. This macroreticular structure in the resin permits ready access of liquid and gaseous reactants to the hydrogen ions present throughout the resin which is not possible to achieve with conventional gel type ion-exchange resin. Amberlyst 15 has a formal resemblance to the conventional sulfonic acid cation-exchange resins due to its bead form and high concentration of hydrogen ions. Amberlyst 15 has excellent resistance to various types of attrition. Its polymer structure offers very good resistance to strong acids, alkalies, aromatic and aliphatic hydrocarbons, alcohols, ethers and other solvents. Amberlyst 15 is sensitive only to high concentrations of chemical oxidants and withstands prolonged use at temperatures up to 150°C. Desulfonation takes place at higher temperatures. It is manufactured by M/S Rohm & Hass Co. USA.⁵⁷

Some of the properties of Amberlyst 15

Appearance - Hard, spherical, dark brown particles.

Particle size -16 +50 U.S. Standard screen

True density gm/ml - 1.4

Hydrogen ion concentration
meq/gm dry resin - 4.9

2. Amberlite IR 120:

Amberlite IR 120, a sulfonated styrene - divinyl benzene copolymer is a strongly acidic resin. Amberlite IR 120 has a few outstanding properties such as high exchange capacity, good chemical resistance and stability at high temperatures. This nuclear sulfonic acid type cation exchanger has a high density and is produced in the form of attrition resistant, bead like particles. Laboratory tests simulating unusually severe process conditions have shown that Amberlite IR 120 is an extremely stable product.

In addition to high exchange capacity and good physical and chemical stability, the unifunctionality, high density and particle size uniformity of Amberlite IR 120 have resulted in widespread acceptance of this exchanger for many speciality uses such as water softening, demineralisation, sugar processing and catalysis. It is manufactured by M/S Rohm & Hass Co. U.S.A.

Properties of IR 120

Appearance	-	Hard, spherical, reddish brown particles
Particle size	-	16 to 50 mesh (U.S. Standard screen)
True density gm/ml	-	1.27
Hydrogen ion concentration		
meq/gm	-	4.8

Zeokarb 215

Zeokarb 215 is classified as a strongly acidic resin. It is a sulfonated phenol formaldehyde resin. Being a polyfunctional resin, it exhibits more exchange capacity in alkaline pH due to phenolic hydroxyl group. It is produced in a granular form and has high density and good attrition resistance. This resin is thermally stable upto 50°C and gradually loses its exchange capacity when heated at high temperatures. In the form of sulfonate salts, the resin is stable at somewhat higher temperatures.

The resin when treated with acids, alkalies and solvents like alcohol, acetone imports brownish colour to the solutions in the initial stages.

It is marketed by M/S Permutit Company, London.

Properties of Zeokarb 215

Appearance - Hard, black granules with a red tinge.

Particle size - 16 to 50 mesh U.S. Standard screen

True density gm/ml 1.33

Hydrogen ion concentration - 2.6 meq/gm of the resin
meq/gm dry resin at 7 pH and
5.0 meq/gm of the resin
at 10 pH

Tulsion 14

Tulsion 14, a sulfonic acid cation exchanger is a strongly acidic resin and is available in granular form. This resin is obtained by sulfonating the cashewnut shell liquid formaldehyde polymer at 100°C. It shows a variation in exchange capacity from neutral to alkaline pH. It is a polyfunctional resin. Tulsion 14, as furnished in the sulfonic acid form, withstands temperature upto 50°C for prolonged use. Gradual desulfonation resulting in the loss of exchange capacity is observed above 50°C. In the form of sulfonate salts, the resin withstands somewhat higher temperatures. It has a good resistance to various type of attrition. Being prepared from a plant material, resin throws colour with solvents, acids and alkalies. It is a completely indigenous product and is manufactured by M/S Tulsu Industries, Poona, as per the patents²² released by National Chemical Laboratory, Poona 8.

Properties of Tulsion 14

Appearance	-	Black, hard granules
Particle size	-	-16 to 50 mesh (U.S. standard screen)
Hydrogen ion concentration meq/gm of the resin		2.2 meq/gm of the resin at 7 pH 4.0-4.1 meqs/gm of the resin at 10 pH.
True density gm/ml	-	1.3

Procedure for the determination of hydrogen ion concentration of Amberlyst 15, Amberlite IR 120, Tulsion 14 and Zeokarb 215.

Before the determination of hydrogen ion concentration of the resin, the resins must be pretreated with hydrochloric acid or with nitric acid or sulphuric acid to convert the resin to the hydrogen form. Unless this acid treatment is carried out properly, the results obtained will be misleading.

In order to obtain reproducible results, 2 litres of each resin sample was treated with acid. The resin sample was placed in a 4 inch diameter column (fitted with a sintered disc and a stop cock) and back washed at 100 percent bed expansion until a clear back wash effluent was obtained. The resin bed was then allowed to settle. Each resin sample was then treated with four litres of 5 % hydrochloric acid. Excess acid was then washed out with deionised water and the resin was dried in an oven at 40°C for twentyfour hours.

Determination of moisture content:-¹⁵⁶

In case of Amberlyst 15 and Amberlite IR 120, accurately weighed 2 to 3 gms of the hydrogen form resin was dried at 110°C overnight to determine the solid contents. But in case of Zeokarb 215 and Tulsion 14, the resins were dried at room temperature over P₂O₅.

Determination of exchange capacity:-¹⁵⁶

Accurately weighed one gram of the above treated resin was taken in a dry 250 milli litre erlenmeyer flask. 200 milli-

litres standardised 0.1 N sodium hydroxide solution prepared in 5 percent sodium chloride solution was added to the erlemeyer flask. Stoppered sample was allowed to stand overnight. 50 millilitres aliquots of the supernatant liquid was titrated against 0.1 N standard acid to the phenolphthalein end point. The cation exchange capacity was calculated as follows:

$$\frac{(200 \times N \text{ NaOH}) - 4 (\text{ Millilitres acid } \times N \text{ acid})}{\text{Sample weight } \times \text{ percent solids}/100}$$

Milliequivalents cation-exchange capacity

Gram of dry hydrogen form resin

Determination of particle size:

In the present investigations, resins of different particle sizes are used as catalysts. Resins of different sizes (-16+20, -20+30, -30+40, -40+50) were obtained by fixing U.S. Standard sieves (16, 20, 30, 40, 50) one above the other on the shaker and resin was placed on the 16 mesh sieve. Shaking was carried out for two hours.

Determination of porosity of the resin catalysts:

The procedure adopted was similar to that reported by Benesi et al.¹⁵⁷ Samples (1 to 2 gms) contained in

small weighing bottles (15 x 20 mm) were first dried in an oven at 130°C for two hours or over phosphorus pentoxide for seven days. Samples were then weighed and with lids removed were transferred to a 16 cm vacuum desiccator containing 210 ml of carbon tetrachloride-centane mixture. The desiccator connected to a cold trap, manometer and vacuum pump, was evacuated until the carbon tetrachloride boiled. After testing the leaks, about 10 ml of carbon tetrachloride was vaporized and collected in the cold trap in order to flush out all the air from the desiccator. The contents were allowed to equilibrate for 16 hours at room temperature. Air was then slowly admitted to the desiccator. The desiccator cover was removed, the weighing bottles were stoppered as rapidly as possible and the resulting samples were weighed. Pore volumes were calculated from the gain in weight of the samples and the density of carbon tetrachloride. The gain in sample weight was first corrected for the weight of carbon tetrachloride vapour entrapped while stoppering the weighing bottle. This correction was evaluated by making a parallel determination using an empty bottle.

Determination of acid number

Accurately weighed sample (about 1 gm.) was dissolved in 50 ccs alcohol-benzene mixture (50 : 50) and titrated against 0.1 N alcoholic potassium hydroxide solution to neutral end point.

Acid number was calculated as follows:

56.1 X N KOH X titre reading

Weight of the sample

It is expressed as mgms of KOH/gm of the substance.

CHAPTER III

EXPERIMENTAL

EXPERIMENTAL

Butanol-oleic acid reaction

Butanol (1 mole), oleic acid (0.25 mole) and resin catalyst were taken in a three necked flask, fitted with a mercury seal stirrer, double walled condenser, a water separator and a thermometer. The reaction mixture was quickly heated to refluxing temperature using a heating mantle with a control. Reflux temperature was found to be 120°C . Zero time was taken as the time when refluxing commenced. Samples (approximately 1 gm) were removed from the reaction mixture and analysed for the acid number at definite intervals of time. Samples were collected in conical flasks with stoppers and chilled immediately. The conical flasks were weighed before taking the sample. After chilling for 10 minutes, samples were brought to room temperature and the conical flasks were again weighed. Samples were analysed for the acid value by the method described earlier.

Different runs were carried out with Amberlyst 15, Amberlite IR 120, Zeokarb 215 and Tulsion 14. Keeping the molar ratios of the reactants and the temperature constant, concentrations of the above mentioned catalysts were varied. Keeping the catalyst concentration and temperature constant, experiments with varying particle size ranging from -16 to

+50 mesh of each of the above described catalysts were carried out. The data obtained is given in Table Nos. 1-6, 8, 9.

Resins Amberlyst 15, Amberlite IR 120, Zeokarb 215 and Tulsion 14 were analysed for their exchange capacities by the method described in Chapter II.

Resins once used were again washed with ethyl alcohol and dried thoroughly. Experiments were carried out using the thoroughly dried resins and results obtained are tabulated in Table Nos. 7, 10.

2-Ethyl-Hexanol - Phthalic anhydride reaction

2 Ethyl hexanol (0.25 moles) and phthalic anhydride (0.118 moles) with different amounts of resins and 100 ccs of toluene were placed in a three necked flask, fitted with a mercury seal stirrer, thermometer and a water separator with condenser. The reaction mixture was rapidly heated to the boiling temperature of toluene, with the help of a mantle and control. This was done in 10 minutes.

Commencement of refluxing was taken as zero time. Samples (approximately 1 gm) were removed from the reaction mixture at regular intervals in 20 ml capacity round bottomed flasks which were initially weighed. All the samples were subjected to heating under reduced pressure to remove all the solvent (toluene). This was done till the flask containing

the reaction mixture gave a constant weight. Sample was then dissolved in 25 ml. dry benzene-alcohol mixture (50:50), transferred to a 100 ml conical flask and analysed for its acid number by the method already described in Chapter II.

Experiments with the variations as mentioned in table Nos. 11-22 were carried out.

Adipic acid - ethylene, diethylene, propylene glycol reaction

Sebacic acid- ethylene, diethylene, propylene glycol reaction

Adipic acid (0.25 mole), glycol (0.313 mole) toluene (100 c.c.) and the catalyst were taken in a three necked flask with a stirring arrangement, thermometer and a water separator with condenser. The whole reaction mixture was quickly heated to refluxing temperature by means of heating mantle supplied with a control. It was possible to bring the refluxing temperature within ten minutes.

Zero time was taken from the time refluxing started. Samples (about 1 gm) were drawn from the reaction mixture from time to time in 20 ml round bottomed flask. Solvent toluene was removed from the sample by heating it over water bath under vacuum. This was continued till a constant weight of the flask containing the sample was obtained. This was to confirm the complete removal of the solvent. Sample was then dissolved in 25 ml dry benzene ; alcohol mixture, transferred to 100 ml. erlenmeyer flask and analysed for its acid number by the method described in Chapter II.

Experiments using adipic acid (0.25 mole) with diethylene glycol (0.313 mole) and propylene glycol (0.313 mole) were carried out in the same fashion.

The same experimental procedure was adopted for sebacic acid (0.1666 mole) and glycol (ethylene, propylene, diethylene 0.208 mole) reaction also.

Table Nos. 23-30 shows the variations of experimental conditions in the adipic acid - glycols and sebacic acid - glycols reaction with all the four resins and the results obtained during these experiments.

CHAPTER - IV

RESULTS AND DISCUSSION

Table No.1

Butanol-oleic acid reaction

Molar ratio - 1 : 0.25

Temperature - 120°C

Particle size - -20 +30 mesh

Resin used - Amberlyst 15.

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log un- reacted acid	k
<u>Resin concentration (dry basis) 3.75 meq.</u>					
1 hr	89.30	0.2345	$\bar{1}.3701$	0.6299	
2 hrs	46.31	0.1090	$\bar{1}.0374$	0.9626	
4 hrs	16.72	0.0439	$\bar{2}.6425$	1.3575	0.00417
5 hrs	9.50	0.0249	$\bar{2}.3969$	1.6021	
6 hrs	6.06	0.0159	$\bar{2}.2017$	1.7983	
<u>Resin concentration (dry basis) 7.5 meq.</u>					
1 hr	56.30	0.1478	$\bar{1}.1698$	0.8302	
2 hrs	25.91	0.0680	$\bar{2}.8325$	1.1675	0.00625
3 hrs	11.83	0.0310	$\bar{2}.4922$	1.5678	
3 hrs.30 min	8.87	0.0233	$\bar{2}.3692$	1.6308	
<u>Resin concentration (dry basis) 11.25 meq</u>					
30 mins.	70.93	0.1862	$\bar{1}.2700$	0.7300	
1 hr.	41.50	0.1090	$\bar{1}.0374$	0.9626	0.00961
2 hr 15 mins	8.08	0.0212	$\bar{2}.3271$	1.6729	
3 hrs.	3.752	0.0098	$\bar{3}.9934$	2.0066	
<u>Resin concentration (dry basis) 15 meq</u>					
30 min	70.62	0.1854	$\bar{1}.2679$	0.6320	
1 hr	40.24	0.1056	$\bar{1}.0238$	0.9762	0.0119
2 hrs	5.95	0.0156	$\bar{2}.1937$	1.8063	
2 hrs 30 mins	2.696	0.0070	$\bar{3}.8500$	2.1500	

Table No. 2

Butanol-oleic acid reaction

Molar ratio 1 : 0.25

Temperature - 120°C

Resin used - Amberlyst 15.

Resin concentration
(dry basis) - 15 meq.

Time	Acid value mgms KOH/gm	Unreacted acid	log unreacted acid	0.0000 -log unreacted acid	k
<u>Particle size = -40+50 mesh</u>					
30 mins	43.77	0.1149	$\bar{1}.0600$	0.9400	0.01760
45 mins	22.43	0.0588	$\bar{2}.7700$	1.2300	
1 hr.	13.98	0.0366	$\bar{2}.5642$	1.4359	
1 hr.30 mins	3.81	0.0100	$\bar{2}.0000$	2.0000	
<u>Particle size = -30+40 mesh</u>					
30 mins	60.40	0.1585	$\bar{1}.2000$	0.8000	
45 mins	36.38	0.0955	$\bar{2}.9800$	1.0200	0.0146
1 hr.	26.87	0.0705	$\bar{2}.8485$	1.1515	
1 hr.30 mins	7.6	0.0199	$\bar{2}.1755$	1.8245	
<u>Particle size = -20+30 mesh</u>					
30 mins	70.62	0.1854	$\bar{1}.2679$	0.6321	
1 hr.	40.24	0.1056	$\bar{1}.0238$	0.9762	0.0119
2 hrs.	5.95	0.0156	$\bar{2}.1937$	1.8063	
2 hrs.30 mins	2.69	0.0070	$\bar{3}.8500$	2.1500	
<u>Particle size = -16+20 mesh</u>					
1 hr.	53.80	0.1413	$\bar{1}.1500$	0.8500	
2 hrs	21.94	0.0576	$\bar{2}.7604$	1.2396	0.0066
3 hrs	9.57	0.0257	$\bar{2}.4000$	1.6000	
4 hrs	3.56	0.0093	$\bar{3}.9715$	2.0285	

Table No.3

Butanol-oleic acid reaction

Molar ratio - 1.0 : 0.25 Temperature - 120°C
 Resin used - Amberlite IR 120. Particle size - -20+30 Mesh

Time	Acid value mgms of KOH/ gm of the substance	Unreacted acid	log unreacted acid	0.0000 -log unreacted acid	k
<u>Resin concentration (dry basis) - 7.5 meq.</u>					
2 hrs	46.15	0.1212	$\bar{1}.0835$	0.9165	
4 hrs	16.23	0.0426	$\bar{2}.6294$	1.3706	0.00382
6 hrs.25 mins	4.43	0.0116	$\bar{2}.0665$	1.9335	
<u>Resin concentration (dry basis) - 15 meq</u>					
1 hr	56.32	0.1475	$\bar{1}.1688$	0.8312	
2 hrs	27.14	0.0712	$\bar{2}.8528$	1.1472	0.00486
3 hrs	11.24	0.0295	$\bar{2}.4701$	1.5299	
4 hrs	5.80	0.0192	$\bar{2}.2833$	1.7167	
5 hrs	3.59	0.0094	$\bar{3}.9747$	2.0253	
<u>Resin concentration (dry basis) - 22.5 meq</u>					
1 hr	51.76	0.1721	$\bar{1}.2358$	0.7642	
2 hrs	17.04	0.0447	$\bar{2}.6506$	1.3494	0.00729
3 hrs.15 mins	5.68	0.0149	$\bar{2}.1741$	1.8259	
4 hrs	2.5	0.0065	$\bar{3}.8171$	2.1829	
<u>Resin concentration (dry basis) - 30 meq.</u>					
1 hr.	47.93	0.1258	$\bar{1}.0997$	0.9003	
2 hrs	13.99	0.0367	$\bar{2}.5651$	1.4349	0.00833
3 hrs	3.97	0.0104	$\bar{2}.0183$	1.9817	
3 hrs.30 mins	2.17	0.0057	$\bar{3}.7574$	2.2426	

Table No.4

Butanol-oleic acid reaction

Molar ratio - 1 : 0.25

Temperature - 120°C

Resin used - Amberlite IR 120.

Resin concentration
(dry basis) - 15 meq

Time	Acid value mgms of KOH/gm of the substance	Unreacted acid	log unreacted acid	0.0000 -log unreacted acid	k
<u>Particle size - -40+50 mesh</u>					
1 hr	52.19	0.1370	$\bar{1}.1367$	0.8633	
2 hrs	28.66	0.0562	$\bar{2}.7500$	1.2500	0.00625
3 hrs	9.891	0.0259	$\bar{2}.4143$	1.5857	
4 hrs	3.582	0.0094	$\bar{3}.9734$	2.0266	
<u>Particle size - -30+40 mesh</u>					
1 hr	54.79	0.1472	$\bar{1}.1679$	0.8321	
2 hrs	25.60	0.0672	$\bar{2}.8274$	1.1726	0.00533
3 hrs	10.92	0.0286	$\bar{2}.4573$	1.5427	
4 hrs	5.43	0.0142	$\bar{2}.1538$	1.8462	
<u>Particle size - -20+30 mesh</u>					
1 hr	56.32	0.1475	$\bar{1}.1688$	0.8312	
2 hrs	27.14	0.0712	$\bar{2}.8528$	1.1472	0.00486
3 hrs	11.24	0.0295	$\bar{2}.4701$	1.5299	
4 hrs	5.80	0.0192	$\bar{2}.2833$	1.7167	
5 hrs	3.59	0.0094	$\bar{3}.9747$	2.0253	
<u>Particle size - -16+20 mesh</u>					
2 hrs	47.23	0.1561	$\bar{1}.1934$	0.8066	
4 hrs	27.75	0.0728	$\bar{2}.8625$	1.1375	0.00250
6 hrs	14.79	0.0388	$\bar{2}.5891$	1.4109	
8 hrs	8.20	0.0215	$\bar{2}.3332$	1.6668	

Table No. 5

Butanol-oleic acid reaction

Molar ratio - 1 : 0.25

Temperature - 120°C

Resin used - Zeokarb 215

Particle size - -20+30 mesh

Time	Acid value mgms of KOH/gm of the substance	Unreacted acid	log unreacted acid	0.0000 -log unreacted acid	k
<u>Resin concentrations (dry basis) - 0.9575 meq</u>					
30 mins.	66.50	0.1746	$\bar{1}.2420$	0.7580	
60 mins	27.67	0.0725	$\bar{2}.8603$	1.1397	0.01455
1 hr.45 mins	6.30	0.0165	$\bar{2}.2185$	1.7815	
2 hrs	3.40	0.0089	$\bar{3}.9507$	2.0393	
<u>Resin concentrations (dry basis) - 1.875 meq.</u>					
30 mins	53.54	0.1406	$\bar{1}.1481$	0.8519	
60 mins	18.62	0.0489	$\bar{2}.6893$	1.3107	0.01759
1 hr.30 mins	6.30	0.0165	$\bar{2}.2185$	1.7815	
1 hr.50 mins	2.56	0.0067	$\bar{3}.8287$	2.1713	
<u>Resin concentrations (dry basis) - 3.75 meq.</u>					
30 mins	30.06	0.0789	$\bar{2}.8971$	1.1029	
45 mins	15.16	0.0398	$\bar{2}.6000$	1.4000	0.01835
1 hr.15 mins	4.86	0.0127	$\bar{2}.1058$	1.8942	
1 hr.30 mins	1.43	0.0057	$\bar{3}.7601$	2.2399	
2 hrs	1.43	0.0057	$\bar{3}.7601$	2.2399	
<u>Resin concentrations (dry basis) - 7.5 meq.</u>					
15 mins	47.95	0.1259	$\bar{1}.1000$	0.9000	
30 mins	19.61	0.0515	$\bar{2}.7118$	1.2882	0.02500
45 mins	6.76	0.0177	$\bar{2}.2500$	1.7500	
60 mins	3.46	0.0090	$\bar{3}.9586$	2.0414	

Table No.6

Butanol-oleic acid reactions

Molar ratio - 1 : 0.25

Temperature - 120°C

Resin used - Zeokarb 215

Resin concentration
(dry basis) - 7.5 meq

Time	Acid value mgms of KOH/gm of the substance	Unreacted acid	log- unreacted acid	0.0000 -log unreacted acid	k
<u>Particle size - -16+20 mesh</u>					
15 mins	67.66	0.1778	$\bar{1}.2500$	0.7500	
30 mins	44.81	0.1176	$\bar{1}.0705$	0.9295	0.01350
1 hr.	16.07	0.0421	$\bar{2}.6250$	1.3750	
1 hr.30 mins	6.76	0.0177	$\bar{2}.2500$	1.7500	
<u>Particle size - -20+30 mesh</u>					
15 mins	47.95	0.1259	$\bar{1}.1000$	0.9000	
30 mins	19.61	0.0575	$\bar{2}.7118$	1.2882	0.02500
45 mins	6.76	0.0177	$\bar{2}.2500$	1.7500	
1 hr.	3.46	0.0090	$\bar{3}.9586$	2.0414	
<u>Particle size - -30+40 mesh</u>					
15 mins	38.10	0.1000	$\bar{1}.0000$	1.0000	
30 mins	10.64	0.0279	$\bar{2}.4461$	1.5539	
45 mins	3.81	0.0100	$\bar{2}.0000$	2.0000	0.02920
60 mins	2.40	0.0062	$\bar{3}.7993$	2.2007	
<u>Particle size - -40+50 mesh</u>					
10 mins	41.30	0.1084	$\bar{1}.0350$	0.9650	
15 mins	21.55	0.0560	$\bar{2}.7485$	1.2515	0.03835
30 mins	6.70	0.0176	$\bar{2}.2455$	1.7545	
40 mins	2.95	0.0079	$\bar{3}.9000$	2.1000	

Table No.7

Butanol oleic acid reactions

Molar ratio - 1 : 0.25

Temperature - 120°C

Resin - Zeokarb 215 (Reused)

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	Log unreacted acid	0.0000 -log unreacted acid	k
<u>Capacity - 1.4 meq/gm dry resin (Salt breaking)</u>					
30 mins	64.66	0.1697	$\bar{1}.2298$	0.7702	
1 hr	23.86	0.0992	$\bar{2}.9969$	1.0031	0.00741
2 hrs	14.00	0.03676	$\bar{2}.5654$	1.4346	
3 hrs	4.60	0.0120	$\bar{2}.0821$	1.9179	
4 hrs	4.60	0.0120	$\bar{2}.0821$	1.9179	
<u>Capacity - salt breaking 1.1 meq/gm dry resin</u>					
1 hr	51.92	0.1363	$\bar{1}.1346$	0.8654	
2 hrs	24.60	0.0646	$\bar{2}.8102$	1.8980	0.00563
2 hrs.30 mins	15.24	0.0399	$\bar{2}.6020$	1.4080	
3 hrs	11.50	0.0301	$\bar{2}.4798$	1.5202	
4 hrs	4.81	0.0126	$\bar{2}.1020$	1.8980	

Table No. 8

Butanol-oleic acid reactions

Molar ratio - 1 : 0.25

Temperature - 120°C.

Resin used - Tulsion 14

Particle size = -20+30 mesh

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	Log unreacted acid	0.0000 -log unreacted acid	k
<u>Resin concentration - 2.5 meq</u>					
15 mins	67.55	0.1409	$\bar{1}.1491$	0.8519	
25 mins	35.90	0.0942	$\bar{2}.9743$	1.0257	
30 mins	25.36	0.0666	$\bar{2}.8238$	1.1762	0.02273
45 mins	12.04	0.0316	$\bar{2}.4997$	1.5003	
1 hr	5.33	0.0140	$\bar{2}.1464$	1.8536	
<u>Resin concentration - 5 meq.</u>					
15 mins	47.90	0.1257	$\bar{1}.0993$	0.9007	
30 mins	23.93	0.0628	$\bar{2}.7982$	1.2018	0.02833
45 mins	6.77	0.0177	$\bar{2}.2498$	1.7502	
1 hr	2.77	0.0072	$\bar{3}.8625$	2.1375	
<u>Resin concentration - 10 meq</u>					
5 mins	63.83	0.1676	$\bar{1}.2242$	0.7758	
15 mins	28.50	0.0799	$\bar{2}.3748$	1.1252	0.03890
30 mins	7.32	0.0192	$\bar{2}.2842$	1.7158	
40 mins	3.02	0.0079	$\bar{3}.8990$	2.1010	
<u>Resin concentration - 15 meq</u>					
10 mins	35.96	0.0944	$\bar{2}.9750$	1.0250	
15 mins	21.40	0.0562	$\bar{2}.7498$	1.2502	0.04800
20 mins	12.05	0.0316	$\bar{2}.4999$	1.5001	
30 mins	3.98	0.0104	$\bar{2}.9190$	1.9810	

Table No. 9

Butanol-oleic acid reaction

Molar ratio - 1 : 0.25

Temperature - 120°C

Resin used - Tulsion 14.

Resin concentration
(dry basis) - 15 meq

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log unreacted acid	0.0000 -log unreacted acid	k
<u>Particle size = -16+20 mesh</u>					
5 mins	75.10	0.1972	$\bar{1}.2949$	0.7051	
15 mins	38.60	0.1014	$\bar{1}.0060$	0.9940	0.02964
30 mins	15.57	0.0408	$\bar{2}.6112$	1.3890	
45 mins	5.20	0.0136	$\bar{2}.1331$	1.8650	
<u>Particle size = -20+30 mesh</u>					
10 mins	35.96	0.0944	$\bar{2}.9750$	1.0250	
15 mins	21.40	0.0562	$\bar{2}.7498$	1.2502	0.04800
20 mins	12.05	0.0316	$\bar{2}.4999$	1.5001	
30 mins	3.98	0.0104	$\bar{2}.0190$	1.9810	
<u>Particle size = -30+40 mesh</u>					
5 mins	52.60	0.1382	$\bar{1}.1405$	0.8595	
10 mins	28.20	0.0739	$\bar{2}.8692$	1.1308	0.05420
15 mins	15.20	0.0398	$\bar{2}.6009$	1.3991	
25 mins	4.25	0.0111	$\bar{2}.0482$	1.9518	
<u>Particle size = -40+50 mesh</u>					
5 mins	44.50	0.1168	$\bar{1}.0675$	0.9325	
10 mins	19.93	0.0524	$\bar{2}.7198$	1.2802	0.06660
15 mins	9.03	0.0237	$\bar{2}.3749$	1.6251	
20 mins	3.80	0.0099	$\bar{3}.9990$	2.0010	

Table No.10

Butanol oleic acid reaction

Molar ratio - 1 : 0.25

Temperature - 120°C

Resin - Tulsion reused.

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log unreacted acid	0.0000 -log unreacted acid	k
<u>Capacity - 0.9 meq/gm dry resin (salt breaking)</u>					
30 mins	63.40	0.1665	$\bar{1}.2215$	0.7795	
1 hr	36.16	0.0949	$\bar{2}.9774$	1.0226	0.00946
2 hrs	5.79	0.0152	$\bar{2}.1820$	1.8180	
3 hrs	2.74	0.0071	$\bar{3}.8534$	2.1466	
4 hrs	2.74	0.0071	$\bar{3}.8534$	2.1466	
6 hrs	2.74	0.0071	$\bar{3}.8534$	2.1466	
<u>Capacity - 0.5 meq/gm dry resin (salt breaking)</u>					
1 hr	43.20	0.1134	$\bar{1}.0548$	0.9452	
2 hrs	18.05	0.0484	$\bar{2}.6758$	1.3242	0.00611
3 hrs	7.17	0.0188	$\bar{2}.2748$	1.7252	
4 hrs	3.33	0.0087	$\bar{3}.9423$	2.0577	
<u>Capacity - 0.3 meq/gm dry resin (salt breaking)</u>					
2 hrs	23.10	0.0606	$\bar{2}.7829$	1.2171	
3 hrs	12.02	0.0315	$\bar{2}.4991$	1.5009	0.00476
4 hrs	6.02	0.0158	$\bar{2}.1986$	1.8014	
5 hrs	3.10	0.0081	$\bar{3}.9107$	2.0893	
6 hrs	3.10	0.0081	$\bar{3}.9107$	2.0893	

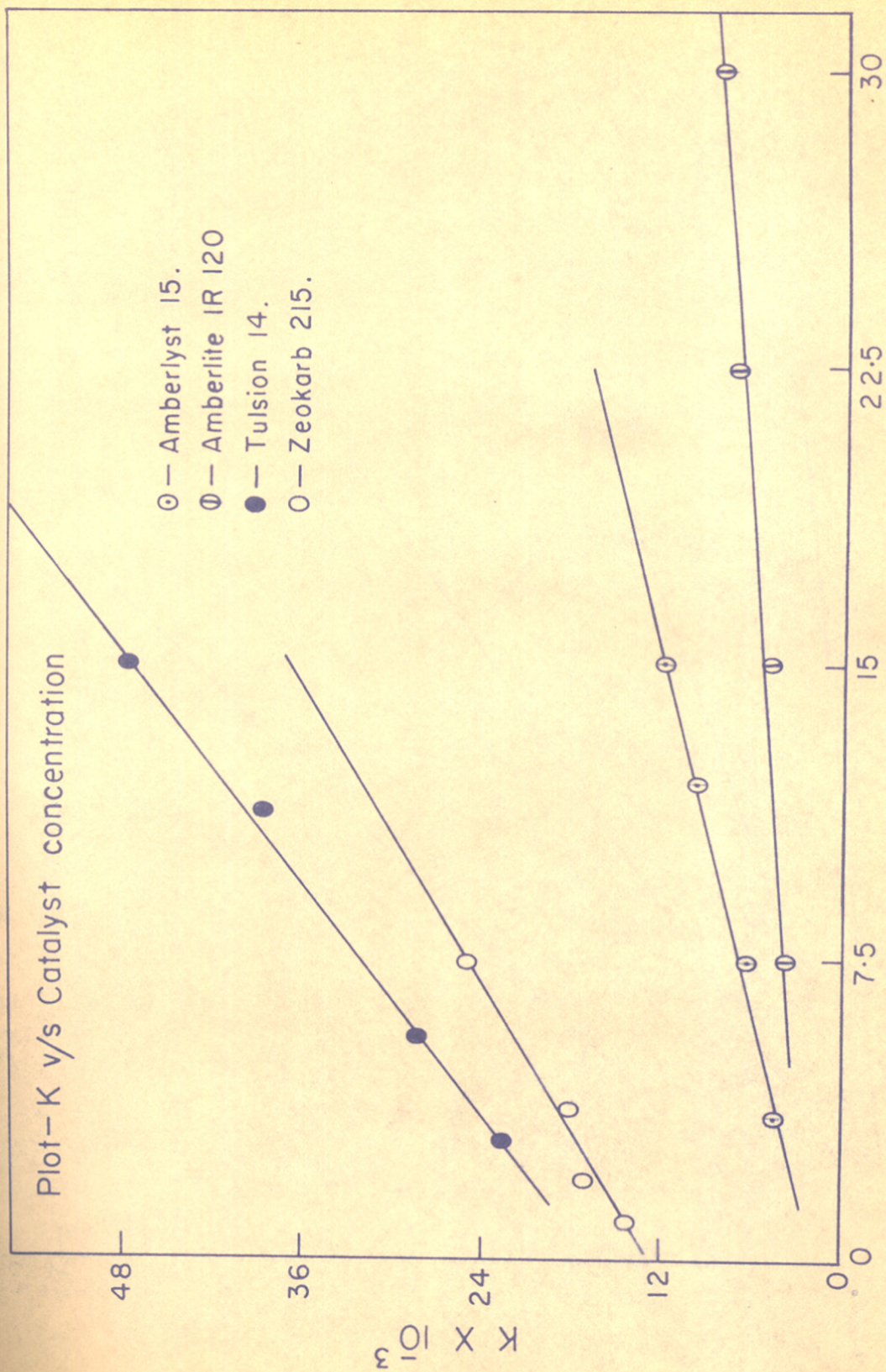


Fig.1 - Butanol - Oleic acid reaction.

RESULTS AND DISCUSSION

1. Butanol-oleic acid reaction

The data collected in this investigation has been utilized to follow the course of reaction between butanol and oleic acid using Amberlyst 15, Amberlite IR 120, Tulsion 14 and Zeokarb 215 hydrogen form cation-exchange resins as catalysts, under different experimental conditions.

By plotting the log unreacted acid concentration against time under the various experimental conditions studied, it has been found that the condensation reaction follows pseudo first order rate law with all the four resin catalysts. By changing the catalyst concentration and particle size of the catalyst, the reaction followed pseudo first order rate law.

In case of Amberlite IR 120, the catalyst concentration was changed from 7.5 meq to 30.0 meq. Although the catalyst concentration was increased four times, k varied from 3.82×10^{-3} to 8.33×10^{-3} . This shows only a marginal effect of the variation of the catalyst concentrations on the rate of esterification. When the catalyst concentration of Amberlyst 15 was changed from 3.7 meq to 15 meq, there was a considerable variation of k from 4.17×10^{-3} to 11.9×10^{-3} which shows that k is directly proportional to the catalyst concentration. Amberlyst 15 is a macroreticular resin especially recommended for use as a catalyst. Hence the variation with increase in catalyst concentration can be

anticipated. Though Amberlite IR 120 and Amberlyst 15 are unfunctional nuclear sulphonic acid resins, the structure of Amberlyst 15 is different from the gel type structure of Amberlite IR 120.

In case of Tulsion 14 and Zeokarb 215, both phenol sulphonic acid type cation exchangers, the catalyst concentration was changed from 2.5 meq to 15 meq. and from 0.9375 meq to 7.5 meq respectively. Change of catalyst concentration had remarkable effect on the values of rate constant in both the cases. A linear relation between the rate constant and catalyst concentration for Tulsion 14 and Zeokarb 215 is revealed in Fig.No.1.

Results in Tables Nos. 1-10 clearly show that with Tulsion 14 and Zeokarb 215, the esterification is completed in much short time as compared to Amberlyst 15 and Amberlite IR 120.

It is also found that Amberlyst 15 and Amberlite IR 120 do not exhibit any change in exchange capacity and their catalytic performance was the same even after repeated use without any regeneration.

But Tulsion 14 and Zeokarb 215, being polyfunctional, are susceptible to higher temperatures and were found to desulphonate with loss in exchange capacity. However it was of interest to study the used resin as preliminary studies had revealed that once used resins could also be reused.¹³⁷ Used Tulsion 14 and Zeokarb 215 were washed with alcohol and

dried thoroughly and again utilized for similar experiments. There was a gradual loss in the exchange capacities of Tulsion 14 and Zeokarb 215 during repeated use. It is very clear from these experiments and the data given in tables Nos. 10 & 7 that although Tulsion 14 and Zeokarb 215 lost their exchange capacities from 2.1 meq to 0.3 meq and from 2.5 meq to 1.1 meq. respectively, they are more effective in the desulphonated forms than Amberlyst 15 and Amberlite IR 120.

When the desulphonated resins (Tulsion 14, Zeokarb 215) were used as catalysts in the butanol-oleic acid reaction, the order of the reaction was unaltered. A straight line was obtained by plotting log unreacted acid against time, which indicates that even with the desulphonated resins, the reaction follows pseudo first order rate law.

The following table indicates the effect of loss of exchange capacity on the rate of reaction.

Salt splitting capacity meq/gm dry resin	Order of reaction	k
<u>Zeokarb 215</u>		
2.5	First order	0.025
1.4	-do-	0.00741
1.1	-do-	0.005631
<u>Tulsion 14</u>		
2.1	-do-	0.048
0.9	-do-	0.00946
0.5	-do-	0.00611
0.3	-do-	0.004762

Results obtained clearly show that Tulsion 14 and Zeokarb 215 are more effective as catalyst than Amberlite IR 120 and Amberlyst 15 even though Amberlyst 15 and Amberlite IR 120 have higher exchange capacities. Therefore it can be concluded that the phenolic hydroxyl and residual sulphonic groups in the polyfunctional resins Tulsion 14 and Zeokarb 215 are responsible for the higher catalyst efficiency than Amberlyst 15 and Amberlite IR 120.

Butanol-oleic acid esterification was studied in presence of the above mentioned catalysts of different particle sizes. Keeping the catalyst concentration constant, the effect of the following particle size of the catalysts was studied

- (1) - 16 + 20
- (2) - 20 + 30
- (3) - 30 + 40
- (4) - 40 + 50

It was found that rate of reaction was accelerated by reducing the particle size of resin catalyst and this was true for Amberlyst 15, Amberlite IR 120, Zeokarb 215 and Tulsion 14.

In Fig. No.2 the values of rate constant k are plotted against the surface area of the catalyst. The surface area was calculated assuming the catalyst particles were either cubes or spheres. In the Fig.No.2, a straight line is obtained for all the four resins showing a linear relationship between the rate constant k and surface area of the catalyst.

Although Amberlyst 15, Amberlite IR 120, Tulsion 14 and Zeokarb 215 behave in a similar fashion as catalysts with the increase in concentration and surface area, it can be concluded from these results that Tulsion 14 and Zeokarb 215 are more efficient as catalysts for butanol-oleic acid esterification than Amberlyst 15 and Amberlite IR 120. Besides surface area, the porosities of the catalysts studied were determined as per procedure described earlier. Results presented below show that Amberlyst 15 (a macroreticular resin) exhibits the highest value and this value is in agreement with the value reported by M/S Rohm & Haas & Co.⁵⁷

<u>Resin</u>	<u>Porosity ml pore/ml bead</u>
Amberlyst 15	0.353
Zeokarb 215	0.0495
Tulsion 14	0.00848
Amberlite IR 120	0.00648

It is very interesting that among the two phenolsulphonic acid resins Zeokarb 215 exhibits higher porosity than Tulsion 14 but the catalytic performance of Tulsion 14 is superior to that of Zeokarb 215.

2 Ethyl hexanol - phthalic anhydride reaction

Table No.11

Molar ratio - 0.25 : 0.118

Temperature - 117°C

Catalyst - Amberlyst 15

Particle size - -20+30 mesh

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 - log unreacted	k
<u>Resin concentration (dry basis) - 7.5 meq</u>					
30 mins	135.60	0.1130	$\bar{1}.0531$	0.9469	
1 hr	126.50	0.1054	$\bar{1}.0229$	0.9771	
1 hr 45 mins	118.00	0.0982	$\bar{2}.9921$	1.0079	0.00073
4 hrs	93.60	0.0779	$\bar{2}.8915$	1.1085	
6 hrs	77.90	0.0649	$\bar{2}.8122$	1.1878	
<u>Resin concentration (dry basis) - 15 meq</u>					
1 hr	123.80	0.1030	$\bar{1}.0128$	0.9872	
2 hrs	106.20	0.0884	$\bar{2}.9465$	1.0535	0.00096
3 hrs.30 mins	86.86	0.0723	$\bar{2}.8591$	1.1409	
5 hrs	72.16	0.0601	$\bar{2}.7789$	1.2211	
<u>Resin concentration (dry basis) - 22.5 meq</u>					
30 mins	123.90	0.1032	$\bar{1}.0136$	0.9864	
1 hr	112.30	0.0938	$\bar{2}.9722$	1.0278	0.00119
2 hrs	95.40	0.0794	$\bar{2}.9998$	1.1002	
3 hrs	76.60	0.0670	$\bar{2}.8261$	1.1739	
<u>Resin concentration (dry basis) - 30 meq.</u>					
30 mins	120.20	0.1001	$\bar{1}.0004$	0.9996	
1 hr.15 mins	100.00	0.8333	$\bar{2}.9206$	1.0794	0.002328
2 hrs	83.70	0.0697	$\bar{2}.8432$	1.1568	
2 hrs.30 mins	76.60	0.0683	$\bar{2}.8344$	1.1656	

Table No.12

2 Ethyl hexanol - Phthalic anhydride

Molar ratio - 0.25 : 0.118

Temperature - 117°C.

Catalyst - Amberlyst 15

Resin concentration
(dry basis) - 15 meq

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log unreacted acid	k
<u>Particle size - -16+20 mesh</u>					
1 hr	126.40	0.1055	$\bar{1}.0233$	0.9767	
2 hr.15 mins	112.60	0.0936	$\bar{2}.9713$	1.0287	
3 hr.15 mins	102.20	0.0851	$\bar{2}.9299$	1.0701	0.00055
4 hrs	95.04	0.0791	$\bar{2}.8982$	1.1018	
7 hrs	74.50	0.0620	$\bar{2}.7924$	1.2076	
<u>Particle size - -20+30 mesh</u>					
1 hr	123.80	0.1030	$\bar{1}.0128$	0.9872	
2 hrs	106.20	0.0884	$\bar{2}.9465$	1.0535	0.00096
3 hr.30 mins	86.86	0.0723	$\bar{2}.8591$	1.1409	
5 hrs	72.16	0.0601	$\bar{2}.7789$	1.2211	
<u>Particle size - -30+40 mesh</u>					
45 mins	117.00	0.0974	$\bar{2}.9886$	1.0114	
2 hrs	90.67	0.0755	$\bar{2}.8779$	1.1221	0.00122
3 hrs	80.50	0.0670	$\bar{2}.8261$	1.1739	
3 hrs.45 mins	71.11	0.0591	$\bar{2}.7716$	1.2284	
<u>Particle size - -40+50 mesh</u>					
30 mins	112.70	0.0938	$\bar{2}.9722$	1.0278	
1 hr	98.92	0.0824	$\bar{2}.9159$	1.0841	0.00207
1 hr.30 mins	86.20	0.0718	$\bar{2}.8561$	1.1439	
2 hrs	73.35	0.0611	$\bar{2}.7860$	1.2140	

Table No. 13

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 : 0.118

Catalyst - Amberlyst 15

Particle size - -20+30 mesh

Resin concentration
(dry basis) - 15 meq

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log unreacted acid	k
<u>Temperature - 85°C</u>					
1 hr.	130.80	0.1088	$\bar{1}.0367$	0.9633	
2 hrs.	127.30	0.1060	$\bar{1}.0253$	0.9748	0.00033
3 hrs	123.80	0.1030	$\bar{1}.0428$	0.9872	
4 hrs	113.10	0.0941	$\bar{2}.9738$	1.0262	
6 hrs	106.70	0.0888	$\bar{2}.9486$	1.0514	
<u>Temperature - 117°C</u>					
1 hr	123.80	0.1030	$\bar{1}.0128$	0.9872	
2 hrs	106.20	0.0889	$\bar{2}.9465$	1.0535	0.00096
3 hrs.30 mins	86.86	0.0723	$\bar{2}.8591$	1.1409	
5 hrs	72.16	0.0601	$\bar{2}.7789$	1.2211	
<u>Temperature - 140°C</u>					
1 hr	110.90	0.0923	$\bar{2}.9652$	1.0348	
1 hr.30 mins	100.90	0.0890	$\bar{2}.9243$	1.0757	
2 hrs.30 mins	81.90	0.0682	$\bar{2}.8338$	1.1662	0.00138
3 hrs.45 mins	70.60	0.0588	$\bar{2}.7694$	1.2306	
4 hrs.	61.40	0.0511	$\bar{2}.7084$	1.2914	

Table No. 14

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 : 0.118.

Temperature - 117°C

Catalyst - Amberlite IR 120.

Particle size - -20+30 mesh

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log unreacted acid	k
<u>Catalyst concentration (dry basis) - 7.5 meq</u>					
1 hr	138.00	0.1150	$\bar{1}.0607$	0.9393	
2 hrs	130.00	0.1080	$\bar{1}.0334$	0.9666	0.000397
6 hrs	104.60	0.0871	$\bar{2}.9400$	1.0600	
8 hrs	94.20	0.0783	$\bar{2}.8943$	1.1057	
<u>Catalyst concentration (dry basis) - 12.9 meq.</u>					
1 hr. 30 mins.	124.00	0.1031	$\bar{1}.0136$	0.9864	
2 hrs	119.70	0.0997	$\bar{2}.9988$	1.0012	0.0004902
4 hrs	104.20	0.0866	$\bar{2}.9375$	1.0625	
5 hrs	98.35	0.0819	$\bar{2}.9134$	1.0866	
6 hrs	91.60	0.0762	$\bar{2}.8820$	1.1180	
<u>Catalyst concentration (dry basis) - 15 meq.</u>					
2 hrs	115.70	0.0962	$\bar{2}.9836$	1.0164	
3 hrs	105.70	0.0880	$\bar{2}.9447$	1.0553	0.0006536
4 hrs. 30 mins	92.66	0.0771	$\bar{2}.8871$	1.1129	
6 hrs.	81.87	0.0682	$\bar{2}.8338$	1.1662	
<u>Catalyst concentration (dry basis) - 22.5 meq</u>					
1 hr.	120.00	0.0999	$\bar{2}.9997$	1.0003	
2 hrs	107.30	0.0893	$\bar{2}.9509$	1.0491	0.0008333
3 hrs	95.25	0.0793	$\bar{2}.8994$	1.1006	
4 hrs	85.39	0.0711	$\bar{2}.8519$	1.1481	
5 hrs	75.64	0.0630	$\bar{2}.7994$	1.2006	

Table No. 15

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 : 0.118

Temperature - 117°C

Catalyst - Amberlite IR 120

Resin concentration
(dry basis) - 15 meq

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log unreacted acid	0.0000 -log unreacted acid	k
<u>Particle size - -16+20 mesh</u>					
1 hr	128.80	0.1073	$\bar{1}.0304$	0.9696	
4 hrs	106.30	0.0884	$\bar{2}.9467$	1.0533	0.0004855
5 hrs	99.40	0.0827	$\bar{2}.9179$	1.0821	
6 hrs	93.96	0.0776	$\bar{3}.8904$	1.1096	
8 hrs	81.80	0.0681	$\bar{2}.8334$	1.1666	
<u>Particle size - -20+30 mesh</u>					
2 hrs	115.70	0.09630	$\bar{2}.9836$	1.0164	
3 hrs	105.70	0.0880	$\bar{2}.9447$	1.0553	0.0006576
4 hrs.30 mins	92.66	0.0771	$\bar{2}.8871$	1.1129	
6 hrs	81.87	0.0682	$\bar{2}.8338$	1.1662	
<u>Particle size - -30+40 mesh</u>					
1 hr	124.00	0.1031	$\bar{1}.0136$	0.9864	
2 hrs	106.90	0.0890	$\bar{2}.9494$	1.0506	0.000877
3 hrs	96.50	0.0803	$\bar{2}.9047$	1.0953	
5 hrs	75.40	0.0628	$\bar{2}.7980$	1.2020	
<u>Particle size - -40+50 mesh</u>					
30 mins	127.00	0.1058	$\bar{1}.0243$	0.9757	
1 hr.	116.80	0.0973	$\bar{2}.9883$	1.0117	0.001234
2 hrs	99.00	0.0823	$\bar{2}.9159$	1.0841	
3 hrs	83.40	0.0694	$\bar{2}.8417$	1.1583	
3 hrs.30 mins	75.50	0.0628	$\bar{2}.7980$	1.2020	

Table No.16

* 2 Ethyl hexanol - phthalic anhydride reaction

Catalyst - Amberlite IR 120

Resin concentration
(dry basis) - 15 meq.

Particle size - -20+30 mesh

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log unreacted acid	0.0000 -log unreacted acid	k
<u>Temperature - 85°C</u>					
1 hr	140.00	0.1165	1.0665	0.9335	
2 hrs.30 mins	134.40	0.1120	1.0492	0.9508	0.0002874
6 hrs	117.20	0.0975	2.9894	1.0106	
9 hrs	108.70	0.0904	2.9566	1.0439	
<u>Temperature - 117°C</u>					
2 hrs	115.70	0.0962	2.9836	1.0164	
3 hrs	105.70	0.0880	2.9447	1.0553	0.0006536
4 hrs.30 mins	92.66	0.0771	2.8871	1.1129	
6 hrs	81.87	0.0682	2.8338	1.1662	
<u>Temperature - 140°C</u>					
1 hr	121.80	0.1014	1.0060	0.9940	
2 hrs	106.80	0.0889	2.9490	1.0510	0.000926
3 hrs	93.20	0.0793	2.8998	1.1002	
4 hrs	86.68	0.06965	2.8429	1.1571	

Table No.17

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 : 0.118

Temperature - 117°C.

Catalyst - Zeokarb 215

Particle size - -20+30 mesh

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log unreacted acid	k
<u>Resin concentration - 0.9375 meq</u>					
2 hrs. 34 mins	129.40	0.1077	$\bar{1}.0324$	0.9676	
4 hrs. 30 mins	120.30	0.1001	$\bar{1}.0005$	0.9995	0.0002344
6 hrs. 5 mins	116.10	0.0966	$\bar{2}.9852$	1.0148	
10 hrs	101.40	0.0844	$\bar{2}.9263$	1.0737	
<u>Resin concentration - 1.875 meq</u>					
2 hrs	126.60	0.1054	$\bar{1}.0229$	0.9771	
4 hrs	110.0	0.0916	$\bar{2}.9619$	1.0381	0.000422
6 hrs	98.35	0.0819	$\bar{2}.9133$	1.0867	
8 hrs. 30 mins	84.30	0.0703	$\bar{2}.8470$	1.1530	
<u>Resin concentration - 3.75 meq</u>					
2 hrs	117.80	0.0981	$\bar{2}.9917$	1.0083	
4 hrs	105.20	0.0876	$\bar{2}.9425$	1.0575	0.0005264
6 hrs	90.40	0.0753	$\bar{2}.8768$	1.1232	
8 hrs. 30 mins	76.40	0.0636	$\bar{2}.8035$	1.1965	
<u>Resin concentration - 7.5 meq</u>					
2 hrs. 30 mins	113.20	0.0942	$\bar{2}.9744$	1.0256	
4 hrs	98.20	0.0817	$\bar{2}.9125$	1.0875	0.0006616
5 hrs. 30 mins.	84.50	0.0708	$\bar{2}.8500$	1.1500	
8 hrs	68.70	0.0572	$\bar{2}.7574$	1.2426	

Table No. 18

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 : 0.118

Temperature - 117°C

Catalyst - Zeokarb 215

Resin concentration
(dry basis) - 7.5 meq

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log unreacted acid	k
<u>Particle size - -16 +20 mesh</u>					
2 hrs.30 mins	118.00	0.0982	$\bar{2}.9921$	1.0079	
3 hrs.30 mins	112.40	0.0936	$\bar{2}.9713$	1.0289	0.0003433
6 hrs	99.10	0.0825	$\bar{2}.9167$	1.0833	
9 hrs	86.21	0.0718	$\bar{2}.8561$	1.1439	
10 hrs	80.53	0.0686	$\bar{2}.8366$	1.1634	
<u>Particle size - -20+30 mesh</u>					
2 hrs.30 mins	113.20	0.09428	$\bar{2}.9744$	1.0256	
4 hrs	98.20	0.0817	$\bar{2}.9125$	1.0875	0.0006616
5 hrs.30 mins	84.50	0.0708	$\bar{2}.8500$	1.1500	
8 hrs	68.70	0.0572	$\bar{2}.7574$	1.2426	
<u>Particle size - -30+40 mesh</u>					
3 hrs.15 mins	100.20	0.0834	$\bar{2}.9212$	1.0788	
5 hrs	84.60	0.0709	$\bar{2}.8509$	1.1491	0.000746
6 hrs.30 mins	71.70	0.0597	$\bar{2}.7760$	1.2240	
11 hrs	43.54	0.0362	$\bar{2}.5591$	1.4408	
<u>Particle size - -40+50 mesh</u>					
3 hrs.30 mins	92.10	0.0767	$\bar{2}.8848$	1.1152	
4 hrs.45 mins	78.00	0.0649	$\bar{2}.8122$	1.1878	0.0008571
6 hrs.45 mins	62.70	0.0522	$\bar{2}.7177$	1.2823	
10 hrs	43.00	0.0358	$\bar{2}.5539$	1.4461	

Table No. 19

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 ; 0.118 Particle size - -20+30 mesh

Resin concentration (dry basis) - 7.5 meq. Resin used -
Zeokarb 215.

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted	0.0000 -log unreacted acid	k
<u>Temperature - 85°C</u>					
1 hr	131.60	0.1095	$\bar{1}.0395$	0.9605	
2 hrs	126.40	0.1052	$\bar{2}.0220$	0.9780	0.0002603
4 hrs	119.70	0.0999	$\bar{2}.9996$	1.0004	
5 hrs	114.90	0.09491	$\bar{2}.9773$	1.0227	
<u>Temperature - 117°C</u>					
2 hrs.30 mins	113.20	0.0942	$\bar{2}.9744$	1.0256	
4 hrs	98.20	0.0817	$\bar{2}.9125$	1.0875	0.0006616
5 hrs.30 mins	84.50	0.0708	$\bar{2}.8500$	1.1500	
8 hrs	68.70	0.0572	$\bar{2}.7574$	1.2426	
<u>Temperature - 140°C</u>					
2 hrs	72.26	0.0601	$\bar{2}.8489$	1.1511	
4 hrs.10 mins	49.22	0.04097	$\bar{2}.6125$	1.3875	0.00174
7 hrs.	26.62	0.02215	$\bar{2}.3454$	1.6546	
10 hrs	12.51	0.0104	$\bar{2}.0170$	1.9930	

Table No. 20

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 : 0.118

Temperature - 117°C

Catalyst - Tulsion 14.

Particle size - -20+30 mesh

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log unreacted acid	k
<u>Resin concentration (dry basis) - 5 meq</u>					
2 hrs	119.60	0.0994	$\bar{2}.9978$	1.0022	
4 hrs	103.90	0.0865	$\bar{2}.9370$	1.0630	0.0007353
8 hrs	67.75	0.0564	$\bar{2}.7515$	1.2485	
10 hrs.30 mins	52.94	0.0441	$\bar{2}.6444$	1.3556	
<u>Resin concentration (dry basis) - 11.3 meq</u>					
2 hrs	110.90	0.0923	$\bar{2}.9652$	1.0348	
4 hrs	86.70	0.0721	$\bar{2}.8585$	1.1415	0.00125
6 hrs	57.61	0.04792	$\bar{2}.6805$	1.3195	
9 hrs.30 mins	32.09	0.0267	$\bar{2}.4265$	1.5735	
<u>Resin concentration (dry basis) - 15 meq</u>					
2 hrs	102.40	0.0852	$\bar{2}.9305$	1.0695	
4 hrs	64.49	0.0537	$\bar{2}.7300$	1.2700	0.001667
6 hrs	39.77	0.0331	$\bar{2}.5198$	1.4802	
9 hrs	19.36	0.0161	$\bar{2}.2074$	1.7926	
<u>Resin concentration (dry basis) - 25 meq</u>					
1 hr	119.90	0.0962	$\bar{2}.9832$	1.0168	
2 hrs	83.35	0.0694	$\bar{2}.8414$	1.1586	0.0025
4 hrs.30 mins	33.36	0.0278	$\bar{2}.4433$	1.5567	
7 hrs	13.80	0.0115	$\bar{2}.0607$	1.9393	
8 hrs	10.51	0.0087	$\bar{3}.9420$	2.0580	

Table No.21

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 : 0.118

Temperature - 117°C

Catalyst - Tulsion 14.

Catalyst concentration
(dry basis) - 15 meq

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log unreacted acid	k
<u>Particle size - -+16 +20 mesh</u>					
2 hrs	108.30	0.0902	$\bar{2}.9552$	1.0448	
4 hrs	73.90	0.0615	$\bar{2}.7889$	1.2111	0.001389
6 hrs	48.00	0.0399	$\bar{2}.6019$	1.3985	
8 hrs	28.20	0.0234	$\bar{2}.3705$	1.6295	
<u>Particle size - -20+30 mesh</u>					
2 hrs	102.40	0.0852	$\bar{2}.9305$	1.0695	
4 hrs	64.49	0.0537	$\bar{2}.7300$	1.2700	0.001667
6 hrs	39.77	0.0331	$\bar{2}.5198$	1.4802	
9 hrs	19.36	0.0161	$\bar{2}.2074$	1.7926	
<u>Particle size - -30+40 mesh</u>					
1 hr	113.50	0.0945	$\bar{2}.9757$	1.0243	
3 hrs	60.05	0.0500	$\bar{2}.6993$	1.3007	0.002083
5 hrs	37.52	0.0312	$\bar{2}.4949$	1.5052	
6 hrs	24.61	0.0205	$\bar{2}.3118$	1.6882	
8 hrs	10.00	0.0083	$\bar{3}.9201$	2.0799	
<u>Particle size - -40+50 mesh</u>					
2 hrs	87.38	0.0578	$\bar{2}.7619$	1.2381	
3 hrs.30 mins	36.43	0.0303	$\bar{2}.4814$	1.5186	0.002777
6 hrs	14.84	0.0123	$\bar{2}.0917$	1.9083	
7 hrs	9.81	0.0081	$\bar{3}.9125$	2.0875	

Table No.22

2 Ethyl hexanol - phthalic anhydride reaction

Molar ratio - 0.25 : 0.118

Particle size - -20+30 mesh

Catalyst - Tulsion 14.

Catalyst concentration
(dry basis) - 15 meq

Time	Acid value mgms KOH/gm of the substance	Unreacted acid	log un- reacted acid	0.0000 -log unreacted acid	k
<u>Temperature - 85°C</u>					
2 hrs	134.00	0.1115	$\bar{1}.0473$	0.9527	
4 hrs	128.30	0.1092	$\bar{1}.0383$	0.9617	0.0002777
8 hrs	108.00	0.0901	$\bar{2}.9547$	1.0453	
12 hrs	91.30	0.0758	$\bar{2}.8798$	1.1203	
<u>Temperature - 117°C</u>					
2 hrs	102.40	0.0852	$\bar{2}.9305$	1.0695	
4 hrs	64.49	0.0537	$\bar{2}.7300$	1.2700	0.001667
6 hrs	39.77	0.331	$\bar{2}.5198$	1.4802	
9 hrs	19.36	0.0161	$\bar{2}.2074$	1.7926	
<u>Temperature - 140°C</u>					
1 hr	60.39	0.0502	$\bar{2}.7011$	1.2989	
2 hrs	27.53	0.0229	$\bar{2}.3598$	1.6402	0.005555
3 hrs	14.74	0.0117	$\bar{2}.0692$	1.9308	
4 hrs	6.92	0.0057	$\bar{3}.7604$	2.2396	

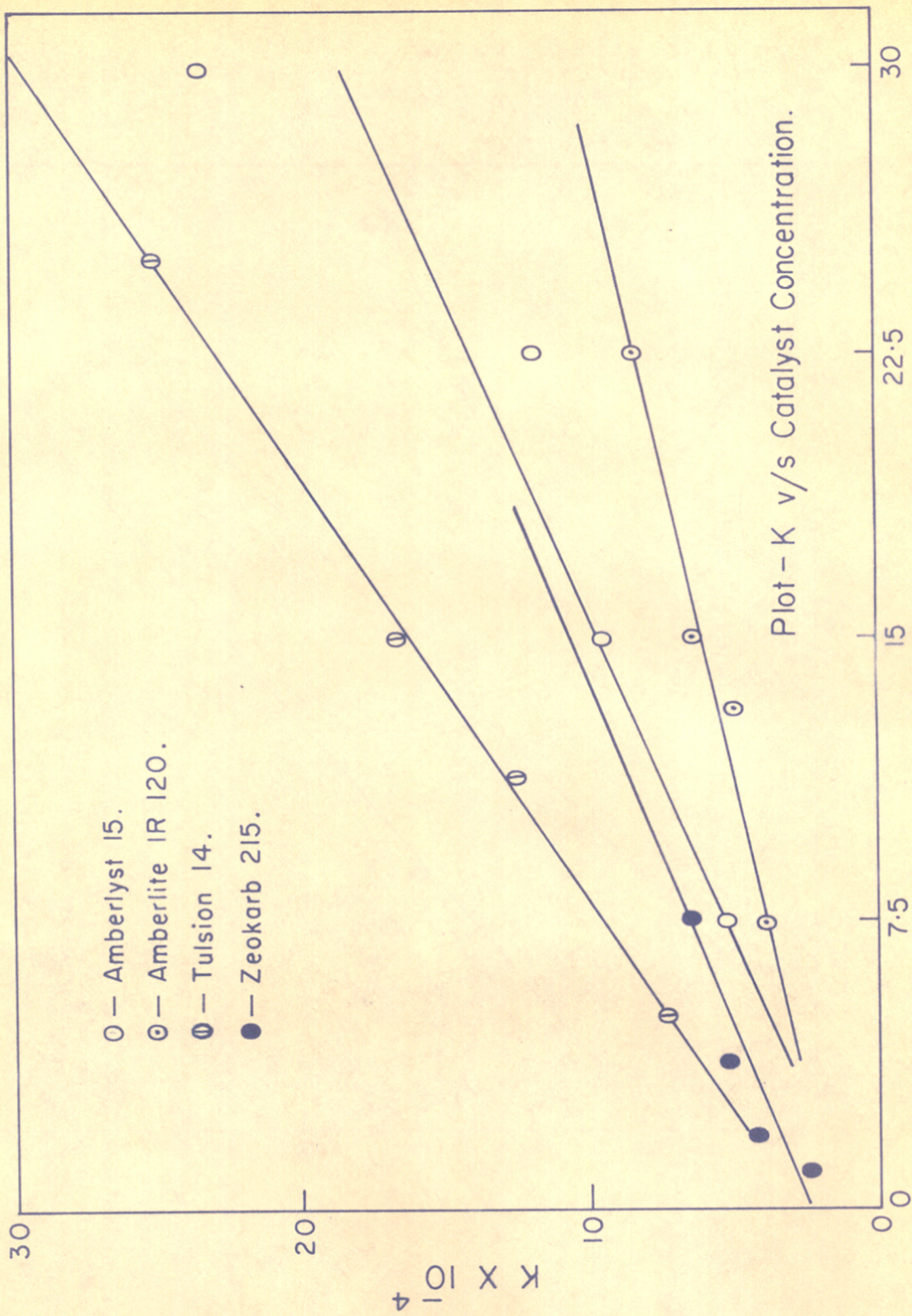


Fig. 3 - 2 Ethyl hexanol - Phthalic anhydride reaction.

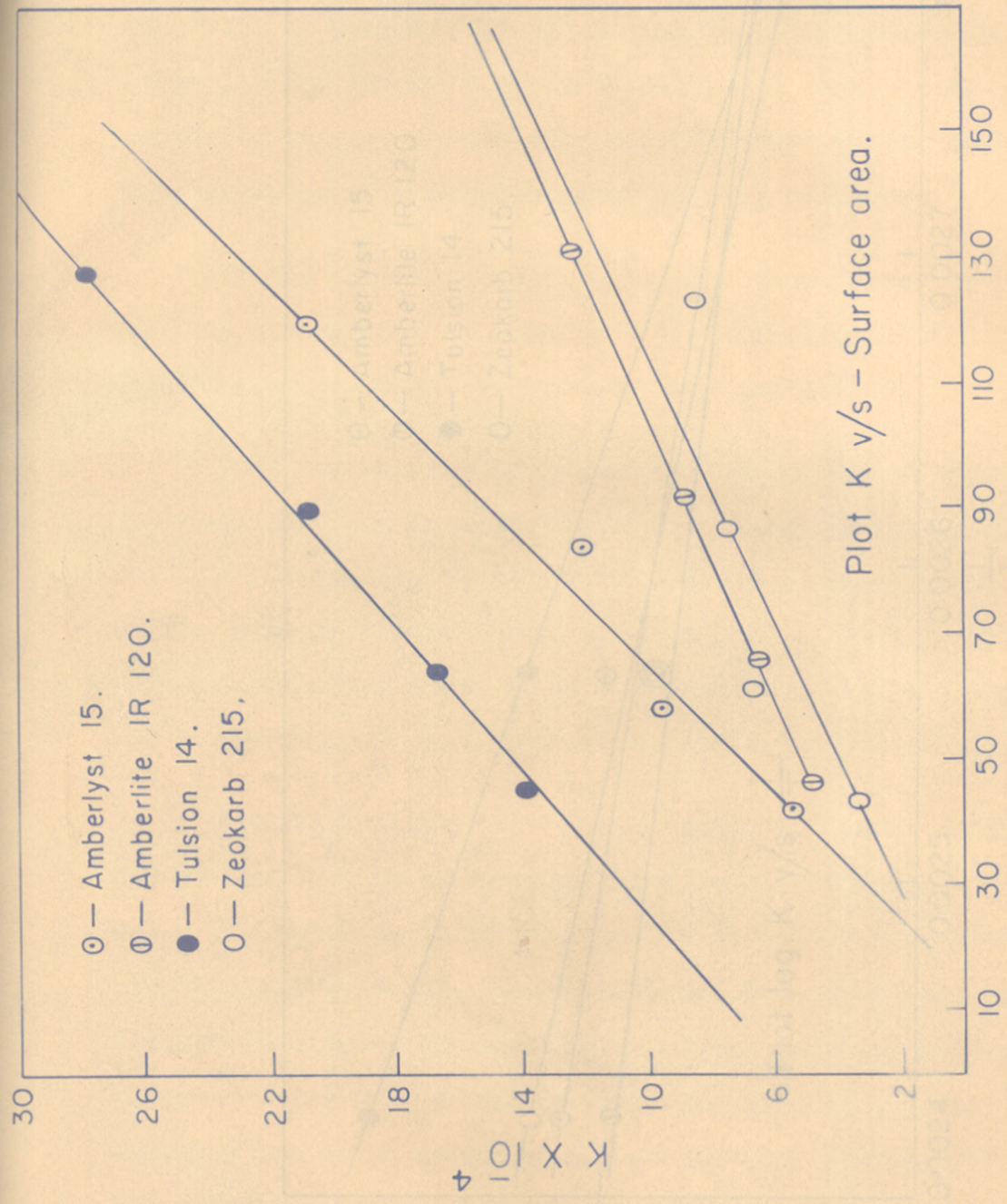


Fig. 4 - 2 Ethyl hexanol - Phthalic anhydride reaction.

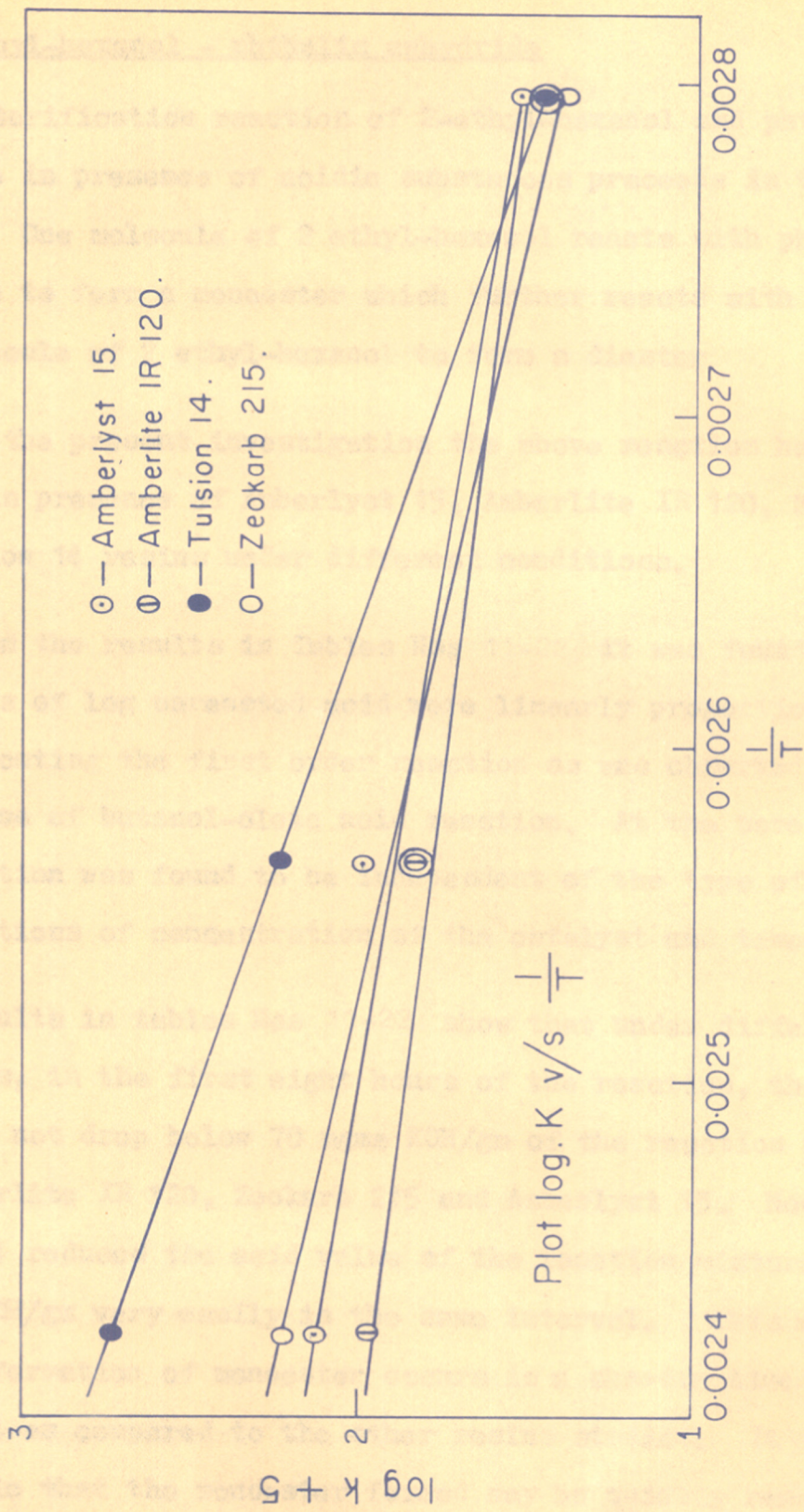


Fig.5 - 2 Ethyl hexanol - Phthalic anhydride reaction.

2. 2-Ethyl-hexanol - phthalic anhydride

Esterification reaction of 2-ethyl-hexanol and phthalic anhydride in presence of acidic substances proceeds in two stages. One molecule of 2 ethyl-hexanol reacts with phthalic anhydride to form a monoester which further reacts with one more molecule of 2 ethyl-hexanol to form a diester

In the present investigation the above reaction has been studied in presence of Amberlyst 15, Amberlite IR 120, Zeokarb 215 and Tulsion 14 resins under different conditions.

From the results in Tables Nos 11-22 it was found that the values of log unreacted acid were linearly proportional to time indicating the first order reaction as was observed earlier in the case of butanol-oleic acid reaction. At the same time, this reaction was found to be independent of the type of catalyst and variations of concentration of the catalyst and temperatures.

Results in tables Nos 11-22 show that under different conditions, in the first eight hours of the reaction, the acid value did not drop below 70 mgms KOH/gm of the reaction mixture with Amberlite IR 120, Zeokarb 215 and Amberlyst 15. However Tulsion 14 reduced the acid value of the reaction mixture below 70 mgms KOH/gm very easily in the same interval. This shows that the formation of monoester occurs in a shorter time with Tulsion 14 as compared to the other resins studied. It may also be possible that the monoester formed may be quickly reacting with another molecule of 2-Ethyl hexanol in presence of Tulsion 14.

On changing the catalyst concentration from 7.5 meq to 28.5 meq with Amberlite IR 120, it was observed that this change had little effect on the k value (Table No. 14) which was in the range of 3.97×10^{-4} to 8.33×10^{-4} .

On the other hand in the case of Amberlyst 15, when the concentration of the catalyst was changed from 7.5 meq to 30 meq, the k value changed from 7.3×10^{-4} to 23.28×10^{-4} , thus confirming the utility of the resin for use as catalyst.

Catalyst concentrations were maintained between 0.9375 meq to 7.5 meq for Zeokarb 215 and between 5 meq to 25 meq for Tulsion 14 resins respectively. It can be seen from Tables Nos.11 & 20 that for equal catalyst concentration of 15 meq, the k value for Tulsion 14 is higher than the value for Amberlyst 15. For equal catalyst concentration of 7.5 meq (tables Nos.11,14,17,20) the efficiencies in decreasing order for these cation-exchange resins can be given as follows:

Tulsion 14 Amberlyst 15 Zeokarb 215 Amberlite IR 120

In the studies on variations of the rate constant with particle size (Fig.4) it was observed that the rate constants were proportional to the area of the catalyst surface. These results clearly support the idea that particle size of the resin is one of the rate controlling factors for the esterification reaction.

Particularly in case of Tulsion 14 (Particle size - 40 + 50), the acid value of the reaction mixture was reduced

to 9 mgms KOH/gm indicating that the reaction had proceeded almost to completion. However in the same time interval, Tulsion 14 (-16 + 20 mesh) could not achieve the same reduction at the same catalyst concentration and temperature.

Results in tables 13, 16, 19, 22 showed that the rate of esterification reaction was greatly increased with increase in temperature. Although at higher temperatures of 140°C, Tulsion 14 and Zeokarb 215 lost their capacities due to desulphonation, this did not interfere much with the catalytic effect of the resins.

Activation energies for 2-ethyl-hexanol - phthalic anhydride reaction in presence of Tulsion 14, Zeokarb 215, Amberlyst 15 and Amberlite IR 120 were calculated from the Arrhenius equation.

Activation energies reported by other authors^{127,132,142,145} in the literature for various esterification reactions in presence of ion-exchange resins vary in the range of 10 kcal to 16 kcals which is observed in these investigations also. The activation energies obtained for 2 ethyl-hexanol - phthalic anhydride reaction were as follows:

Amberlyst 15	7.997 kcal
Amberlite IR 120	6.854 kcal
Tulsion 14	16.33 kcal
Zeokarb 215	10.28 kcal

It can be concluded from the results obtained in this catalysis study that Tulsion 14 resin, which is indigenously available, will be very much useful as a catalyst for 2 ethyl-hexanol - phthalic anhydride reaction.

Table No. 22

Adipic acid - ethylene glycol reaction

Resin used - Amberlyst 15.

Molar ratio - 0.25 : 0.313

Particle size.	Resin concentration	Temperature	Time Hrs. Mins	Acid value	Unreacted acid moles	p	$\frac{1}{1-p}$	k
1	2	3	4	5	6	7	8	9
-20+30 mesh	7.5 meq	107°C	2- 00	153.0	0.0665	0.734	3.76	1
			3- 15	116.0	0.058	0.768	4.31	0.008323
			4- 30	100.0	0.0501	0.7995	4.986	1
			5- 45	88.98	0.0445	0.823	5.65	1
			8- 00	72.38	0.0367	0.8533	6.815	1
-20+30 mesh	20 meq	107°C	2- 00	79.16	0.0396	0.8415	6.31	1
			3- 15	65.28	0.0326	0.87	7.696	0.01777
			3- 45	60.19	0.0301	0.8796	8.267	1
			4- 15	57.57	0.0288	0.885	8.695	1
			7- 45	40.56	0.0202	0.919	12.34	1

Continued.....

Table No. 23 (Contd). Adipic acid - ethylene glycol reaction (Resin used - Amberlyst 15)

1	2	3	4	5	6	7	8	9
-20+30 mesh	30 meq	107°C	2 - 00	74.03	0.0370	0.852	6.756	
			3 - 00	62.95	0.0315	0.874	7.935	0.02333
			3 - 30	56.44	0.0282	0.8873	8.872	
			4 - 15	51.12	0.0256	0.8976	9.766	
			5 - 00	45.12	0.02296	0.9581	10.87	
			6 - 30	38.96	0.0194	0.9225	12.9	
-40+20 mesh								
-16+20 mesh	15 meq	107°C	2 - 00	92.64	0.0463	0.8148	5.403	
			2 - 45	82.12	0.04105	0.8358	6.09	0.014
			3 - 45	73.72	0.03686	0.8526	6.785	
			4 - 00	70.53	0.03527	0.8589	7.09	
			8 - 00	48.4	0.0241	0.9036	10.37	
-20+30 mesh	15 meq	107°C	2 - 00	87.44	0.0437	0.8251	5.718	
			3 - 15	72.46	0.03622	0.855	6.896	0.01524
			4 - 00	67.82	0.0339	0.868	7.575	
			4 - 30	62.81	0.0314	0.8746	7.973	
			8 - 45	42.7	0.02126	0.915	11.76	

Table No. 23 (contd) Adipic acid - ethylene glycol reaction (Resin used - Amberlyst 15)

1	2	3	4	5	6	7	8	9
-30+40 mesh	15 meq	107°C	2-00	84.76	0.04288	0.8305	5.9	
			3-00	68.48	0.05424	0.855	6.9	0.01666
			3-30	67.69	0.05382	0.8665	7.49	
			4-00	63.77	0.0519	0.8726	7.85	
			8-00	41.37	0.0206	0.9176	12.14	
-40+50 mesh	15 meq	107°C	2-00	82.51	0.0411	0.836	6.1	
			3-15	66.40	0.0532	0.8673	7.535	0.01833
			3-40	62.63	0.0513	0.875	8.000	
			4-15	56.22	0.0281	0.8876	8.896	
			5-45	47.96	0.023970	0.904	10.42	
			8-00	38.96	0.0194	0.9225	12.9	
-20+30 mesh	15 meq	85°C	2-00	145.50	0.0727	0.7095	3.442	
			5-00	89.97	0.045	0.815	5.464	0.01222
			6-00	77.34	0.0387	0.845	6.45	
			6-30	74.04	0.037	0.852	6.756	
			8-00	64.46	0.0321	0.8718	7.8	

(Contd...)

6-00 ←

Table No. 23 (Contd) Adipic acid - ethylene glycol reaction (Resin used - Amberlyst 15)

1	2	3	4	5	6	7	8	9
-20+30 mesh	15 meq	140°C	2-00	68.06	0.034	0.864	7.354	
			4-00	49.64	0.0248	0.901	10.1	0.02222
			5-30	42.52	0.02126	0.915	11.76	
			7-30	33.85	0.01692	0.932	14.7	

Adipic acid - Diethylene glycol reaction.

				Molar ratio - 0.25 : 0.313				
-20+30 mesh	15 meq	107°C	1-15	54.26	0.0337	0.8655	7.435	
			4-00	16.99	0.0101	0.96	25.0	0.1
			6-00	11.42	0.0071	0.9716	35.22	
			7-00	7.85	0.00488	0.9805	40.74	

Adipic acid - propylene glycol reaction.

				Molar ratio - 0.25 : 0.313				
-20+30 mesh	15 meq	107°C	2-00	135.4	0.0742	0.703	3.367	
			4-00	126.4	0.068	0.7282	3.68	0.006666
			5-00	114.3	0.0614	0.7545	4.067	
			8-00	109.1	0.0587	0.7652	4.26	

(Contd.....)

Table No. 23 (Contd)

1	2	3	4	5	6	7	8	9
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Adipic acid - ethylene glycol reaction Molar ratio - 0.25 : 0.376

-20+30 mesh	15 meq	107°C	2-00	83.3	0.04149	0.8358	6.09
			3-40	59.44	0.0317	0.8755	7.902
			4-30	52.98	0.0283	0.887	8.85
			4-45	51.14	0.0273	0.891	9.175
			5-14	45.94	0.0245	0.902	10.2
			8-00	39.36	0.0196	0.9215	12.74

Adipic acid - ethylene glycol reaction. Molar ratio - 0.25 : 0.395

-20+30 mesh	15 meq	107°C	2-00	77.70	0.0387	0.845	6.45
			4-15	50.74	0.0276	0.890	9.09
			4-30	48.88	0.0266	0.894	9.436
			5-15	44.26	0.0241	0.9036	10.37
			5-35	42.31	0.02305	0.9076	10.82
			7-00	40.56	0.0202	0.919	12.34

Table No. 24

Adipic acid - ethylene glycol reaction

Resin used - Amberlite IR 120.

Molar ratio - 0.25 : 0.313

1	2	3	4	5	6	7	8	9
Particle size	Resin concentration	Temperature	Time Hrs.Mins.	Acid value	Unreacted acid moles	p	$\frac{1}{1-p}$	k
-20+30 mesh	3.75 meq	107°C	2-00	179.4	0.0897,	0.6412	2.787	
			3-45	158.2	0.0791	0.6836	3.16	0.003333
			6-00	140.2	0.0702	0.7195	3.647	
			8-0	127.4	0.0637	0.745	3.922	
-20+30 mesh	7.5 meq	107°C	2-00	154.0	0.0774	0.6905	3.231	
			4-00	112.4	0.0612	0.7552	4.085	0.006666
			6-00	103.5	0.0517	0.7934	4.838	
			10-00	97.23	0.0486	0.8455	6.473	

(Contd....)

Table No. 24 (Contd.) Adipic acid - ethylene glycol reaction (Resin used - Amberlite IR 120)

1	2	3	4	5	6	7	8	9
-20+30 mesh	20.5 meq	107°C	2-0	86.42	0.0432	0.8273	5.79	
			4-0	69.02	0.0345	0.8620	7.246	0.0125
			6-0	57.84	0.0288	0.8850	8.695	
			8-0	49.8	0.0248	0.9010	10.10	
-16+20 mesh	15.0 meq	107°C	1-30	116.5	0.058	0.768	4.31	
			3-0	104.3	0.0521	0.7917	4.801	
			5-30	88.49	0.0442	0.8234	5.663	0.005416
			7-00	82.26	0.04111	0.836	6.1	
			8-00	78.16	0.0391	0.8435	6.39	
-20+30 mesh	15 meq	107°C	2-00	106.6	0.0531	0.7878	4.713	
			3-0	95.55	0.0478	0.809	5.236	
			5-15	78.14	0.0391	0.8435	6.39	0.00875
			6-00	72.09	0.036	0.856	6.944	
			7-15	67.01	0.0335	0.8661	7.468	

(Contd.....)

Table No. 24 (Contd.) Adipic acid - ethylene glycol reaction (Resin used - Amberlite IR 120)

1	2	3	4	5	6	7	8	9
-50+40 mesh	15 meq	107°C	2-30	89.92	0.045	0.8201	5.556	
			4-00	76.4	0.0382	0.8471	6.54	0.01028
			4-45	71.6	0.0358	0.857	6.993	
			8-00	56.43	0.0281	0.8876	8.896	
-40+50 mesh	15 meq	107°C	2-00	82.54	0.04111	0.836	6.1	
			3-00	71.82	0.0359	0.8563	6.96	
			3-30	68.94	0.0344	0.862	7.256	0.01217
			4-15	64.23	0.0321	0.8718	7.8	
			5-15	58.01	0.029	0.884	8.62	
			8-00	47.8	0.0238	0.905	10.5	
-20+30 mesh	15 meq	85°C	2-00	156.9	0.0784	0.6864	3.19	
			4-00	127.2	0.0636	0.7456	3.931	0.005555
			6-30	106.1	0.0531	0.7878	4.713	
			8-00	94.1	0.0471	0.8117	5.31	

(Contd.....)

Table No. 24 (Contd) Adipic acid - ethylene glycol reaction (Resin used - Amberlite IR 120)

1	2	3	4	5	6	7	8	9
-20+30 mesh	15 meq	140°C	2-00	85.1	0.04238	0.8505	5.9	
			3-15	72.65	0.0363	0.8547	6.881	
			4-00	68.04	0.034	0.8641	7.358	0.01111
			5-15	61.37	0.0307	0.8773	8.149	
			8-00	49.71	0.0249	0.9006	10.06	

Adipic acid - propylene glycol reaction - Molar ratio - 0.25 : 0.313.

-20+30 mesh	15 meq	107°C	2-00	198.8	0.107	0.572	2.18	
			3-40	169.4	0.0911	0.629	2.695	0.04762
			5-10	152.4	0.0819	0.6725	3.053	
			6-30	126.5	0.068	0.7281	3.594	
			8-00	116.1	0.0625	0.75	4.000	

Adipic acid - diethylene glycol reaction - Molar ratio - 0.25 : 0.313

30 mesh	15 meq	107°C	2-0	58.04	0.0361	0.8555	6.92	
			5-0	26.44	0.0164	0.9346	18.05	0.06
			6-0	18.94	0.0118	0.953	21.28	
			8-0	14.16	0.0088	0.965	28.57	

Table No. 24 (Contd).

(Resin used - Amberlite IR 120)

1	2	3	4	5	6	7	8	9
<u>Adipic acid - Ethylene glycol.</u>								
30 mesh	15 meq	107°C	2-0	85.6	0.0455	0.818	5.5	
			3-0	79.34	0.0423	0.831	5.917	
			4-0	71.57	0.0382	0.8471	6.541	0.01042
			5-15	63.78	0.034	0.864	7.358	
			6-0	60.95	0.0324	0.8708	7.74	
			8-0	51.06	0.0275	0.891	9.15	
<u>Adipic acid - Ethylene glycol.</u>								
30 mesh	15 meq	107°C	2-00	77.79	0.04238	0.8305	5.9	
			4-30	60.22	0.0328	0.869	7.633	0.01083
			5-45	54.63	0.0298	0.8803	8.39	
			6-45	50.26	0.0274	0.8906	9.142	
			7-00	46.11	0.0251	0.892	9.26	

Table No. 25

Adipic acid - ethylene glycol reaction

Resin used - Zeokarb 215

Molar ratio - 0.25 : 0.513

Particle size	Resin concentration	Temperature	Time Hrs.Mins	Acid value	Unreacted acid moles	p	$\frac{1}{1-p}$	k
1	2	3	4	5	6	7	8	9
-16+20 mesh	7.5 meq	107°C	2-00	59.03	0.0294	0.8825	8.5	
			6-00	51.50	0.02575	0.897	9.71	0.004792
			9-00	47.8	0.0238	0.905	10.5	
			12-00	43.94	0.0220	0.912	11.36	
-20+30 mesh	7.5 meq	107°C	2-00	63.26	0.0315	0.8945	9.45	
			3-00	49.71	0.02485	0.9003	10.03	
			4-30	46.45	0.0232	0.9073	10.78	0.01
			6-00	42.62	0.0215	0.915	11.77	
8-00	38.73	0.0194	0.9225	12.9				

(Contd ...)

Table No. 25 (Contd)

Adipic acid - ethylene glycol reaction

(Resin used - Zeokarb)

1	2	3	4	5	6	7	8	9
-30+40 mesh	7.5 meq	107°C	1-30	23.46	0.0117	0.9535	21.5	
			2-00	22.73	0.0114	0.9546	22.04	0.02572
			6-00	18.05	0.00903	0.9640	27.77	
			8-00	15.96	0.00798	0.968	31.25	
-40+50 mesh	7.5 meq	107°C	2-00	16.42	0.00821	0.9672	30.49	
			4-00	14.55	0.00728	0.971	34.48	0.03056
			5-00	13.72	0.00686	0.9725	36.37	77
			8-00	12.12	0.00606	0.976	41.67	
-20+30 mesh	3.75 meq	107°C	2-00	92.23	0.0461	0.8156	5.424	
			5-30	74.61	0.0373	0.8567	6.697	0.006666
			7-15	68.39	0.0342	0.8631	7.305	
			8-00	65.95	0.03299	0.8681	7.581	

(Contd ...)

Table No. 25 (Contd) Adipic acid - ethylene glycol reaction (Resin used - Zeokarb 215)

1	2	3	4	5	6	7	8	9
-20+30 mesh	11.65 meq	107°C	2-00	43.45	0.0217	0.9132	11.52	
			4-45	36.2	0.0181	0.9276	13.82	0.01333
			7-00	32.25	0.0161	0.936	15.62	
			10-00	27.7	0.0139	0.9445	18.04	
-20+30 mesh	15 meq	107°C	2-00	37.15	0.0185	0.926	13.5	
			3-00	35.29	0.0175	0.93	14.29	
			4-00	32.28	0.0164	0.9346	15.29	0.015
			5-15	30.36	0.0152	0.9392	16.46	
			8-00	26.59	0.0133	0.9472	18.94	
-20+30 mesh	7.5 meq	85°C	1-00	188.0	0.094	0.624	2.66	
			2-00	167.5	0.0834	0.6666	3.00	0.007777
			5-30	107.0	0.0535	0.786	4.673	
			9-00	76.76	0.0384	0.8464	6.51	

(Contd ...)

Table No.25 (contd) Adipic acid - ethylene glycol reaction (Resin - Zeckarb 215)

1	2	3	4	5	6	7	8	9
-20+30 mesh	7.5 meq	140°C	1-00	16.47	0.00823	0.9672	30.49	
			1-30	15.97	0.00799	0.968	31.25	0.03833
			3-00	14.13	0.00706	0.9716	35.32	
			8-00	10.88	0.00544	0.9786	46.71	

Adipic acid - Diethylene Glycol

Molar Ratio - 0.25 : 0.313

1	2	3	4	5	6	7	8	9
-20+30 mesh	7.5 meq	107°C	1-00	23.62	0.0147	0.941	17.00	
			2-00	11.41	0.0071	0.975	35.00	0.2917
			4-30	4.982	0.0031	0.9876	80.65	
			6-00	3.905	0.00243	0.9959	106.2	

Adipic acid - propylene Glycol

Molar Ratio - 0.25 : 0.313

1	2	3	4	5	6	7	8	9
-20+30 mesh	7.5 meq	107°C	2-00	88.74	0.0477	0.828	5.814	
			5-00	63.60	0.0342	0.863	7.3	0.007406
			6-00	59.22	0.0318	0.873	7.873	
			9-30	51.05	0.00275	0.89	9.09	

(Contd)

Table No. 25 Contd. Adipic acid - ethylene glycol reaction (Resin used - Zeokarb 215)

1	2	3	4	5	6	7	8	9
<u>Adipic acid - ethylene glycol</u>								
-20+30 mesh	7.5 meq	107°C	2-00	27.18	0.0145	0.942	17.24	
			4-00	18.57	0.00925	0.963	27.03	0.06666
			6-30	15.81	0.00899	0.9665	29.86	
			8-00	11.93	0.00637	0.9745	39.22	
<u>Adipic acid - ethylene glycol</u>								
-20+30 mesh	7.5 meq	107°C	2-00	5.644	0.00307	0.9876	80.65	
			6-00	4.006	0.00218	0.991	111.1	0.125
			7-15	3.943	0.00215	0.9916	119.0	
			8-00	3.51	0.00191	0.9966	125	

(Contd.)

Table No. 26

Adipic acid - ethylene glycol reaction

(Resin used - Tulsion 14)

Molar ratio - 0.35 : 0.313

Particle size	Resin concentration	Temperature	Time Hrs. Mins.	Acid value	Unreacted acid moles	p	$\frac{1}{1-p}$	k
1	2	3	4	5	6	7	8	9
-20+30 mesh	3.75 meq	85°C	2-15	54.75	0.0274	0.8906	9.143	
			4-00	42.52	0.0213	0.9154	11.82	0.02055
			6-00	36.15	0.0181	0.928	13.89	
			8-00	30.79	0.0154	0.9385	16.26	
-20+30 mesh	3.75 meq	140°C	1-00	19.73	0.00986	0.9605	25.32	
			2-45	16.39	0.00819	0.968	31.25	0.055
			3-15	15.47	0.00773	0.9693	32.57	
			4-00	14.16	0.00708	0.9716	35.22	
8-00	10.45	0.0052	0.979	48.00				

(Contd)

Table No. 26 (Contd) Adipic acid - ethylene glycol reaction (Resin used - Division 14)

1 2 3 4 5 6 7 8 9

Adipic acid - diethylene glycol reaction Molar ratio - 0.25 : 0.313

-20+30 mesh	3.75 meq	107°C	1-00	33.07	0.0206	0.918	7.28	
			2-30	20.05	0.0125	0.95	20.0	0.1633
			3-00	16.06	0.00998	0.96	25.0	
			3-45	12.64	0.00786	0.969	32.25	
			5-50	8.345	0.0052	0.98	48.5	

Adipic acid - propylene glycol reaction Molar ratio - 0.25 : 0.313

-20+30 mesh	3.75 meq	107°C	1-00	124.8	0.0671	0.7516	3.726	
			3-00	79.62	0.0438	0.825	5.715	0.03334
			5-00	66.00	0.0344	0.8625	7.27	
			5-30	59.89	0.0322	0.8715	7.78	
			8-00	41.86	0.0225	0.9000	10.00	

(Contd....)

Table No. 26 (Contd)

(Resin used - Tulsion 14)

1 2 3 4 5 6 7 8 9

Adipic acid - ethylene glycol reaction

Molar ratio - 0.25 : 0.376

-20+30 mesh	3.75 meq 107°C	1-00	28.93	0.0143	0.943	17.54
		3-00	20.23	0.01	0.96	25.00
		4-00	18.48	0.00913	0.9636	27.47
		8-00	12.14	0.006	0.9765	42.00
						0.06

Adipic acid - ethylene glycol reaction

Molar ratio - 0.25 : 0.395

-20+30 mesh	3.75 meq 107°C	1-00	18.05	0.00983	0.961	25.64
		4-15	9.495	0.0051	0.9793	48.31
		6-00	7.52	0.00410	0.9838	61.73
		8-00	6.89	0.00375	0.9853	74.52
						0.12

-16+20 mesh 3.75 meq 107°C

1-00	36.59	0.0183	0.927	13.7
4-00	28.89	0.01445	0.942	17.24
6-30	24.83	0.0124	0.9505	20.2
11-00	19.42	0.00971	0.9615	25.97
				0.02039

(Contd)

Table No. 26 (Contd)

(Resin used - Tulsion 14)

1	2	3	4	5	6	7	8	9
-20+30 mesh	3.75 meq	107°C	2-00	26.77	0.0134	0.9465	18.68	
			5-30	20.88	0.0103	0.959	24.39	0.02666
			7-00	18.72	0.00936	0.9625	26.67	
			8-30	17.1	0.00855	0.9656	29.07	
-30+40 mesh	3.75 meq	107°C	1-30	23.36	0.0117	0.9535	21.5	
			2-00	22.76	0.0114	0.9546	22.01	0.0375
			6-00	15.96	0.0798	0.968	31.25	
			8-00	14.05	0.0702	0.972	35.7	
-40+50 mesh	3.75 meq	107°C	1-00	20.50	0.0104	0.9585	24.1	
			1-30	19.75	0.00987	0.9605	25.32	0.0431
			4-30	15.25	0.00762	0.9696	32.9	
			8-00	12.4	0.0062	0.9763	42.2	

(Contd...)

Table No. 26 (Contd)

(Resin used - Tulsion 14)

1	2	3	4	5	6	7	8	9
-20+30 mesh	0.75 meq	107°C	1-00	171.4	0.0857	0.6572	2.918	
			5-00	88.57	0.0442	0.8233	5.56	0.01111
			7-30	11.45	0.0357	0.857	6.992	
			8-00	69.90	0.03495	0.86	7.144	
-20+30 mesh	1.5 meq	107°C	1-00	86.75	0.0432	0.8275	6.8	
			4-00	45.2	0.0225	0.9000	10.00	0.01777
			6-00	41.25	0.0206	0.9176	12.14	
			7-00	37.65	0.0189	0.9245	13.25	
			8-00	35.24	0.0176	0.9256	14.2	
-20+30 mesh	7.5 meq	107°C	1-00	18.42	0.00921	0.9633	27.24	
			4-00	10.62	0.00531	0.9788	47.18	0.1
			6-00	8.62	0.00431	0.9828	58.14	
			8-00	7.29	0.00364	0.9856	69.44	

Table No. 27

Sebacic acid - ethylene glycol reaction

Resin used - Amberlyst 15.

Molar ratio - 0.1666 : 0.208

Particle size	Resin concentration	Temperature	Time Hrs. Mins	Acid value	Unreacted acid moles	p	$\frac{1}{1-p}$	k
1	2	3	4	5	6	7	8	9
-20+30 mesh	3.75 meq	107°C	2-00	134.3	0.0557	0.666	2.994	
			3-00	129.2	0.0536	0.6767	3.112	0.001666
			4-00	128.9	0.0524	0.686	3.185	
			6-00	126.2	0.0491	0.706	3.402	
			8-00	112.4	0.0466	0.7206	3.58	
-20+30 mesh	7.5 meq	107°C	2-00	129.8	0.054	0.675	3.077	
			2-45	125.1	0.05195	0.6882	3.207	0.0025
			4-00	118.4	0.0491	0.706	3.402	
			8-00	97.66	0.0405	0.7572	4.12	

92.43

91.16

(Contd ...)

Table No. 27 (Contd) Sebacic acid - ethylene glycol reaction (Resin used - Amberlyst 15)

1	2	3	4	5	6	7	8	9
-20+30 mesh	15 meq	107°C	2-00	108.3	0.045	0.73	3.703	
			3-00	98.95	0.0411	0.7537	4.061	0.00613
			5-45	83.45	0.0347	0.804	5.101	
			6-00	77.5	0.0322	0.807	5.181	
			8-00	68.18	0.02828	0.8305	5.9	
-20+30 mesh	20 meq	107°C	2-00	100.2	0.0416	0.7506	4.01	
			4-00	79.86	0.0332	0.801	5.025	0.008750
			4-45	73.67	0.0306	0.8165	5.45	
			5-30	68.68	0.0285	0.829	5.85	
			9-30	52.08	0.0216	0.8706	7.727	
-16+20 mesh	15 meq	107°C	2-00	118.5	0.0493	0.7043	3.305	
			4-00	105.92	0.043	0.7421	3.877	0.004166
			6-00	92.41	0.0384	0.7700	4.348	
			8-00	81.16	0.0357	0.798	4.95	

Table No. 27 (contd) Sebecic acid - ethylene glycol reaction (Resin used - Amberlyst 15)

1	2	3	4	5	6	7	8	9
-50+40 mesh	15 meq	107°C	2-00	98.56	0.04095	0.7542	4.068	
			2-30	91.89	0.0382	0.771	4.567	0.007915
			3-45	82.6	0.0343	0.7944	4.863	
			6-00	67.47	0.02805	0.832	5.953	
			9-00	54.96	0.0228	0.8633	7.315	
-40+50 mesh	15 meq	107°C	2-00	93.2	0.0387	0.768	4.31	
			2-30	88.22	0.03665	0.78	4.545	0.009165
			3-45	76.8	0.0319	0.8087	5.227	
			5-30	64.85	0.02693	0.8384	6.19	
			6-15	61.05	0.0254	0.8475	6.56	
			9-30	49.01	0.02033	0.8785	8.231	
-20+30 mesh	15 meq	85°C	1-00	180.8	0.0749	0.5384	2.117	
			6-00	115.2	0.0479	0.713	3.484	0.004166
			8-30	98.19	0.0408	0.7556	4.092	
			10-00	89.73	0.0373	0.7765	5.227	

Table No. 27 (Contd) Sebacic acid - ethylene glycol reaction (Resin used - Amberlyst 15)

1	2	3	4	5	6	7	8	9
-20+30 mesh	15 meq	140°C	2-00	76.83	0.0319	0.8087	5.227	
			3-00	64.73	0.02685	0.839	6.212	0.01667
			6-30	42.39	0.0176	0.8946	9.486	
			7-00	39.41	0.0164	0.9016	10.16	
			8-00	36.34	0.0151	0.9095	11.08	

Ethylene glycol - sebacic acid reaction

Molar ratio - 0.252 : 0.1666

1	2	3	4	5	6	7	8	9
-20+30 mesh	15 meq	107°C	2-00	86.35	0.03413	0.7955	4.89	
			3-30	75.90	0.03	0.8200	5.555	0.007223
			4-15	68.23	0.0286	0.8287	5.837	
			5-00	65.04	0.02685	0.8390	6.2111	
			8-00	61.10	0.0222	0.8665	7.5	

(Contd..)

Table No. 27 (Contd) Sebacic acid - ethylene glycol reaction (Resin used - Amberlyst 15)

1	2	3	4	5	6	7	8	9
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Sebacic acid - ethylene glycol reaction
Molar ratio - 0.1666 : 0.2663

-20+30 mesh	15 meq	107°C	2-00	57.42	0.0256	0.8464	6.51
			2-15	56.27	0.0252	0.849	6.622
			2-45	53.95	0.0242	0.8545	6.872
			4-30	47.89	0.02144	0.872	7.812
			8-00	38.28	0.01717	0.897	9.71

Sebacic acid - propylene glycol reaction
Molar ratio - 0.1666 : 0.208

-20+30 mesh	15 meq	107°C	2-00	174.6	0.0771	0.5377	2.166
			4-00	148.5	0.0656	0.6067	2.543
			5-00	134.3	0.0593	0.6446	2.814
			7-10	126.5	0.05585	0.671	3.04
			10-00	107.4	0.04755	0.715	3.51

Sebacic acid - diethylene glycol reaction
Molar ratio - 0.1666 : 0.208

-20+30 mesh	15 meq	107°C	1-05	93.78	0.04755	0.715	3.51
			2-45	38.73	0.01965	0.8025	8.492
			6-40	15.75	0.00799	0.9525	21.05
			7-30	14.01	0.00711	0.9576	23.59
			8-00	12.97	0.00658	0.9605	25.72

Table No. 23

Sebacic acid - ethylene glycol reaction

Resin used - Amberlite IR 120

Molar ratio - 0.1666 : 0.208

Particle size	Resin concentration	Temperature	Time Hrs.Mins	Acid value	Unreacted acid moles	$\frac{1}{1-p}$	k
1	2	3	4	5	6	7	8 9
-20+30 mesh	3 meq	107°C	2-00	192.2	0.0799	0.5216	2.09
			4-00	181.4	0.0753	0.5487	2.215 0.00125
			5-00	173.3	0.072	0.5684	2.317
			8-00	156.4	0.065	0.6103	2.567
-20+30 mesh	7.5 meq	107°C	2-00	185.3	0.077	0.5384	2.166
			2-45	179.4	0.0745	0.5534	2.24 0.001806
			3-45	172.3	0.0716	0.5706	2.329
			8-00	142.9	0.0594	0.6439	2.808

(Contd...)

1	2	3	4	5	6	7	8	9
-20+30 mesh	20.5 meq	107°C	2-00	158.5	0.0659	0.6048	2.53	
			5-00	117.1	0.04753	0.715	3.51	
			6-30	103.0	0.0428	0.7433	3.896	0.005138
			7-00	99.24	0.04123	0.7522	4.068	
			8-00	92.58	0.0384	0.77	4.348	
-16+20 mesh	15 meq	107°C	2-00	182.00	0.0749	0.569	2.227	
			4-30	153.1	0.0636	0.6187	2.623	0.002717
			7-30	127.3	0.0529	0.683	3.154	
			9-30	115.0	0.0473	0.7133	3.487	
-20+30 mesh	15 meq	107°C	2-00	178.0	0.074	0.5562	2.253	
			4-30	149.1	0.062	0.6283	2.69	0.003194
			7-00	125.7	0.05220	0.687	3.195	
			9-00	112.2	0.0466	0.7206	3.59	

(Contd ...)

Table No. 28 (Contd) Sebacic acid - ethylene glycol reaction (Resin used - Amberlite IR 120)

1	2	3	4	5	6	7	8	9
-30+40 mesh	15 meq	107°C	2.00	174.2	0.0724	0.5562	2.305	
			4-00	146.7	0.061	0.6345	2.736	0.003472
			6-30	124.7	0.0518	0.6895	3.22	
			8-30	110.4	0.0459	0.725	3.637	
-40+50 mesh	15 meq	107°C	2-00	169.6	0.0705	0.581	2.386	
			4-00	142.9	0.0594	0.644	2.81	0.00375
			6-00	122.5	0.0509	0.695	3.279	
			9-00	100.7	0.0418	0.7494	3.991	
-20+30 mesh	15 meq	85°C	2-00	314.9	0.121	0.2146	1.373	
			6-00	254.0	0.1055	0.3675	1.581	0.001146
			7-00	246.1	0.1022	0.3846	1.625	
			8-00	238.2	0.0989	0.406	1.686	

(Contd....)

Table No. 28 (Contd) (Resin used -Amberlite IR 120)

1	2	3	4	5	6	7	8	9
-20+30 mesh	15 meq	140°C	2-00	147.8	0.0613	0.6325	2.72	
			4-00	125.3	0.0521	0.6876	3.2	0.00375
			5-00	117.7	0.0489	0.7072	3.415	
			6-00	109.7	0.0456	0.7266	3.657	
			8-00	97.4	0.0405	0.7572	4.12	

Sebacic acid - ethylene glycol reaction Molar ratio - 0.1666 : 0.252

-20+30 mesh	15 meq	107°C	2-00	162.6	0.0715	0.5847	2.403	
			3-30	141.4	0.0622	0.627	2.681	0.003403
			6-00	117.6	0.0517	0.69	3.225	
			8-00	104.5	0.0459	0.725	3.637	

Sebacic acid - ethylene glycol reaction Molar ratio - 0.1666 : 0.2663

-20+30 mesh	15 meq	107°C	2-00	150.7	0.0675	0.5953	2.47	
			3-45	128.6	0.0576	0.6546	2.895	0.00389
			5-45	111.4	0.0499	0.701	3.345	
			8-00	96.2	0.0431	0.7416	3.87	

(Contd)

Table No. 28 (Contd)

(Resin used - Amerlite IR 120)

1 2 3 4 5 6 7 8 9

Sebacic acid - diethylene glycol reaction Molar ratio - 0.1666 : 0.208

Mesh	Meq	Temp (°C)	Reaction	Molar ratio	Value	Value	Value
-20+30	15	107	2-00	0.0789	0.53	2.128	
			4-00	0.0349	0.7907	4.78	0.01875
			6-00	0.0247	0.852	6.756	
			7-00	0.0213	0.8725	7.844	
			8-30	0.01753	0.8952	9.545	

Sebacic acid - propylene glycol reaction

Molar ratio - 0.1666 : 0.208

Mesh	Meq	Temp (°C)	Reaction	Molar ratio	Value	Value	Value
-20+30	15	107	2-00	0.118	0.2926	1.414	
			3-00	0.115	0.3105	1.45	0.001296
			6-00	0.1002	0.3993	1.665	
			8-00	0.0892	0.4652	1.87	

1
9
1

Table No. 29

Sebacic acid - ethylene glycol reaction

Resin used - Zeokarb 215

Molar ratio - 0.1656 : 0.208

1	2	3	4	5	6	7	8	9
Particle size	Resin concentration	Temperature	Time Hrs.Mins	Acid value	Unreacted acid moles	p	$\frac{1}{1-p}$	k
-20+30 mesh	0.9375 meq	107°C	2-00	156.5	0.0650	0.6097	2.563	
			4-00	153.5	0.0638	0.6174	2.614	0.001515
			6-10	137.3	0.0584	0.6500	2.857	96
			8-35	130.2	0.0546	0.6726	3.055	
-20+30 mesh	1.875 meq	107°C	1-50	121.6	0.0506	0.697	3.3	
			3-00	117.0	0.0497	0.702	3.356	0.001852
			6-00	106.0	0.0441	0.7355	3.78	
			8-00	101.0	0.042	0.748	3.968	

(Contd ...)

Table No. 29 (Contd) Sebacic acid - ethylene glycol reaction (Resin used - Zeokarb 215)

1	2	3	4	5	6	7	8	9
-20+30 mesh	6 meq	107°C	1-30	95.52	0.0397	0.762	4.202	
			4-00	77.27	0.0321	0.8075	5.195	0.006666
			6-45	64.28	0.0267	0.840	6.25	
			8-00	58.86	0.0245	0.853	6.803	
-20+30 mesh	7.5 meq	107°C	0-30	90.1	0.0374	0.776	4.465	
			1-00	86.22	0.0358	0.7853	4.657	0.007777
			4-45	62.53	0.026	0.844	6.41	
			10-00	45.26	0.01880	0.8875	8.89	
-16+20 mesh	7.5 meq	107°C	2-00	166.0	0.069	0.5863	2.418	
			2-45	156.2	0.0649	0.611	2.571	0.003333
			4-15	139.2	0.0578	0.6535	2.886	
			8-00	108.8	0.0452	0.729	3.69	

(Contd...)

Table No. 29 (Contd): Sebacic acid - ethylene glycol reaction (Resin used - Zeokarb 215)

1	2	3	4	5	6	7	8	9
-30+40 mesh	7.5 meq	107°C	0-30	85.16	0.0354	0.788	4.75	
			1-45	74.41	0.0309	0.8147	5.396	0.009165
			4-45	57.38	0.02384	0.857	6.993	
			10-00	40.08	0.01695	0.8985	9.856	
-40+50 mesh	7.5 meq	107°C	2-00	63.93	0.02656	0.8403	6.26	
			3-45	54.91	0.0228	0.8633	7.315	0.01083
			4-30	51.91	0.0216	0.8706	7.727	
			8-00	40.10	0.01665	0.9000	10.00	
-20+30 mesh	7.5 meq	85°C	2-00	134.5	0.0559	0.665	2.986	
			5-15	93.2	0.0387	0.768	4.31	0.006664
			7-30	82.10	0.0341	0.8075	5.195	
			8-00	74.30	0.0309	0.815	5.415	

(Continued ...)

Table No. 23 (Cont). Sebacic acid - ethylene glycol reaction (Resin used - Zeokarb 215)

1	2	3	4	5	6	7	8	9
-20+30 mesh	7.5 meq	140°C	0-30	75.83	0.0313	0.812	5.32	
			1-00	71.17	0.0298	0.8214	5.66	
			1-15	70.41	0.02925	0.8256	5.728	0.01
			2-00	64.34	0.02685	0.839	6.212	
			8-00	44.71	0.01845	0.897	9.7	

Sebacic acid - propylene glycol reaction

1	2	3	4	5	6	7	8	9
-20	+30 mesh	7.5 meq	107°C	2-00	158.06	0.0699	0.581	2.586
				4-00	144.05	0.0637	0.618	2.618
				6-00	138.3	0.0613	0.6325	2.72
				8-00	120.05	0.0534	0.68	3.125

Molar ratio - 0.1666 ; 0.208

Sebacic acid - diethylene glycol reaction

1	2	3	4	5	6	7	8	9
-20	+30 mesh	7.5 meq	107°C	2-00	128.04	0.0651	0.6097	2.563
				5-45	43.18	0.0219	0.8685	7.603
				6-15	37.86	0.0192	0.8806	8.375
				10.00	24.85	0.0126	0.9245	13.25

Molar ratio - 0.1666 ; 0.208

(Continued...)

Table No. 29. (Contd) Sebacic acid - ethylene glycol reaction (Resin - Zeokarb 215)

1	2	3	4	5	6	7	8	9
-20+30 mesh	7.5 meq	107°C	2-00	39.1	0.0172	0.9113	11.28	
			4-30	28.99	0.01275	0.923	12.98	0.01111
			6-00	27.00	0.0119	0.9286	14.01	
			6-30	26.04	0.0116	0.9305	14.39	
			8-00	24.38	0.0107	0.935	15.38	

Molar ratio - 0.1666 : 0.252

Sebacic acid - ethylene glycol reaction

Sebacic acid - ethylene glycol reaction

Molar ratio - 0.1666 : 0.2663

-20+30 mesh	7.5 meq	107°C	1-00	28.12	0.01275	0.923	12.98	
			4-45	20.58	0.00922	0.945	18.18	0.02387
			6-45	18.15	0.00814	0.952	20.84	
			8-00	16.48	0.00733	0.956	22.75	

Table No. 30

Sebacic acid - ethylene glycol reactionResin used - Tulsion 14

Molar ratio - 0.1666 : 0.208

1	2	3	4	5	6	7	$\frac{1}{1-p}$	8	9
Particle size	Resin concentration	Temperature	Time Hrs.Mins	Acid value	Unreacted acid moles	p			k
-20+30 mesh	0.75 meq	107°C	1-00	140.3	0.0583	0.6505		2.861	
			2-00	151.1	0.0545	0.6705		3.062	0.002361
			5-00	116.9	0.0483	0.7106		3.455	
			12-00	87.9	0.0365	0.781		4.566	
-20+30 mesh	1.5 meq	107°C	1-00	115.8	0.0481	0.7116		3.467	
			4-00	100.9	0.0419	0.7486		3.95	0.003334
			6-00	92.4	0.0385	0.77		4.348	
			8-00	83.43	0.0347	0.792		4.797	
-20+30 mesh	7.5 meq	107°C	1-0	36.2	0.015	0.91		11.11	
			3-00	30.4	0.0126	0.9245		13.25	0.0175
			5-45	25.2	0.01045	0.9376		16.02	
			9-30	20.1	0.00835	0.95		20.00	

Table No. 30 (Contd.) Sebacic acid - ethylene glycol reaction (Resin used - Tulsion 14)

1	2	3	4	5	6	7	8	9
-16+20 mesh	3.75 meq	107°C	1-00	44.39	0.01845	0.89	9.09	
			3-00	41.33	0.01717	0.897	9.71	0.004167
			8-00	37.54	0.0156	0.9066	10.71	
			12-00	34.33	0.01435	0.9143	11.67	
-20+30 mesh	3.75 meq	107°C	1-00	40.12	0.0167	0.90	10.00	
			3-00	38.24	0.0159	0.905	10.53	0.004444
			3-30	37.08	0.0157	0.906	10.63	
			11-00	31.06	0.0131	0.9215	12.74	
-30+40 mesh	3.75 meq	107°C	2-00	36.11	0.015	0.91	11.11	
			4-00	33.06	0.01395	0.9166	11.99	0.00722
			7-00	30.05	0.0125	0.925	13.33	
			10-00	27.08	0.01155	0.9313	14.55	

(Contd ...)

Table No. 30 (Contd.) Sebacic acid - ethylene glycol reaction (Resin used - Tulsion 14)

1	2	3	4	5	6	7	8	9
-40+50 mesh	3.75 meq	107°C	1-30	36.73	0.0148	0.9113	11.28	
			4-00	31.06	0.0131	0.9215	12.78	0.01055
			5-00	29.15	0.0121	0.9255	13.42	
			10-00	23.97	0.00996	0.94	16.66	
-20+30 mesh	3.75 meq	85°C	2-00	71.85	0.0298	0.8215	5.6	
			4-00	66.32	0.02755	0.8352	6.067	0.003055
			7-00	60.05	0.02515	0.8492	6.033	
			16-00	48.93	0.02033	0.8785	8.231	
-20+30 mesh	3.75 meq	140°C	2-00	33.51	0.0139	0.9166	12.0	
			4-00	31.34	0.013	0.922	12.8	0.006806
			6-00	29.42	0.0122	0.9266	13.6	
			10-00	26.28	0.0109	0.935	15.35	

Ethylene glycol - sebacic acid reaction Molar ratio - 0.252 : 0.1666

-20+30 mesh	3.75 meq	107°C	2-00	15.62	0.00687	0.5882	24.87	
			2-30	14.79	0.0065	0.6103	25.38	0.01805
			4-15	13.63	0.00599	0.641	27.14	
			7-45	12.17	0.00535	0.6793	30.86	

(Contd.....)

Table No. 30 (Contd.)

1	2	3	4	5	6	7	8	9
<u>Sebacic acid - Ethylene glycol reaction</u>								
-20+30 mesh	3.75 meq	107°C	1-00	15.04	0.00673	0.59565	25.00	
			1-15	14.58	0.00653	0.6083	25.36	0.025
			1-45	14.02	0.00636	0.6187	26.04	
			4-00	12.54	0.005615	0.6619	29.5	
			8-00	10.28	0.0046	0.972	35.75	
<u>Sebacic acid - propylene glycol reaction</u>								
-20+30 mesh	3.75 meq	107°C	1-00	164.7	0.0727	0.5641	2.294	
			4-00	124.2	0.0548	0.6715	3.044	0.004167
			8-00	92.7	0.0409	0.755	4.081	
			12-00	79.6	0.03435	0.7943	4.861	
<u>Sebacic acid - diethylene glycol reaction</u>								
-20+30 mesh	3.75 meq	107°C	0-45	61.91	0.0314	0.8117	5.31	
			2-00	25.45	0.0129	0.923	12.98	0.1133
			6-50	7.156	0.00363	0.9786	46.73	
			7-30	6.66	0.00338	0.9805	51.28	

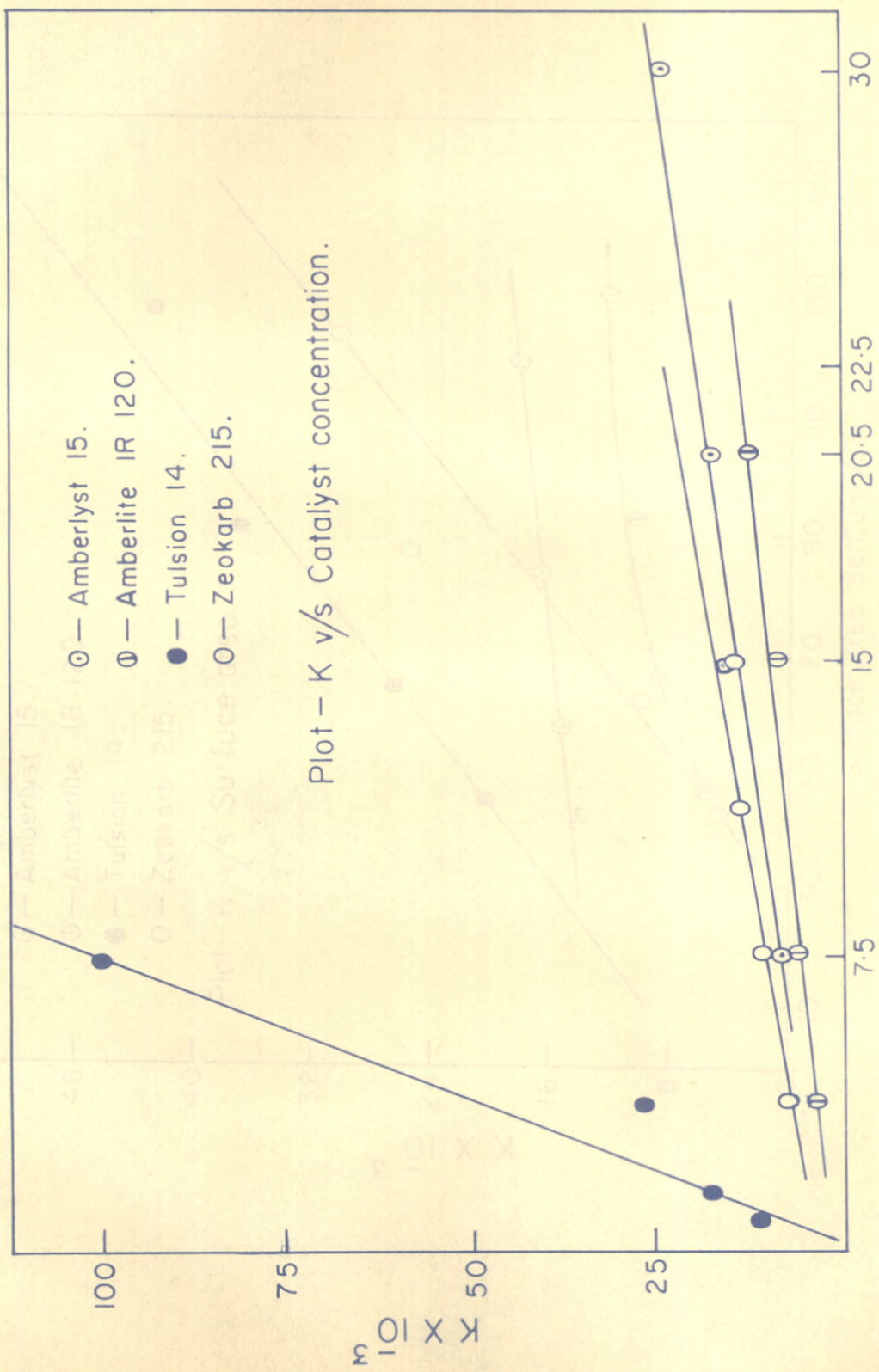


Fig. 6 - Adipic acid - Ethylene glycol reaction.

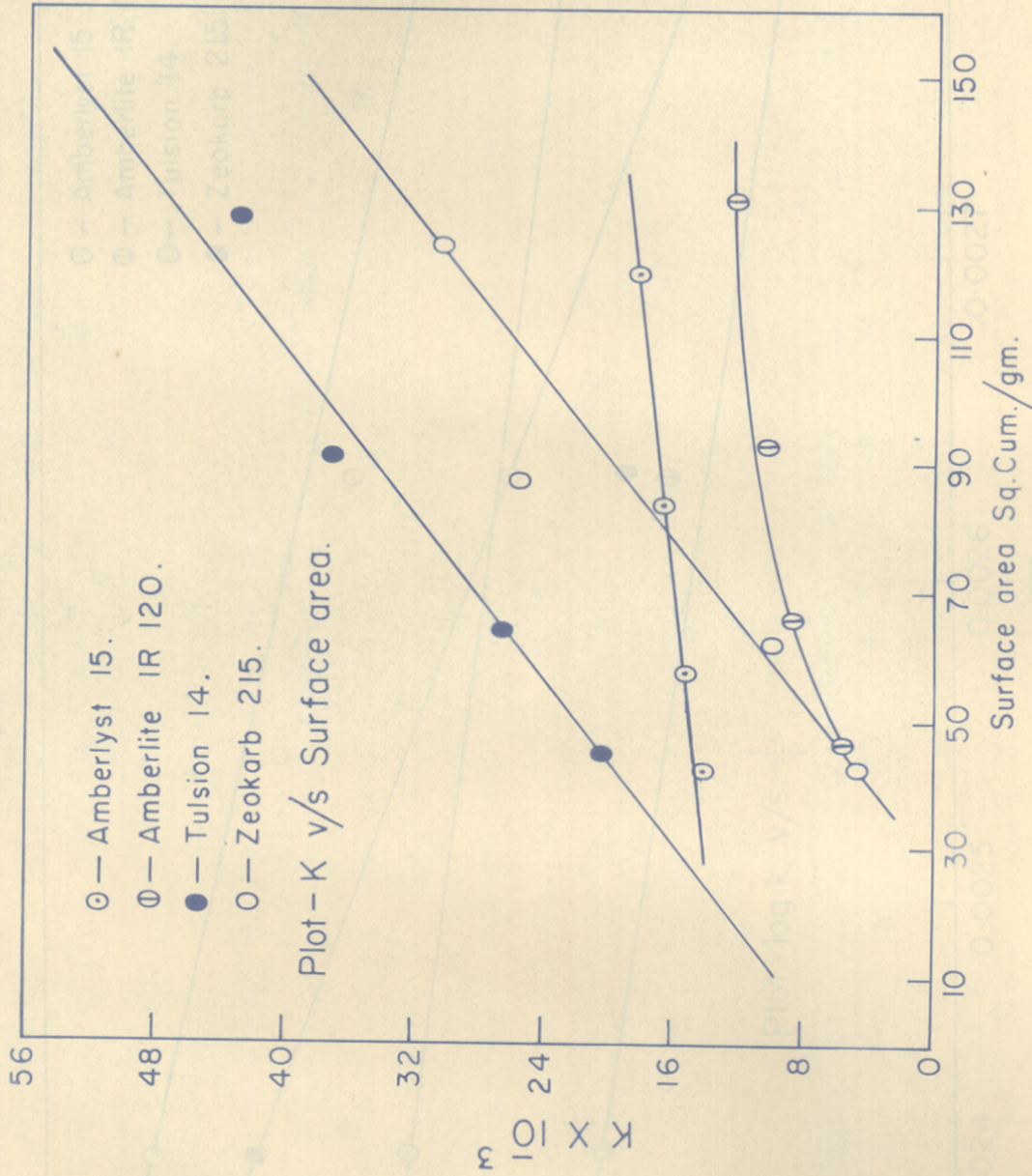


Fig. 7 — Adipic acid - Ethylene glycol reaction.

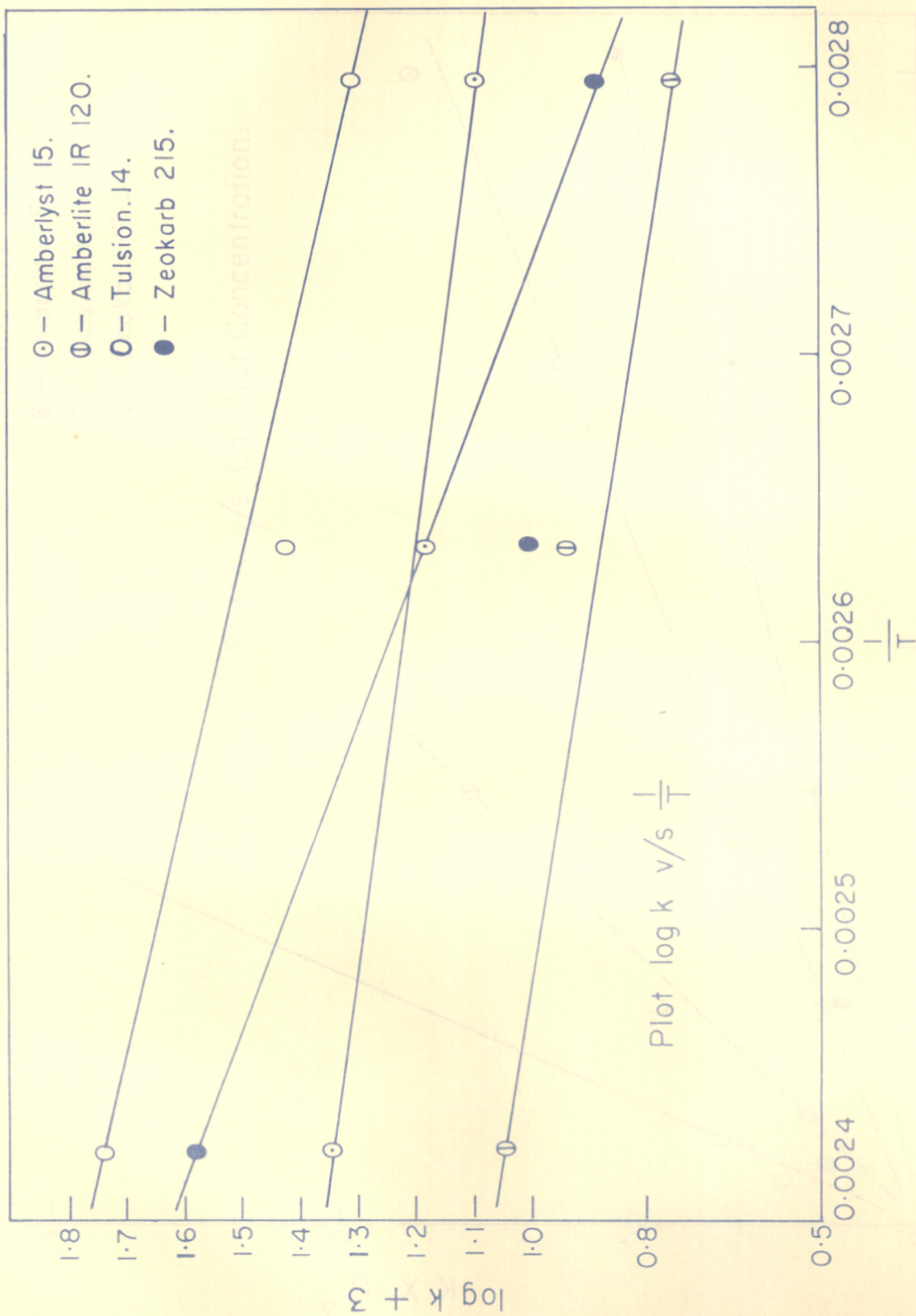


Fig.8 — Adipic acid-Ethylene glycol reaction.

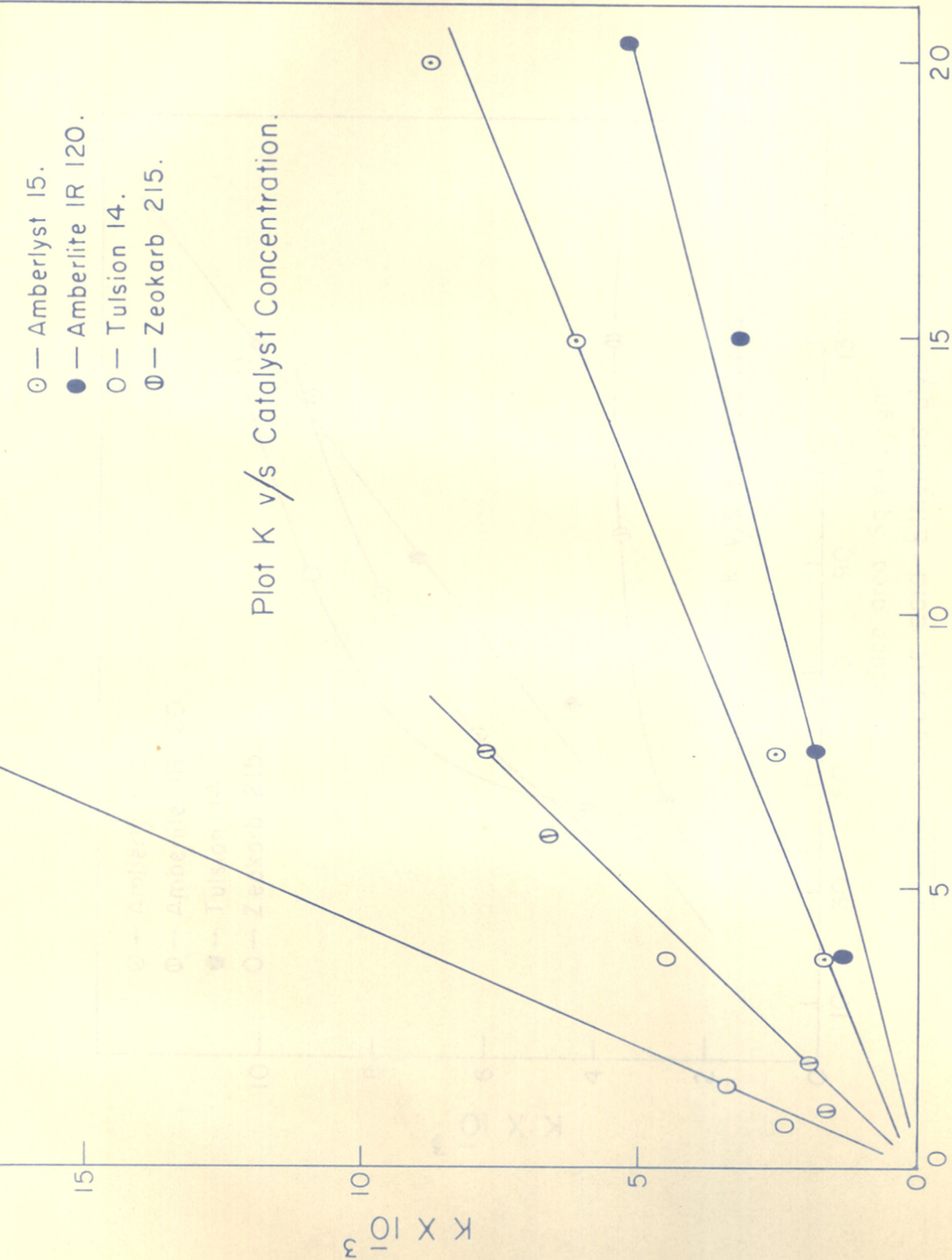


Fig. 9 — Sebacic acid - Ethylene glycol reaction.

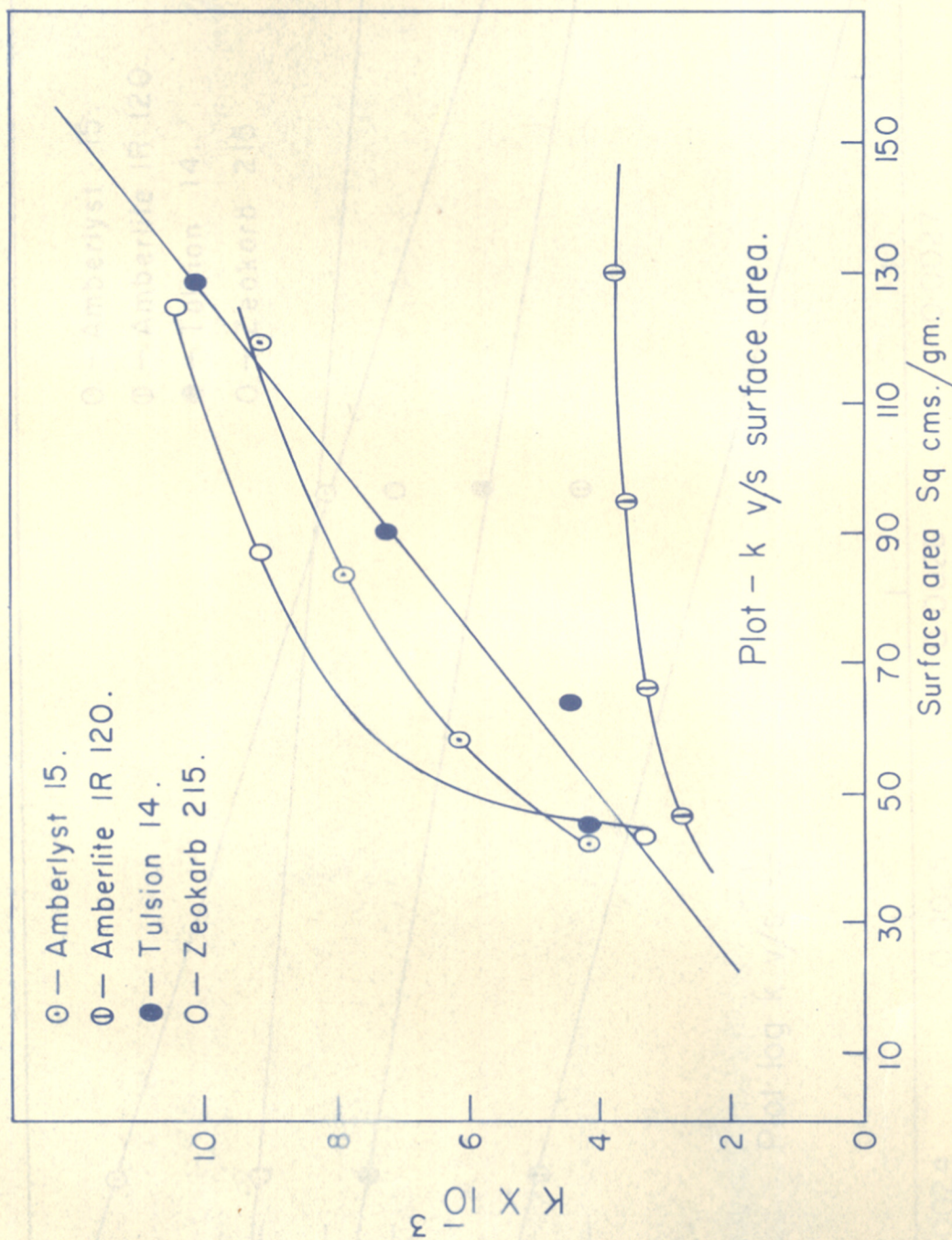


Fig. 10 — Sebacic acid - Ethylene glycol reaction.

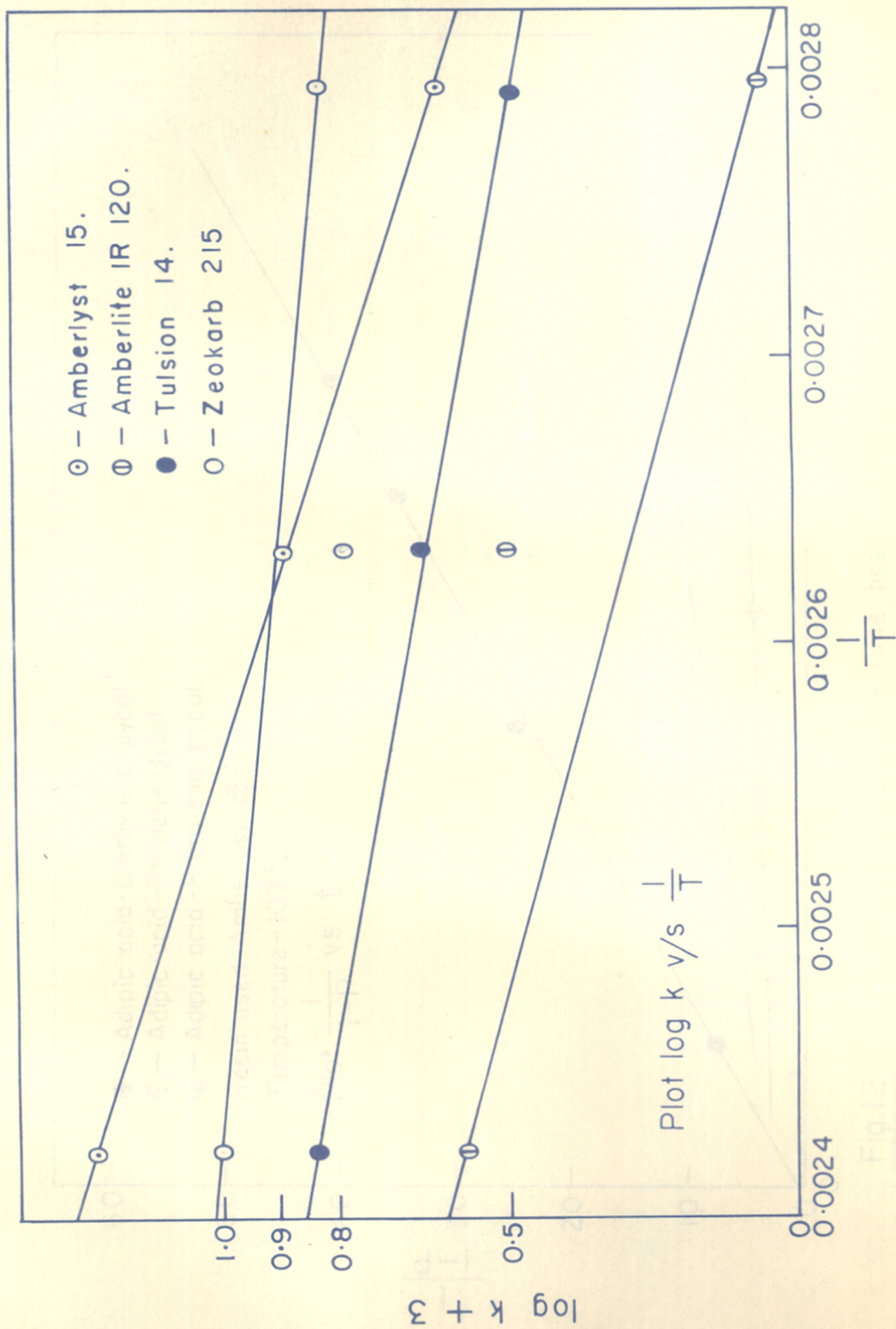


Fig.11 - Sebacic acid - Ethylene glycol reaction.

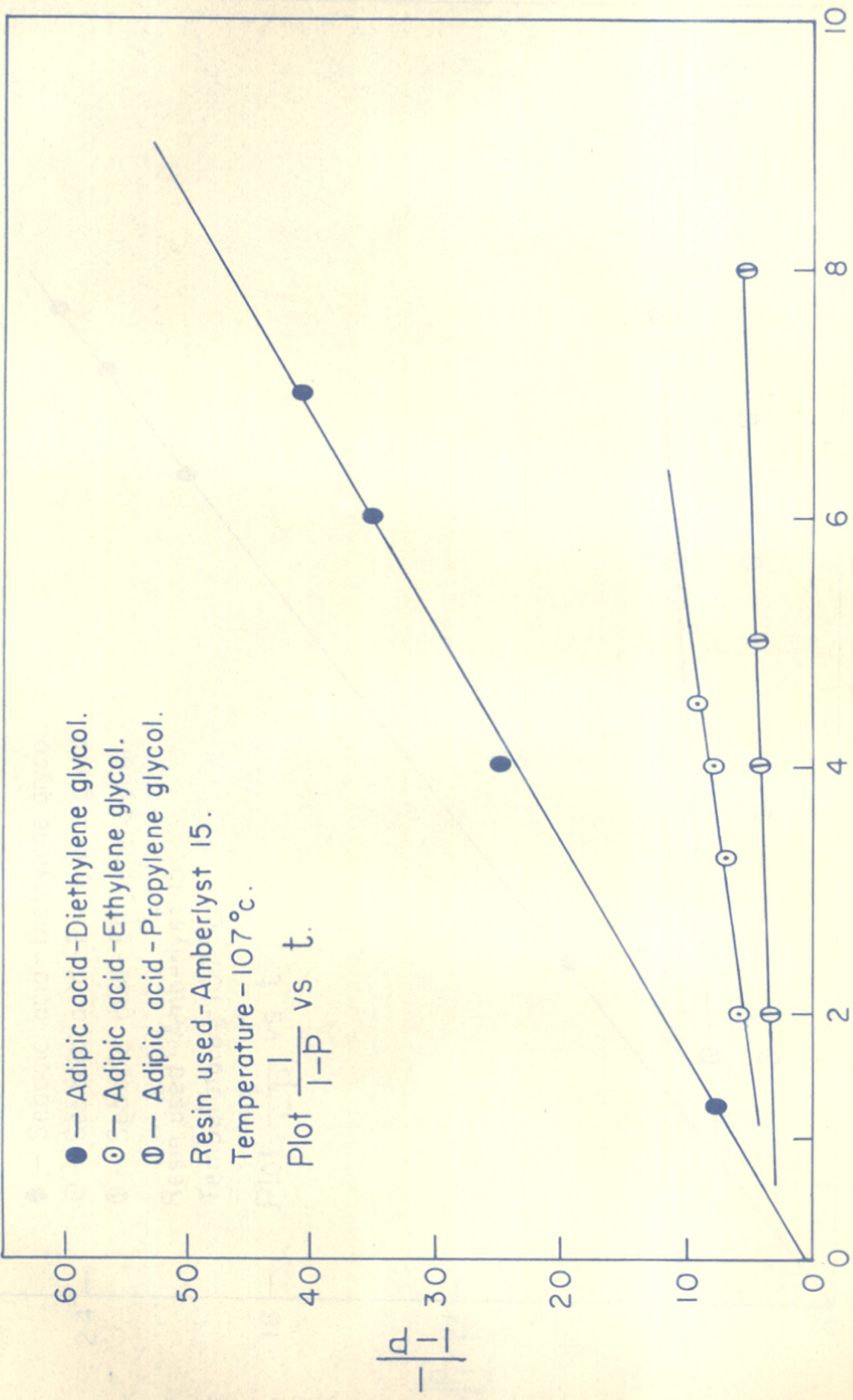


Fig.12

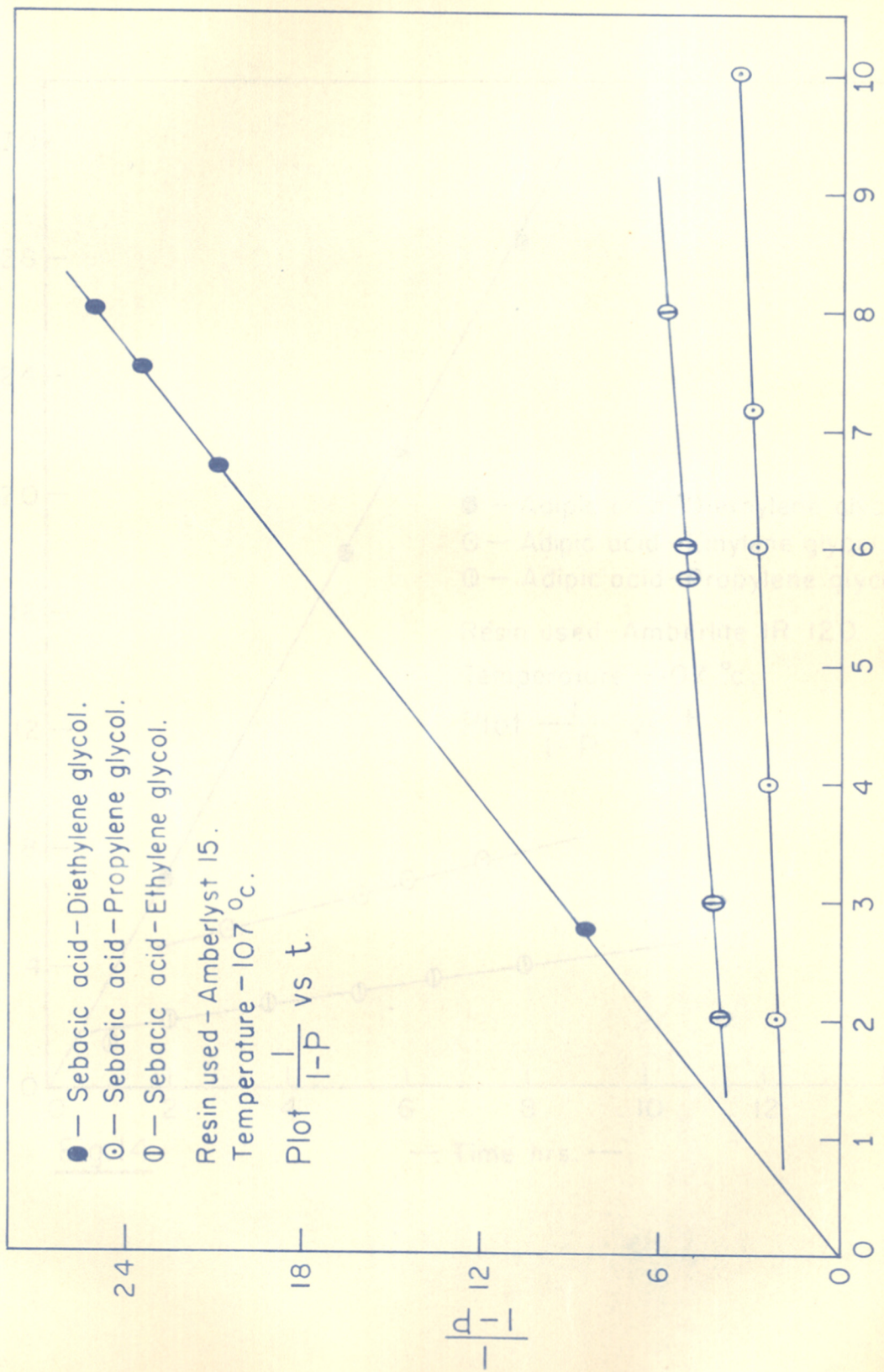


Fig.13

— Time hrs. —

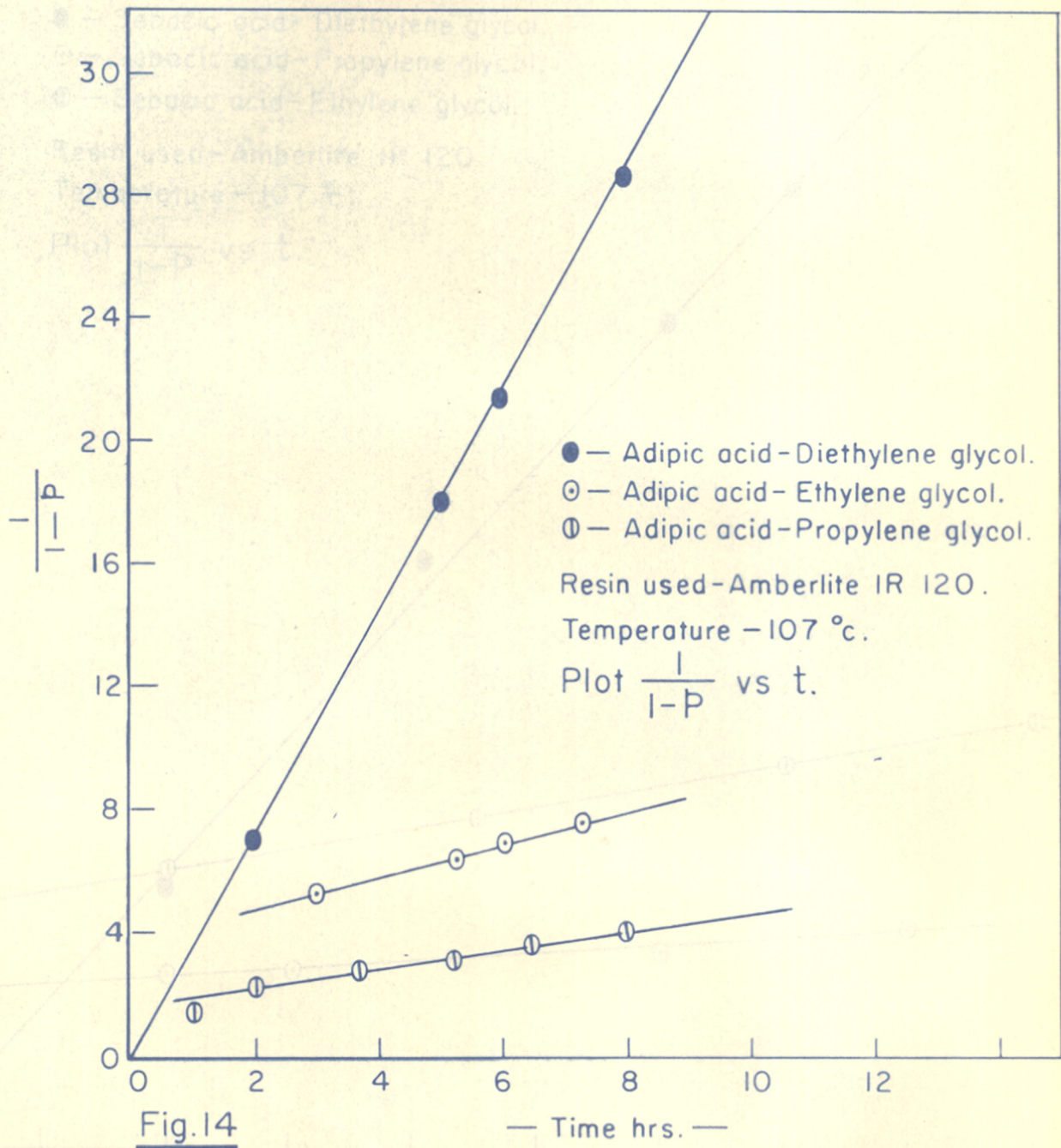


Fig. 14

— Time hrs. —

- — Sebacic acid-Diethylene glycol.
- — Sebacic acid-Propylene glycol.
- ⊙ — Sebacic acid-Ethylene glycol.

Resin used - Amberlite IR 120.
 Temperature - 107 °C.

Plot $\frac{1}{1-p}$ vs t.

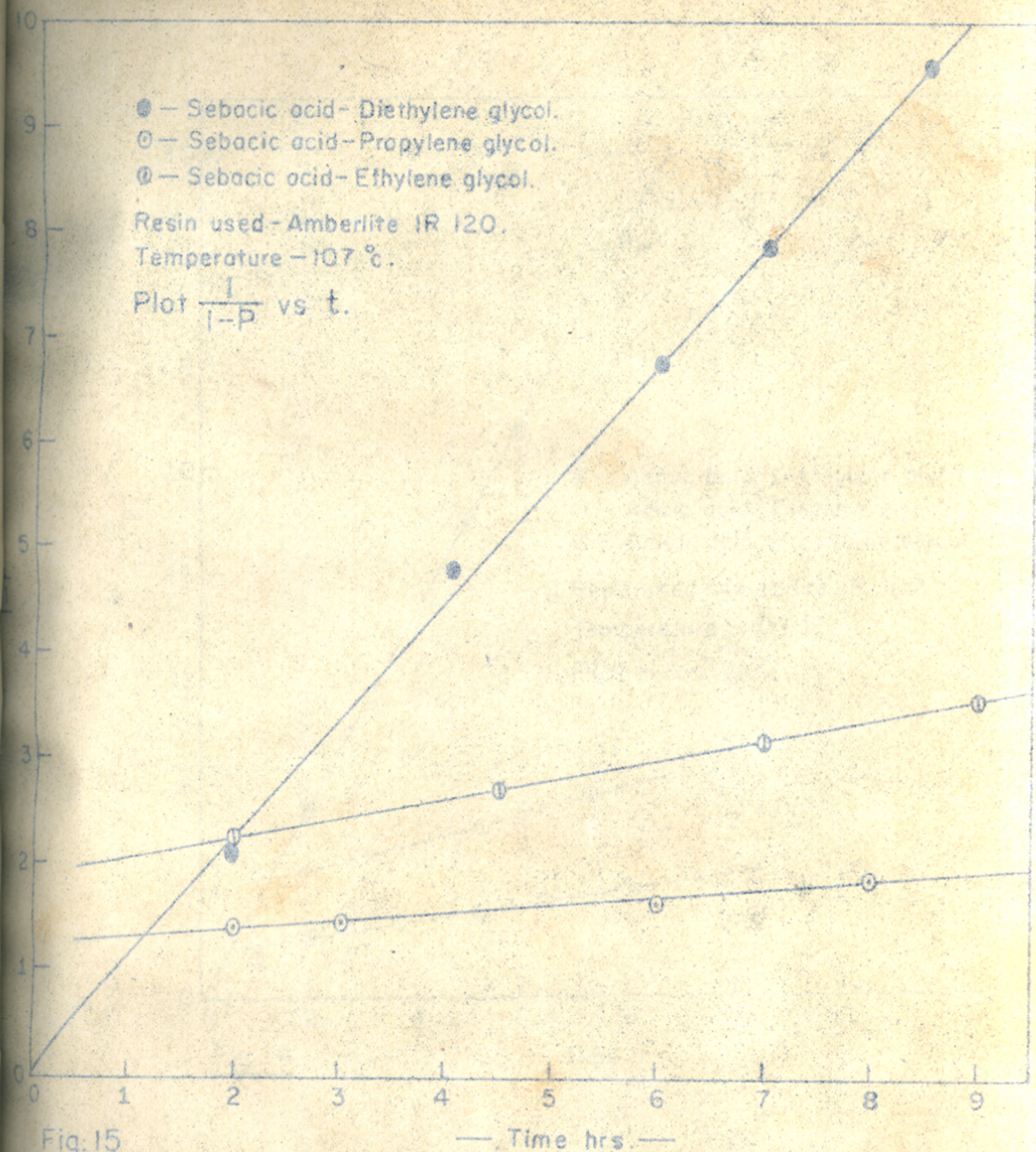


Fig. 15

— Time hrs. —

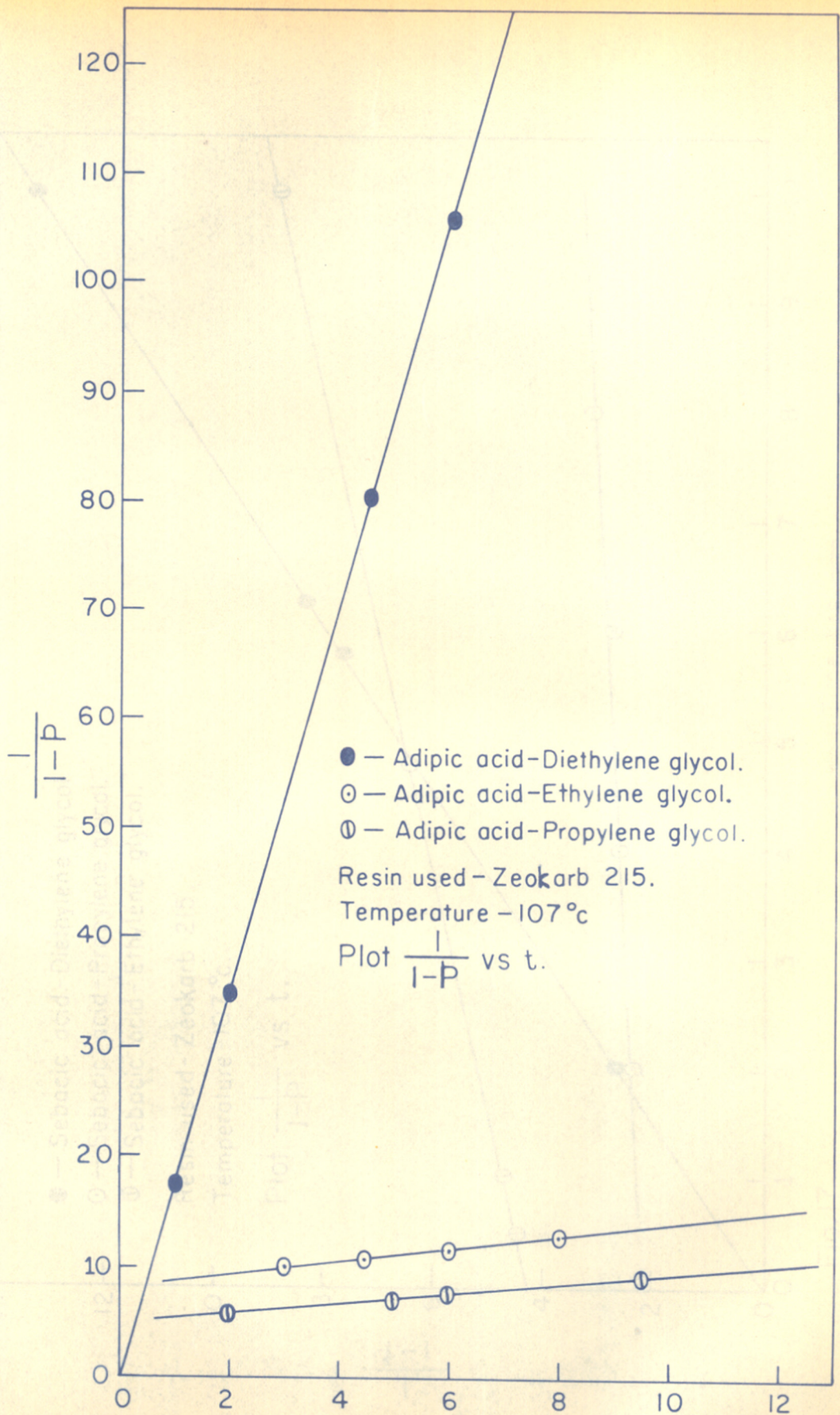


Fig.16

— Time hrs. —

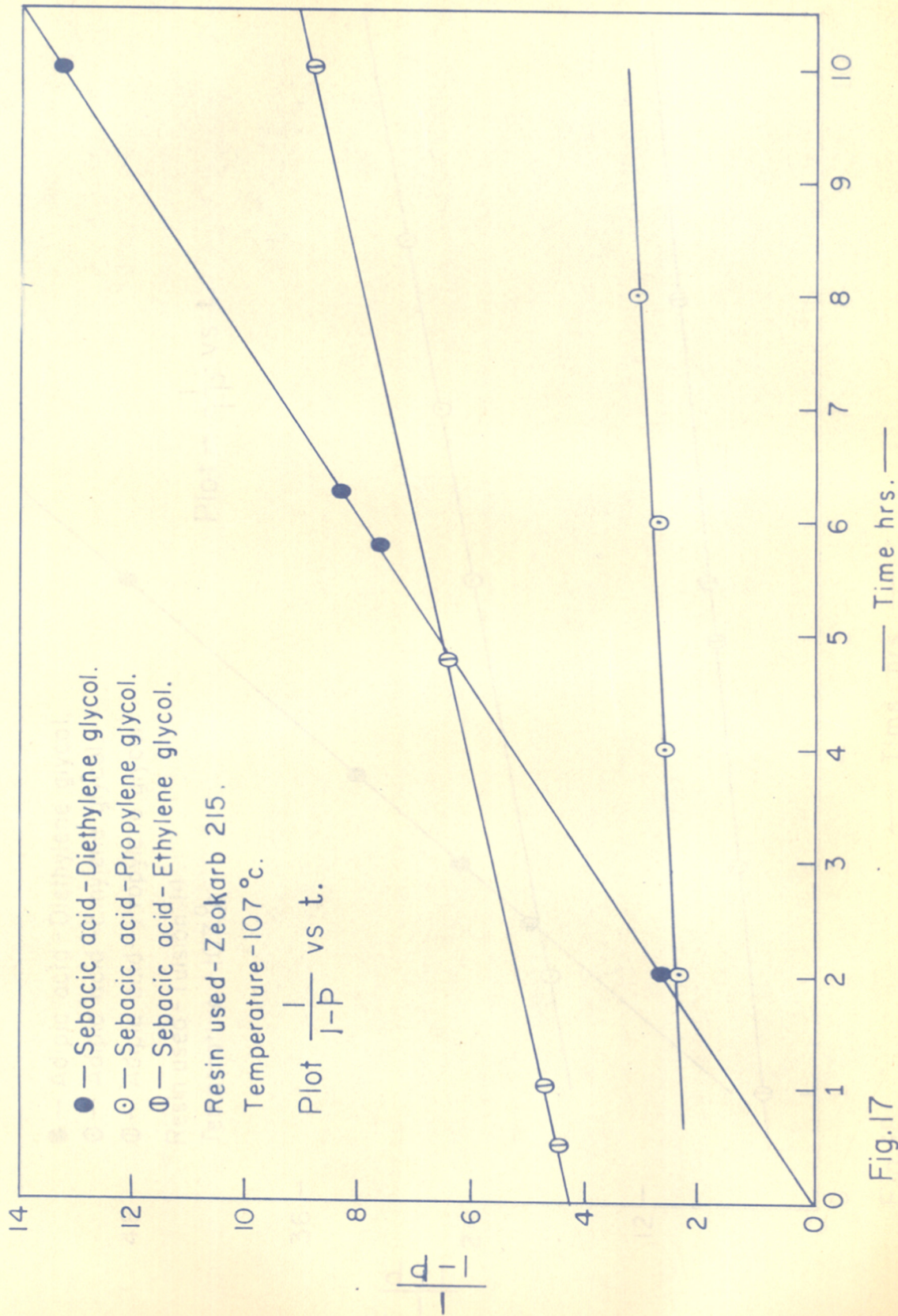


Fig. 17

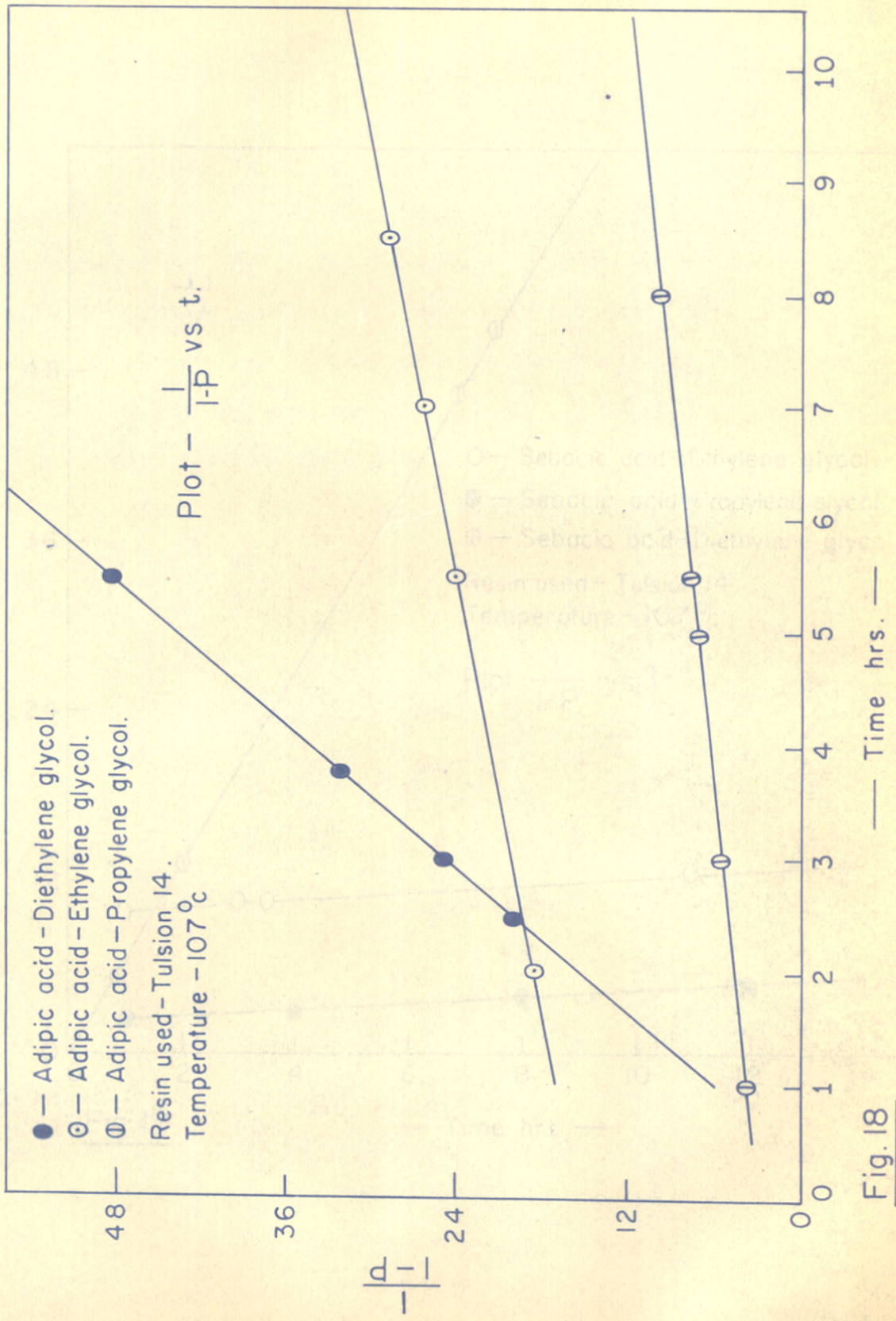


Fig. 18

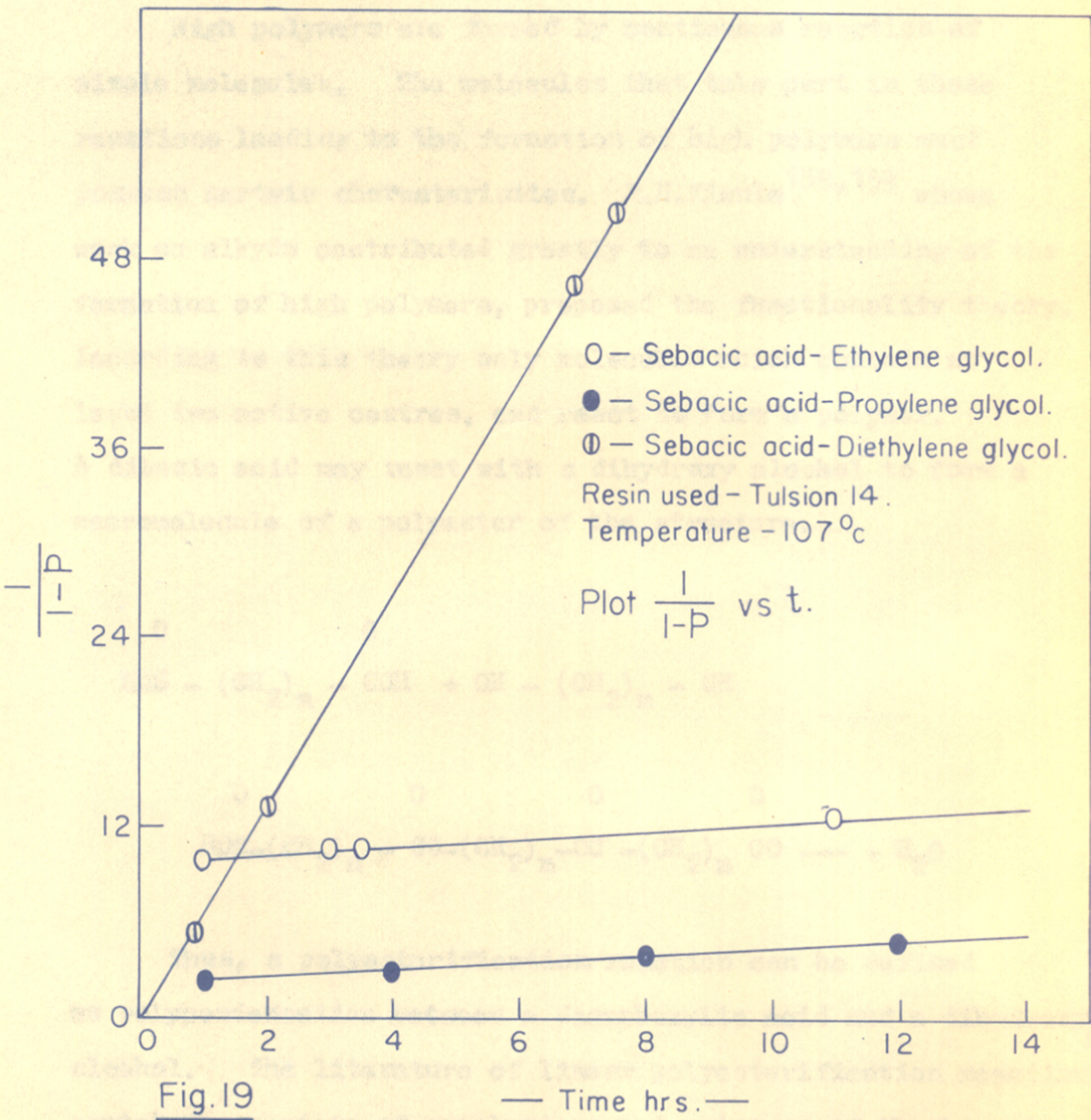
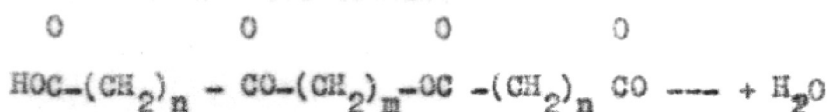
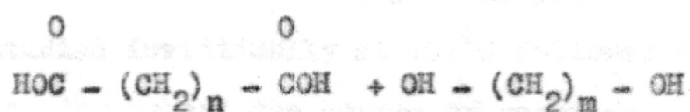


Fig.19

— Time hrs. —

3. Polyesterification:

High polymers are formed by continuous reaction of simple molecules. The molecules that take part in these reactions leading to the formation of high polymers must possess certain characteristics. R.H.Kienle^{158,159} whose work on alkyds contributed greatly to an understanding of the formation of high polymers, proposed the functionality theory. According to this theory only molecules which contain at least two active centres, can react to form a polymer. Thus a dibasic acid may react with a dihydroxy alcohol to form a macromolecule of a polyester of the structure.—



Thus, a polyesterification reaction can be defined as polycondensation between a dicarboxylic acid and a dihydroxy alcohol. The literature of linear polyesterification reactions contains a variety of conclusions and opinions of the kinetic order of the reaction. The kinetics of polyesterification were studied extensively from various angles by P.H.Flory^{160,161} and his co-workers.

In the present investigations, esterification of adipic acid with ethylene glycol, propylene glycol and diethylene glycol were carried out at the refluxing temperature of toluene. To study the effect of temperature and to determine the activation energy, the reaction of ethylene glycol - adipic acid and ethylene glycol - sebacic acid were also carried out at the refluxing temperatures of benzene and xylene. Reactions were catalysed with the help of the four cation-exchange resins in hydrogen form viz. Amberlyst 15, Amberlite IR 120, Zeokarb 215 and Tulsion 14.

It was found during these investigations that the reactions of adipic acid with diethylene glycol and sebacic acid with diethylene glycol in presence of the four resins studied individually at 107°C followed the 2nd order rate law throughout the course of reaction. Figs. 12-19 show that straight lines were obtained by plotting $1/1-p$ against time.

From the results reported on simple esterifications and from the observations on the influence of the added acid catalysts on simple and polyesterifications, Flory¹⁶¹ noticed that the reactions were acid catalysed. In the absence of any catalyst, a second molecule of acid acted as a catalyst.

Flory therefore suggested that the rate of polyesterification process without added catalyst should be written as

$$\frac{-d(\text{COOH})}{dt} = k(\text{COOH})^2(\text{OH})$$

If the carboxyl and hydroxyl group concentrations are equal and of a concentration C, then the form of the equation becomes

$$\frac{-d(\text{COOH})}{dt} = kC^3$$

or

$$2kt = \frac{1}{C^2} - \text{constant}$$

A factor p, called extent of reaction, represents the fraction of the functional groups reacted in time t. It was further introduced in the given equation as follows:

Then $C = (1 - p)C_0$ where C_0 is the initial concentration of functional groups. Hence the equation becomes

$$2C_0kt = \frac{1}{(1-p)^2} - \text{constant}$$

Flory therefore presented his results by plotting $1/(1-p)^2$ against time.

But when the reaction was catalysed by acid catalyst viz. p-toluene sulphonic acid, the kinetic equation is that of second order reaction.

$$\frac{-d(\text{COOH})}{dt} = k(\text{COOH})(\text{OH})$$

or

$$k_0 k t = 1/1-p - \text{constant.}$$

In the uncatalysed condensation of exactly equivalent amounts of adipic acid and diethylene glycol at 166°C, it is reported by Flory¹⁶¹ that the condensation reaction follows the third order rate law. Results obtained by Flory for the reaction of adipic acid, diethylene glycol in the presence of para toluene sulfonic acid at 109°C are plotted as a second order reaction, where a straight line is obtained by plotting $\frac{1}{1-p}$ against time. Flory¹⁶¹ also reported that the rate of reaction was greatly accelerated.

In the present investigation, the polycondensation reactions of adipic acid, with diethylene glycol as well as sebacic acid with diethylene glycol have been observed to follow in the same way as mentioned by Flory in the presence of ion-exchange resin catalysts.

Flory¹⁶¹ had studied adipic acid - diethylene glycol reactions in presence of para toluene sulfonic acid without any solvent. In the present investigations the reactions of sebacic acid and adipic acid with diethylene glycol were carried out in presence of toluene and the catalyst. As the

results obtained during this investigation are agreeing with the results of Flory in terms of the order of reactions, it can be understood that dilution effect (due to use of solvent) is not involved in the reaction.

In the case of adipic acid - propylene glycol and sebacic acid - propylene glycol esterifications, it was observed that the reaction did not obey the 2nd order rate law in the beginning but followed in the later stages. It can be seen from Figs 12-19 that rates of esterification of dibasic acids with propylene glycol are very much lower than those obtained in the reaction of dibasic acids with diethylene glycol.

In the polyesterification studies of adipic acid with ethylene glycol and that of sebacic acid with ethylene glycol it was observed that these reactions obeyed the second order rate law during the final stages in presence of Amberlyst 15, Amberlite IR 120, Zeokarb 215 and Tulsion 14 resins. Second order rate law was not followed in the initial stages. The same behaviour was noted by variation of temperature, catalyst concentration and using different molar ratios of the reactants.

Results in tables Nos 23-30 indicate clearly that for all the resin catalysts, increase in the catalyst concentration increased the rate of reaction between adipic acid - ethylene glycol and between sebacic acid - ethylene glycol proportionately.

It was revealed from these results (Fig.12-19 Tables 23-30) that the rates of polyesterification reactions of adipic acid and sebacic acid with diethylene glycol are much higher than those obtained in the esterification reactions of adipic acid and sebacic acid with ethylene and propylene glycols.

By changing the molar ratios of adipic acid and ethylene glycol and sebacic acid-ethylene glycol, it was found that the rate of reaction increased with the increase in the glycol concentration. Amberlyst 15, Amberlite IR 120, Zeokarb 215 and Tulsion 14 resins present the same behaviour on changing the glycol concentrations.

In the adipic acid - ethylene glycol reaction, catalysed with Tulsion 14, Zeokarb 215 and Amberlyst 15, the rate constants are linearly proportional to the surface area of the catalyst, indicating the dependence of the activity on the available surface area of the catalyst.

However with Amberlite IR 120, this effect was not noted after a surface area of 60 sq. cms. The value of k tended towards saturation showing that the increase in surface area produced negligible change in the activity of the catalyst system. (Fig.No.7).

In the sebacic acid-ethylene glycol series, except with Tulsion 14, surface area above 60 sq.cms levels off the variation of k value. (Fig.No.10).

From results in Tables 23-30 and Figs it is evident that with all the resin catalysts, the rate of polyesterification of adipic acid - ethylene glycol and sebacic acid - ethylene glycol increased considerably with the increase in the reaction temperature. Activation energy for the reaction of adipic acid - ethylene glycol and sebacic acid - ethylene glycol was calculated from the Arrhenius equation and following values have been obtained.

Reaction studied	Catalyst used	Activation energy
Adipic acid - ethylene glycol	Amberlyst 15	3.047 kcals
	Amberlite IR 120	3.81 kcals
	Tulsion 14	5.484 kcals
	Zeokarb 215	8.57 kcals
Sebacic acid - ethylene glycol	Amberlyst 15	5.255 kcals
	Amberlite IR 120	6.286 kcals
	Tulsion 14	4.57 kcals
	Zeokarb 215	2.38 kcals

It appears from these values which are in the range of 3 kcal to 9 kcal, that the reaction phenomenon is the same for all the resins and the lower value of activation energy suggests mostly the physical adsorption on the ion-exchange resin.

It can be concluded from the above investigation that Tulsion 14, an indigenously available ion-exchange resin can be efficiently used as a catalyst in these polycondensation reactions.

SUMMARY AND CONCLUSIONS

- (1) In the butanol-oleic acid esterification reaction, it is found that at constant catalyst concentration and temperature, the rate of reaction is dependent on the surface area of the catalysts.
- (2) In the above reaction, reuse of the polyfunctional resins which have been desulphonated was found to yield almost the same results as obtained with fresh unifunctional resins. Thus the presence of sulphonic groups alone is perhaps not entirely responsible for the catalytic behaviour.
- (3) When a macroreticular resin of the type useful for catalysis is employed, it is found that its usefulness increased with increasing concentration employed.
- (4) The effect of surface area has been shown significant in (1) Butanol-oleic acid reaction, and (2) 2-ethyl-hexanol - phthalic anhydride reaction with all the four catalysts studied.
- (5) In adipic acid-ethylene glycol reaction, the effect of surface area is significant only with the resin Amberlyst 15, Tulsion 14 and Zeokarb 215.
- (6) In sebacic acid - ethylene glycol reaction, the effect of surface area is significant only with Tulsion 14.
- (7) Higher temperatures are shown to hasten the rates of esterification catalysed by ion exchange resins.

(8) The polystyrene based sulphonic acid type cation exchangers are seen to be unaffected by the temperature of the reaction, while polyfunctional resins lose their exchange capacities with loss in their catalytic activity.

(9) Values of activation energy determined for 2-ethyl hexanol - phthalic anhydride reaction are almost equal to the values obtained for other simple esterification reactions reported in the literature.

(10) The order of reaction for all the resins as determined graphically were found to be

- | | |
|---|--------------------------------|
| (a) Butanol-oleic acid reaction | - Pseudo first order |
| (b) 2-ethyl hexanol - phthalic anhydride reaction | - First order |
| (c) Adipic acid - ethylene glycol | - Second order in last stages. |
| (d) Adipic acid - propylene glycol | - -do- |
| (e) Adipic acid - diethylene glycol | - Second order |
| (f) Sebacic acid - diethylene glycol | - -do- |
| (g) Sebacic acid - ethylene glycol | - Second order in last stages. |
| (h) Sebacic acid - propylene glycol | -do- |

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