III. RESULTS AND DISCUSSION

III.1 Polyvinyl alcohol

Polyvinyl alcohol has been used by me as a starting material for many of my investigations. It is available commercially in different grades depending on its degree of polymerization and degree of hydrolysis. Some companies offer more than ten different major grades and more than hundred subgrades of polyvinyl alcohol. Their classification is based on (i) percentage hydrolysis and (ii) degree of polymerization. They fall into (i) fully hydrolysed group having about 98% hydrolysis, (ii) partly hydrolysed group with (a) 87-89% hydrolysis or (b) 78-80% hydrolysis. In terms of degree of polymerization (d.p.), the major groups are (i) low viscosity group with d.p. of about 500 (ii) medium viscosity group with d.p. of about 1700 and (iii) high viscosity group with d.p. of about 2400 with subgroups having d.p. of about 1000 and 2000.

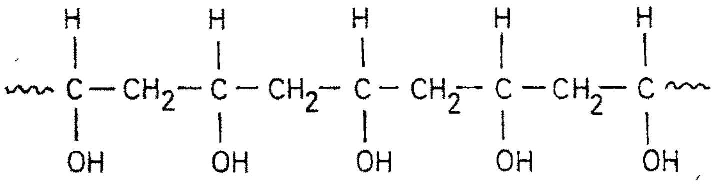
I have used three makes of polyvinyl alcohol. The characteristics of Koch-Light make (KL grade), SD Chem make (SD grade) and Loba Chemie make (LC grade) are presented in table III.1.

Stereoregular forms of polyvinylalcohol are shown in fig III.1(a).

Stereoregularity of polyvinyl alcohol depends on the method of preparation. Polyvinyl trifluoroacetate,

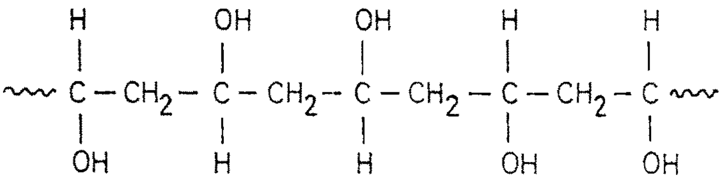
Table III.1

	Poly (Vinyl alcohol)		
	KL grade	SD grade	LC grade
% hydrolysis	97	80	97.6
degree of polymerization	1640	2840	1800
% sodium acetate	4.2	2.4	3.2
% volatile matter	0.7	0.7	0.4



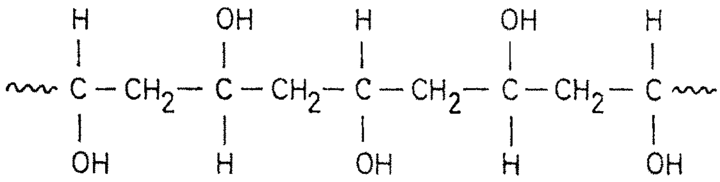
$$\sim\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\sim$$

isotactic



$$\sim\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\sim$$

atactic



$$\sim\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\sim$$

syndiotactic

steoregular forms of polyvinyl alcohol

Fig III.1(a)

on hydrolysis, was found to yield syndiotactic polyvinyl alcohol with low 1,2-glycol content (131,132). Ionic polymerization of vinyl ethers (133) produced isotactic polyvinyl ethers and polymerization of divinyloxy compounds yielded mixed products (134,135).

The crystallinity of polyvinyl formate is sensitive to differences in tacticity. The highly syndiotactic polymer has an X-ray pattern repeat of 5.0 A while highly isotactic polymer has a repeat of 6.55 A (136,137).

Polyvinylalcohol gives characteristic colour reaction with iodine, depending on its tacticity, degree of polymerization, etc. (138,139). The colouration is related to alcohol-iodine complex and has an absorption maximum at 620nm. The intensity decreases with both 1,2-glycol content and isotacticity and is almost zero when isotacticity exceeds 70%.

Polyvinyl alcohol readily undergoes (i) etherification reaction (ii) esterification reaction and (iii) formalization reaction. Formalization (or acetalization) reaction is the reaction with formaldehyde (or acetaldehyde) and generally represents reaction with carbonyl group. It has been observed that isotactic polyvinyl alcohol is more readily formalized and less readily deformalized. Polyvinylalcohol having 1,3-glycol groups undergoes (i) intramolecular formalization to the extent of 70-80% in presence of acid catalyst and (ii) intermolecular formalization causing gelation. In homogeneous formalization, formal groups are distributed randomly along the molecules and in fibres formal group distributes collectively and selectively only in amorphous areas. Variation in (i) density or (ii) degree of swelling with degree of formalization was investigated by Sakurada (140) (Fig III.1(b), 1(c) and 1(d)).

Formalization reaction was studied (i) using formaldehyde, acetaldehyde, butyraldehyde, etc. by Sakaguchi (141), Matsuzawa (142), Kawase (143), Sakurada (144), Imoto (145), etc. (ii) using glyoxal by Okamura (146), etc. (iii) using salicylaldehyde, benzaldehyde, etc. by Motoyama (147), Noma (148), etc. (iv) using furfural by Hachihama (149), etc.

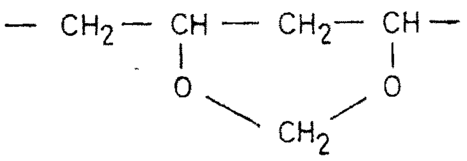
Formalization reactions fall into four types:

(i) precipitation method

The reaction is carried out in an aqueous solution of poly vinyl alcohol, causing the formal to precipitate at about 30% formalization after which the reaction is continued in the heterogeneous system.

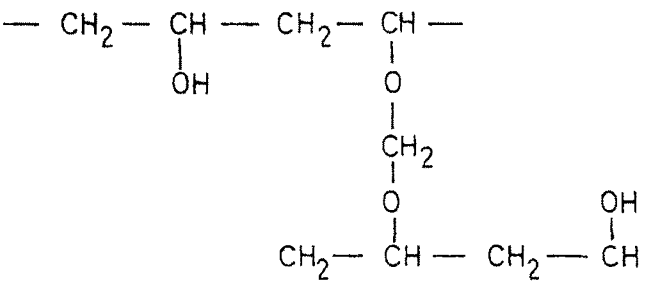
(ii) dissolution method

The reaction is carried out by allowing powdered poly vinyl alcohol to dissolve as acetalization proceeds, then continuing the reaction in the homogeneous system.



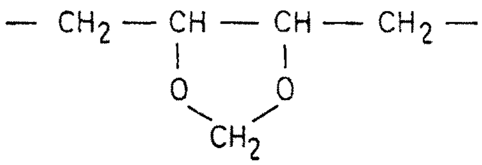
intramolecular formalization of 1,3 glycols in PVA

(i)



intermolecular formalization in PVA

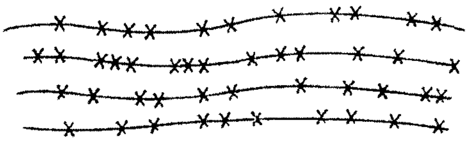
(ii)



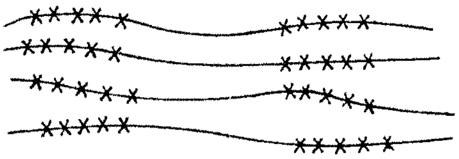
intramolecular formalization of 1,2 glycols in PVA

(iii)

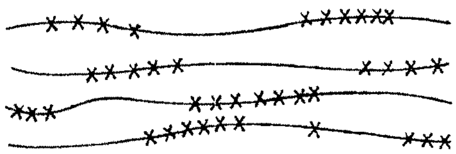
Fig III.1(b) Formalization of poly(vinyl alcohol)



(i) random state of random molecules



(ii) selected state of ordered molecules



(iii) random state of ordered molecules

Fig III.1(c)

(iii) homogeneous method

The reaction is carried out in solution and the formal formed does not precipitate out.

(iv) heterogeneous method

The reaction is carried in a heterogeneous phase system.

Properties of the formals obtained vary considerably with the method of preparation, although the degree of formalization is the same. The precipitation method is generally adopted for ease of purification after reaction and for preparing cross-linked gels (Fig III. 1(e)). The cross-link density increases with the concentration of formaldehyde and it increases with the reaction time until a maximum is reached and then decreases gradually. Inter molecular cross-linking by formal bonds is also more unstable to acid treatment than intramolecular formal bonds.

Poly vinyl formals and their derived products with chelating ligands and various condensation reactions have been prepared and studied by me as presented below.

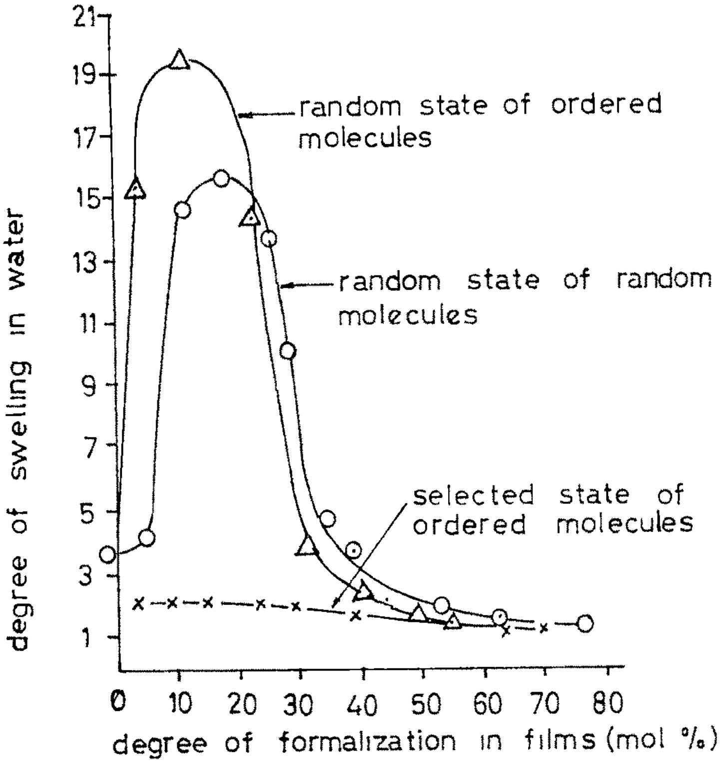
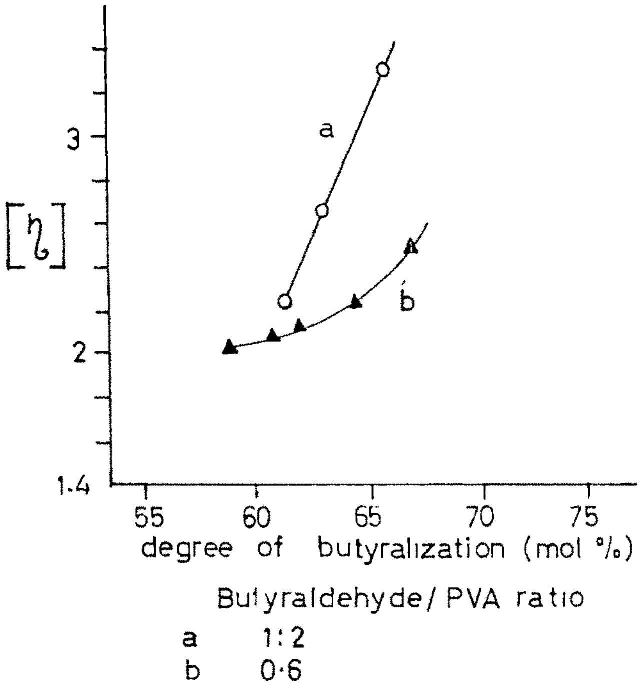


Fig III.1(d)



Butyraldehyde/PVA ratio

a 1:2

b 0·6

Fig III.1(e)

III.2 Polyformals

Poly vinyl formals have been prepared using a wide range of conditions. The yields of products give us a relative idea of the effects of proportions of reactants, nature of media, time of reactions, conditions of reactions, nature of poly vinyl alcohol, etc. The results are presented in (i) fig III.2 for alkaline conditions, (ii) fig III.3 for acid conditions and (iii) fig III.4 for alkali-acid conditions.

Media used for the reaction are water (W), aqueous glycerine (AG), glycerine (G) and poly ethylene glycol (Pg). The media have increasing viscosity in the order suggested ($W < AG < G$) and Pg has relatively higher molecular weight. Reaction rate would get reduced as viscosity or molecular weight of the medium and degree of polymerization of poly vinyl alcohol increase. This has been generally reflected in figs III.2(a) and (b), 3(a) and (b) and 4(a) and (b). The reaction between vinyl alcohol unit and formaldehyde involving cross-linking and leading to gelation is presented in eq.III.1.

Uniform results have been obtained for the reactions under acidic conditions (fig III.3 (a) and (b)).

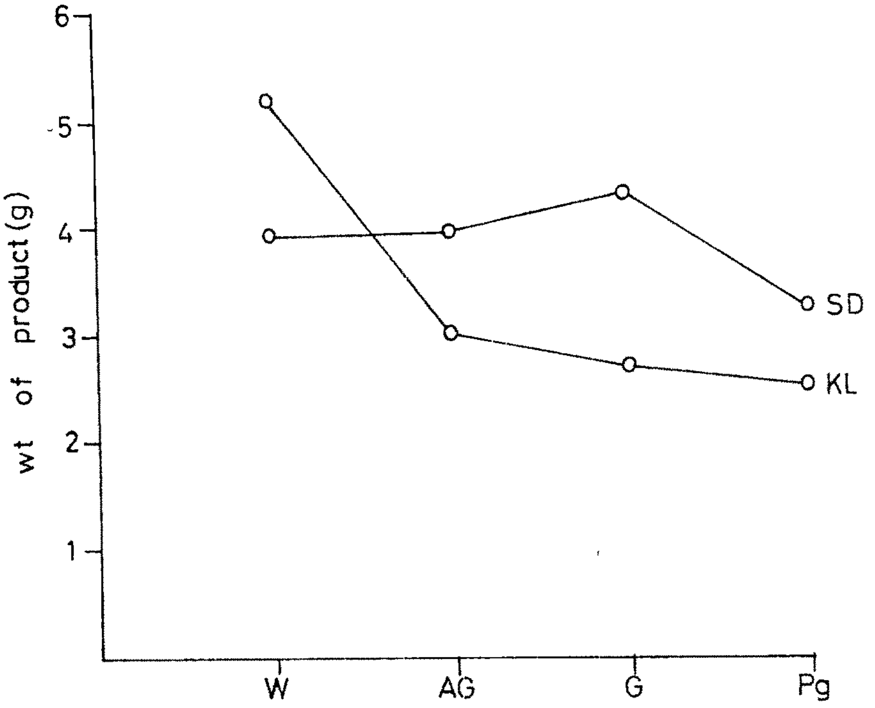


Fig III.2(a) data from table II.2(a)

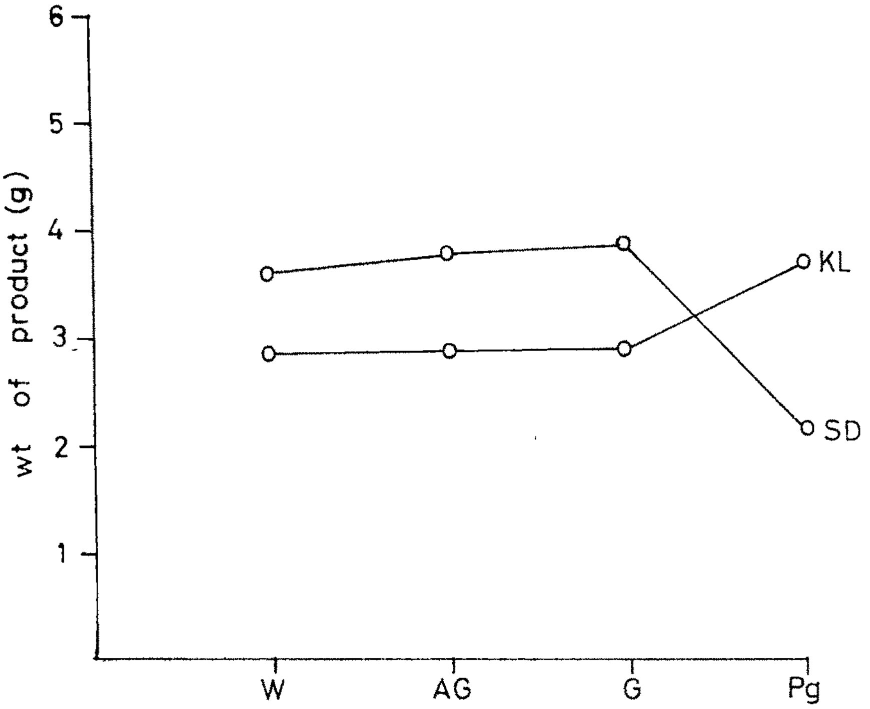
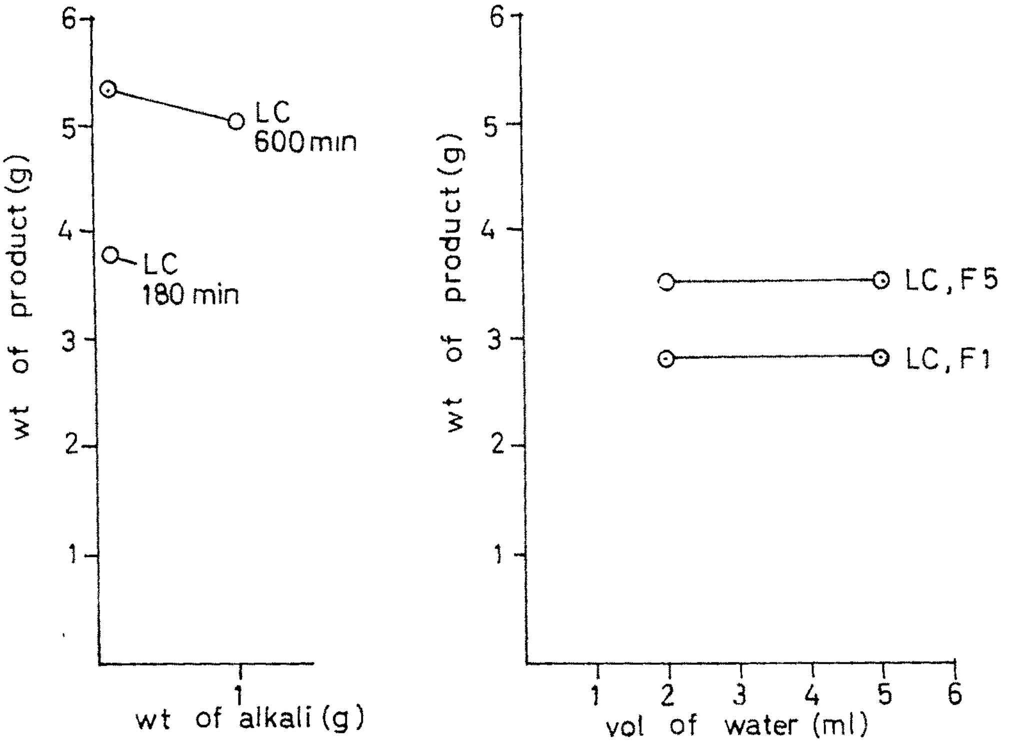


Fig III.2(b) data from table II 2(d)



(i) (ii)

Fig III.2(c) data from table II.2(a)

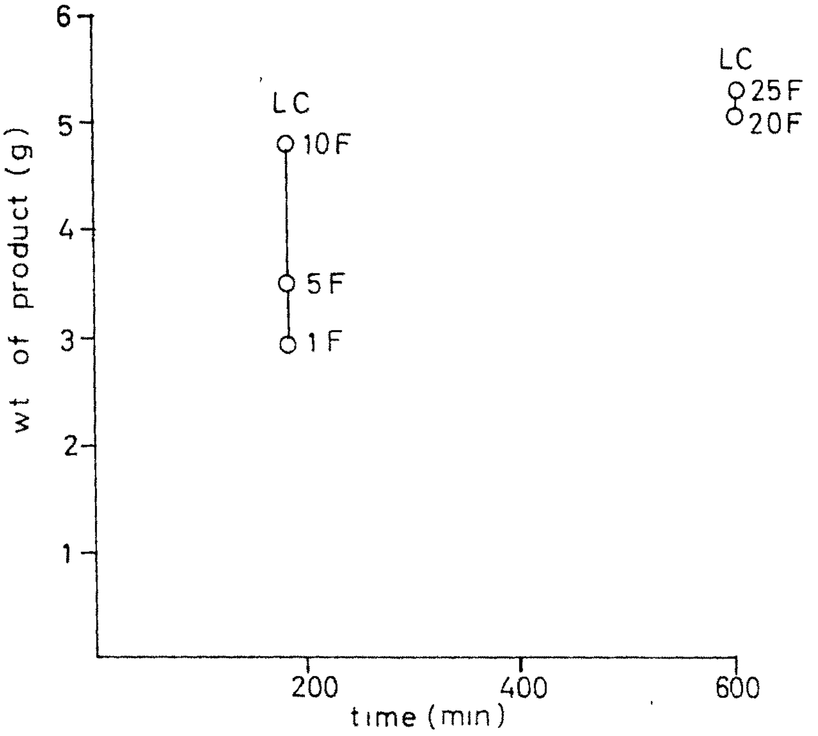


Fig III.2(d) data from table II 2(a)

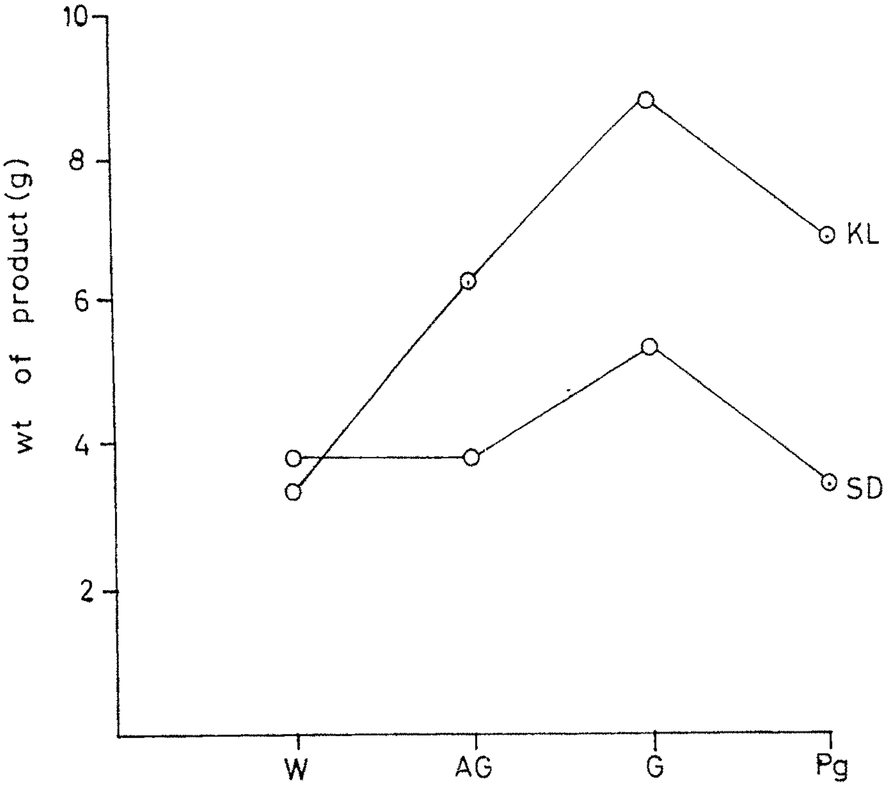


Fig III.3(a) data from table II 2(b)

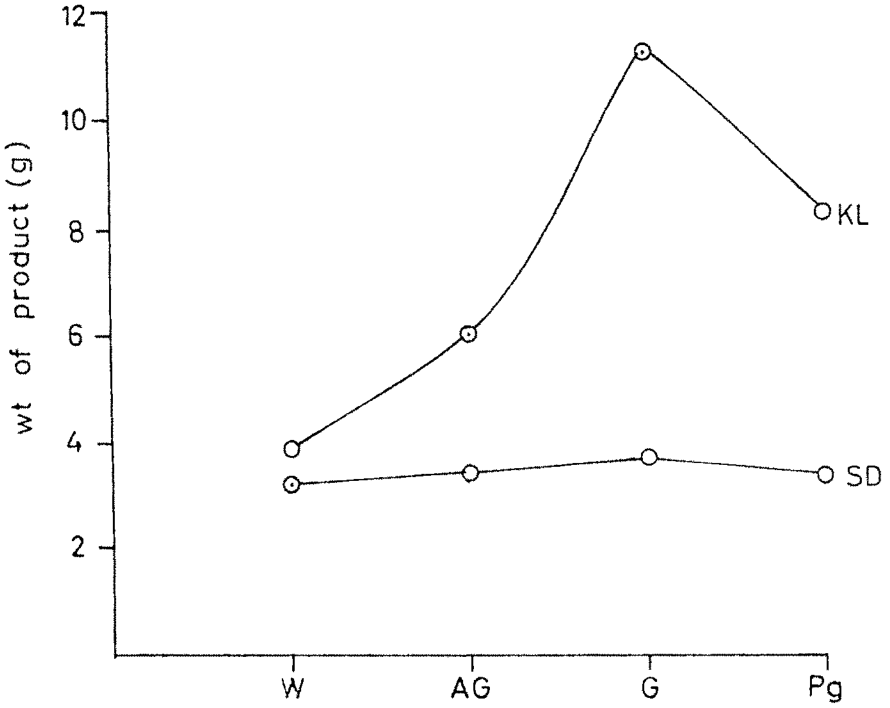


Fig III.3(b) data from table II 2(e)

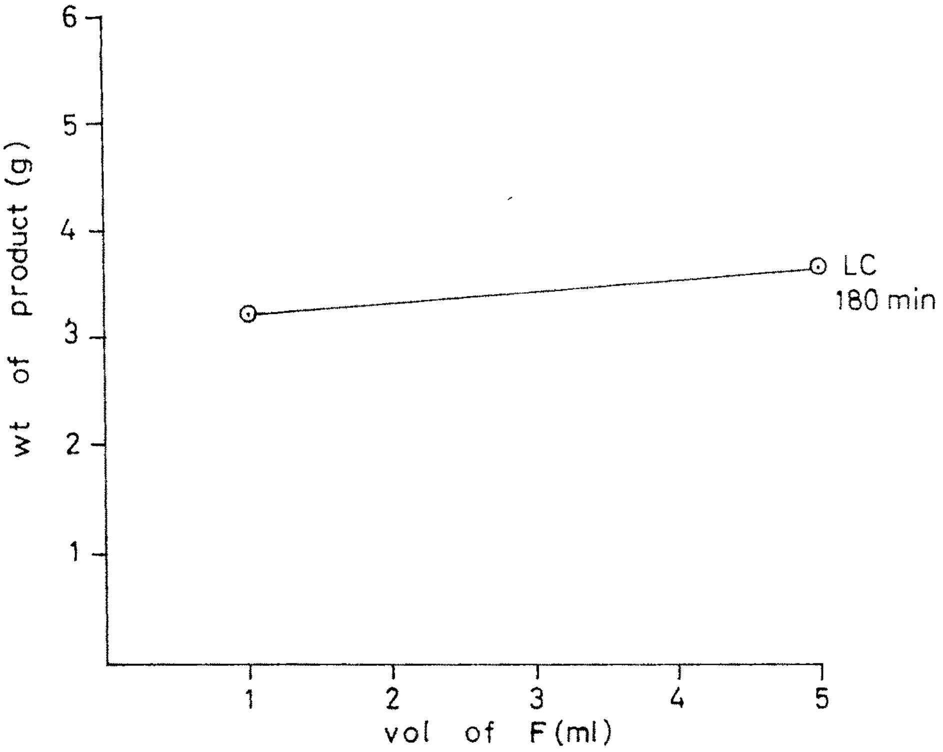


Fig III.3(c) data from table II 2(b)

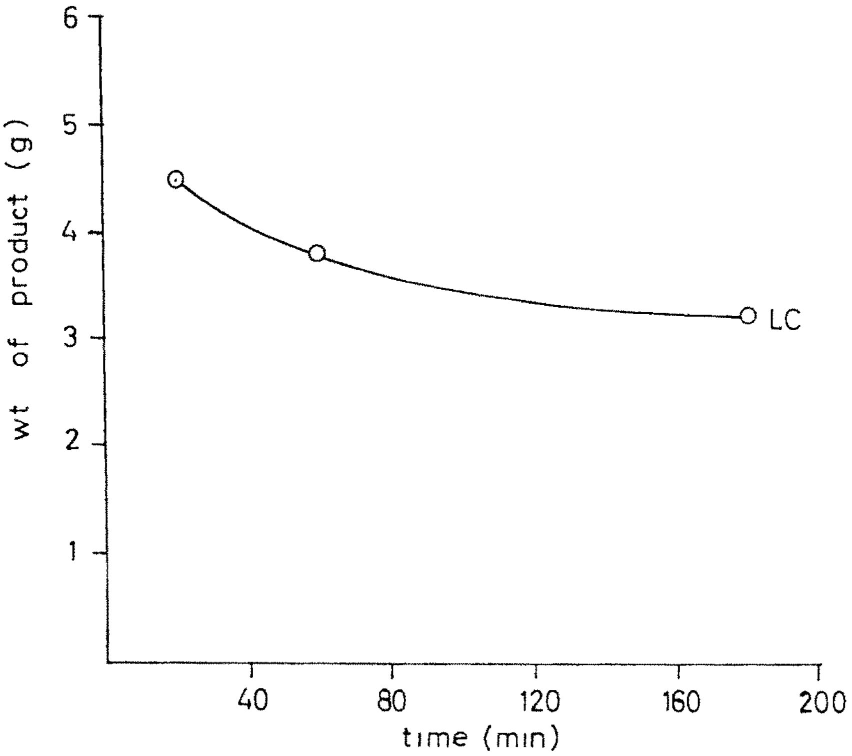


Fig III. 3(d) data from table II 2(b)

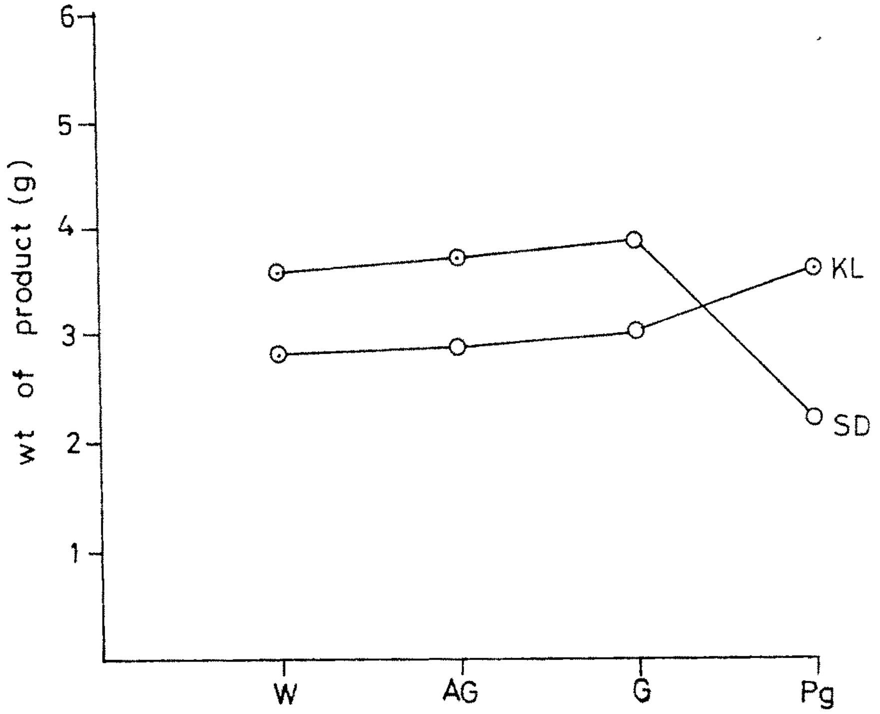


Fig III.4(a) data from table II 2(c)

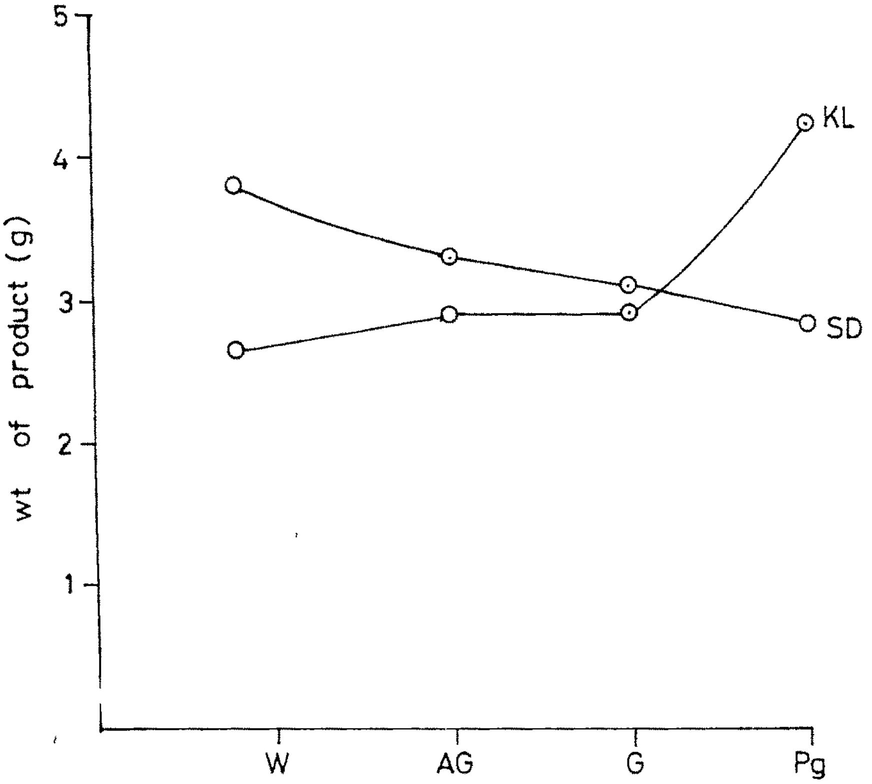


Fig III.4(b) data from table II.2(f)

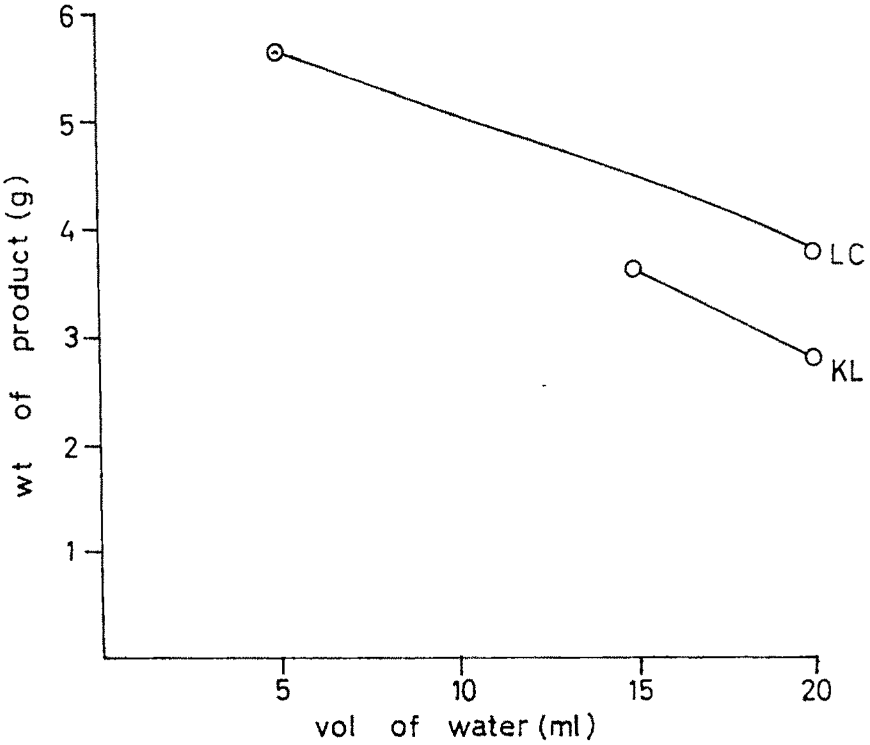


Fig III.4 (c) data from table II.2(c)

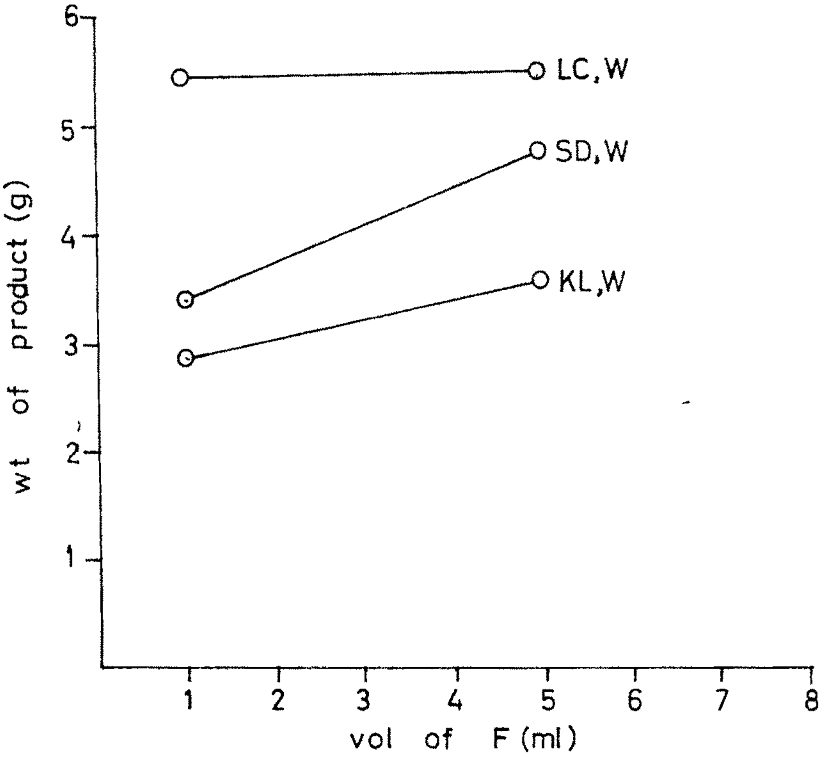


Fig III.4 (d) data from table II 2(c)

Thus the yield for G medium is higher than for W medium or for Pg medium, the yield for AG medium is intermediate between those for W and G media, the yield for KL grade is higher than that for SD grade and the yield for reaction in presence of starch is higher than that in absence of starch. Lower yield in W medium can be attributed to the common mass effect as water is one of the products of reaction.

Higher yield in presence of glycerine can be explained in terms of the side reaction suggested in eq.III.2.

Also starch can undergo reaction with formaldehyde increasing yield in favourable conditions and poly vinyl alcohol with higher d.p. can have lower degree of formalization than one with lower d.p..

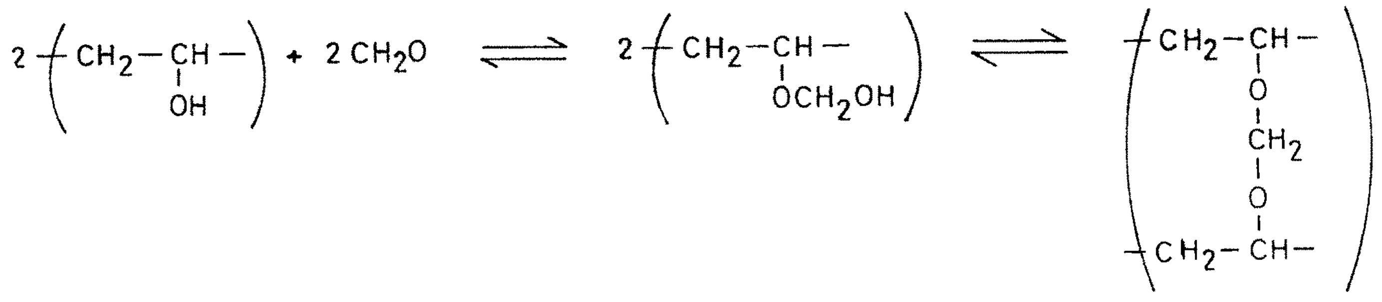
Under alkaline conditions (fig III.2(a) and (b)) and alkali-acid conditions (fig.III.4 (a) and (b)) the yield of products for SD grade alcohol is generally increasing as

$W < AG < G > Pg$

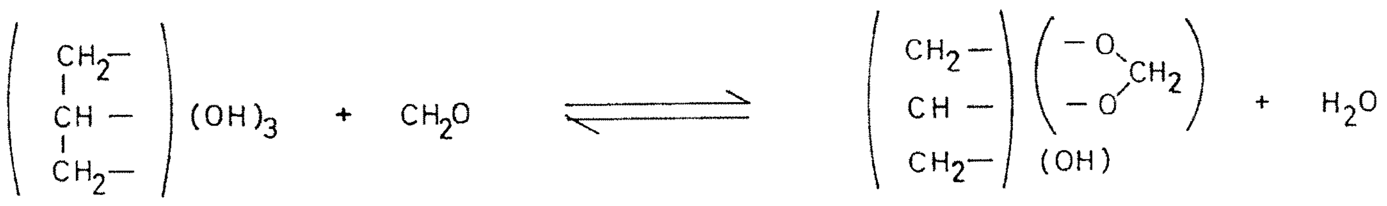
except for alkali-acid-starch conditions where

$W > AG > G$

The yield in case of products for KL-grade alcohol



Eq. III.1



Eq. III.2

is generally increasing in order

$W < AG < G < Pg$

except for alkali and alkali-acid-starch conditions where

$W > AG > G$

In contrast to acidic conditions, in alkaline and alkali-acid conditions, the yield for products in W, AG or G medium is higher for SD alcohol than for KL alcohol.

Increase in the time of reaction increases the yield under alkaline conditions but decreases the yield under acidic conditions. It is suggested that under alkaline conditions hemi formals are substantially formed and under acidic conditions, the initial product would be hemi formal which would undergo condensation to yield cyclic formal and cross-linked formal (150).

Increase in the amount of formaldehyde for the reaction increases the yield of the product under alkaline, acidic and alkali-acid conditions. This is to be attributed to the formation of poly oxy-methylenes in the rings and cross-links.

Increase in the amount of water decreases the yield of the product in general as water is one of the products of reaction.

Increase in the amount of alkali for the reaction decreases the yield. It can be attributed to the increased formation of poly oxy methylenes in the products.

All these products are white or brown in colour and are insoluble in various solvents but are affected slightly by acids and alkalis. Hence chelating ligands were introduced into the reaction systems so that chelating poly formals with less unstability would be obtained.

III.3 Chelating poly formals

3(a) 8-hydroxy quinoline

8-Hydroxy quinoline dissolved in minimum amount of acid was reacted with poly vinyl alcohol and formaldehyde under basic conditions and the products were cured (figs III.5 and 6). It has been observed that increase in the amount of 8-hydroxy quinoline (and of formaldehyde, if necessary) increases the yield of the product. The increase in yield is much higher when the increase in the amount of 8-hydroxy quinoline is from 0.5 to 1 g than when it is from 1 to 3 g.

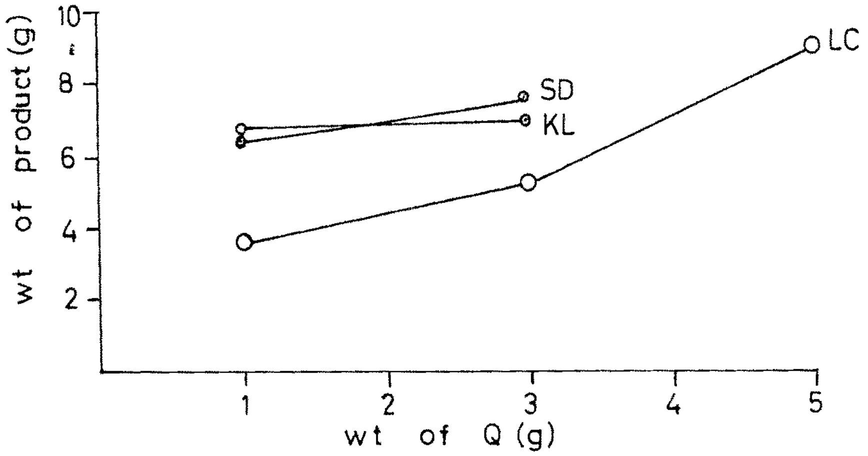


Fig III.5(a) data from table II.4(a)

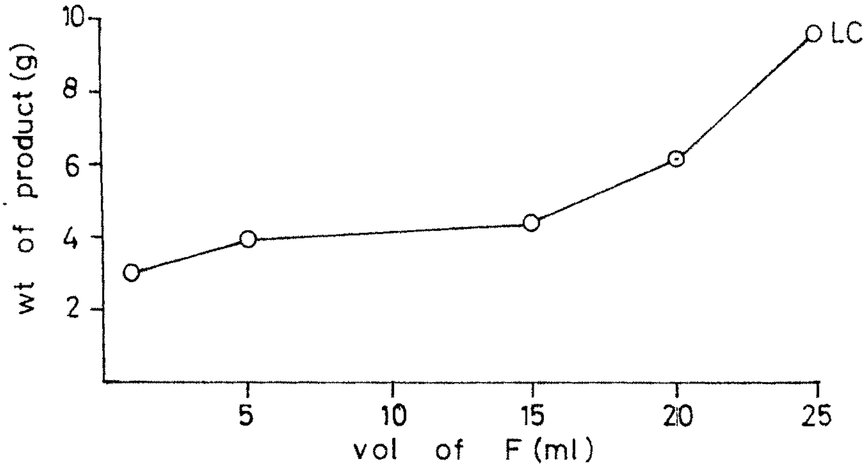


Fig III.5(b) data from table II.4(a)

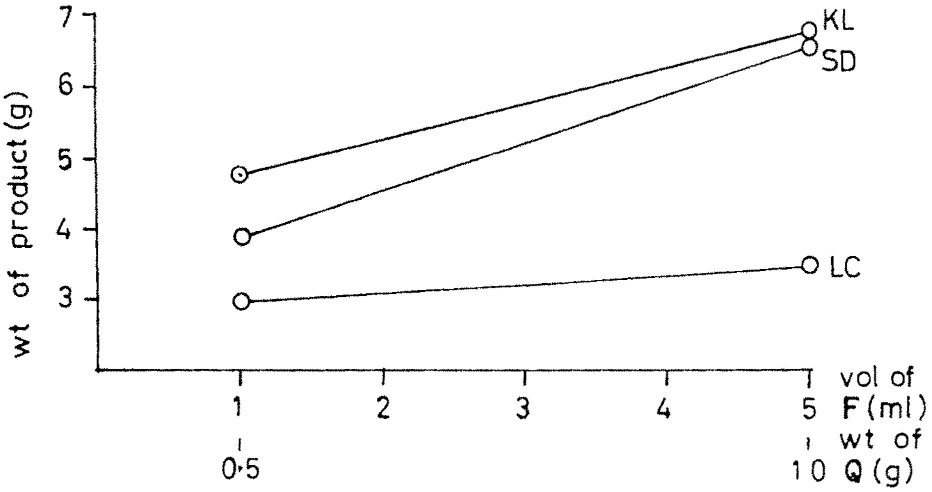


Fig III.5(c) data from table II 4(a)

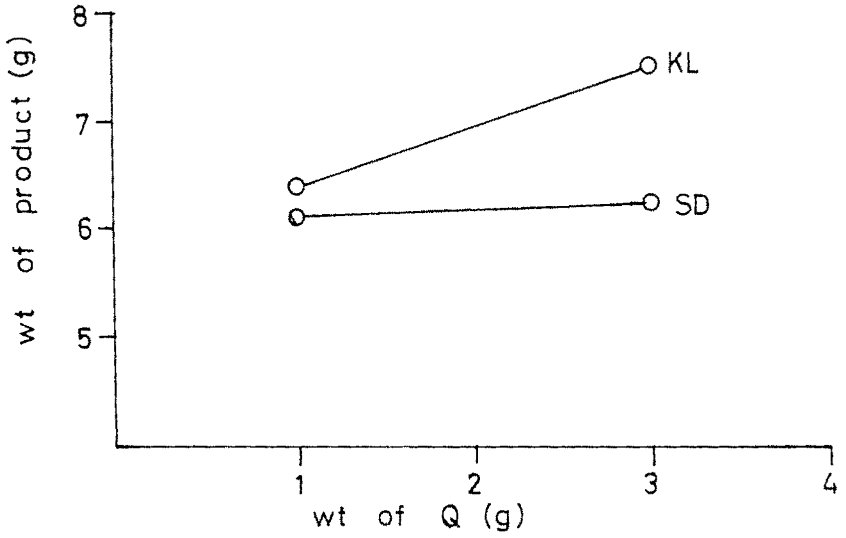


Fig III.6(a) data from table II 4(b)

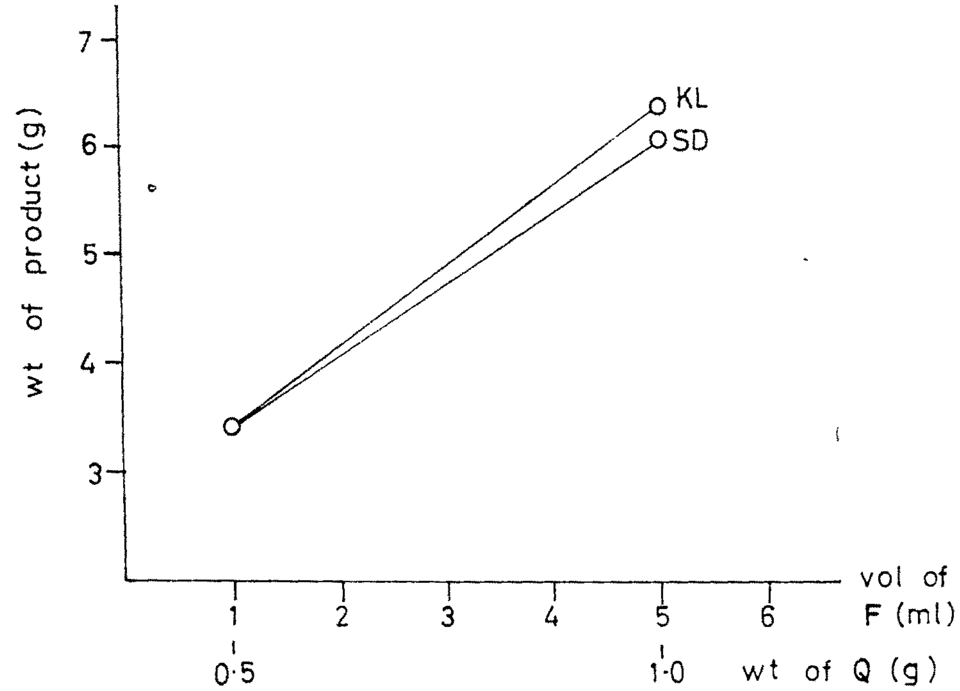


Fig III.6(b) data from table II 4(b)

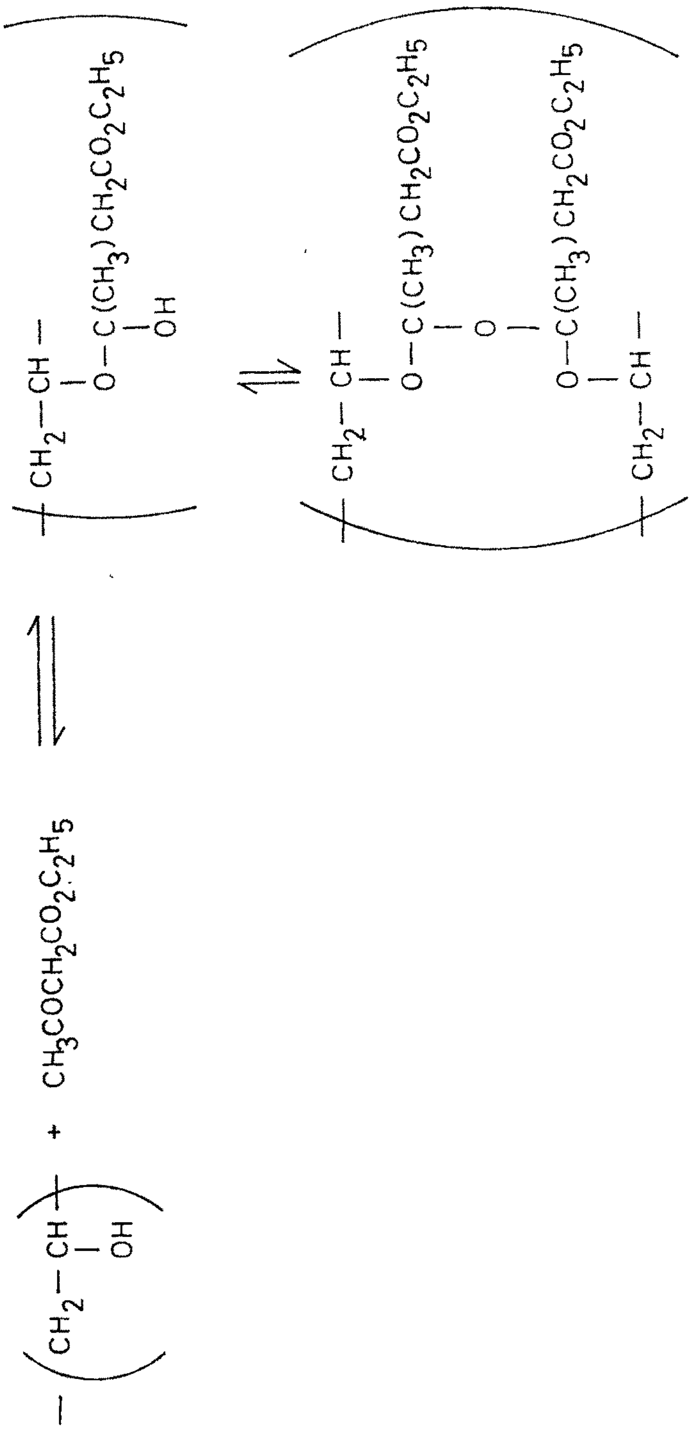
It is also observed that increase in the amount of formaldehyde in the reaction system increases the yield of the product and the formation of poly oxymethylenes in the cross-links is suggested.

3(b) Ethyl aceto acetate

Ethyl aceto acetate has been used both as a condensing agent for formalization and as a chelating agent. It is assumed that the reaction would take place as shown in eg.III.3.

When the amount of ethyl aceto acetate in the reaction system is increased, the yield increases, reaches a maximum and then decreases (figs III.5 and 6). It is assumed that hemi-formal type of product would be formed initially; it would react further in presence of more amount of ethyl aceto acetate to yield poly oxy-methylene type of product. With larger excess of ethyl aceto acetate other reactions such as hydrolysis of the ester can become of importance.

It is also observed that the addition of starch increases the yield of the product under alkaline, acidic and alkali-acid conditions (figs III.7, 8 and 9). The increase is indicative of the possible reaction of starch with ethyl aceto acetate.



Eq. III.3

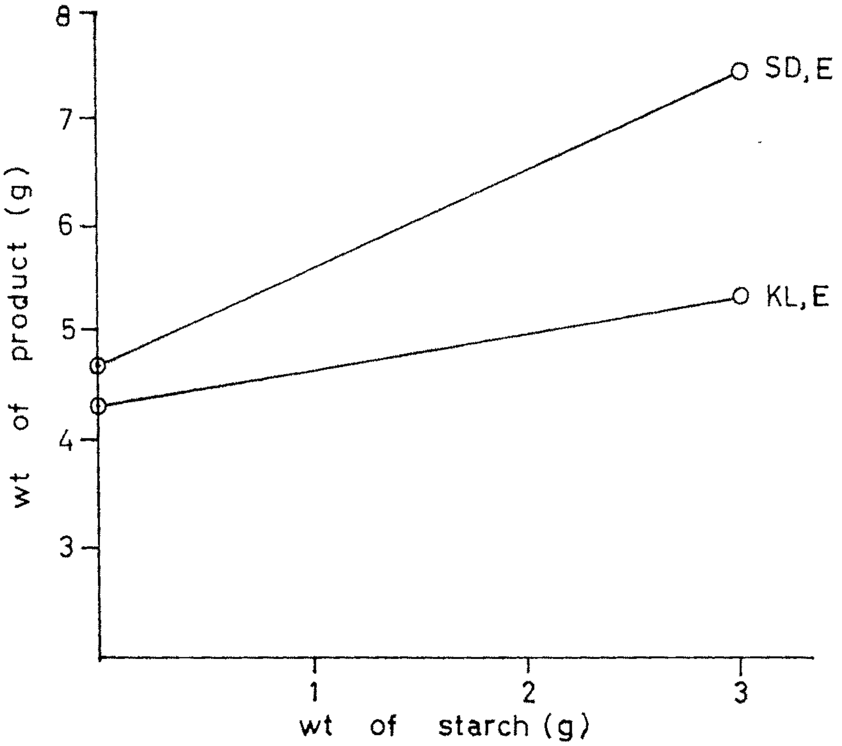


Fig III.7(a) data from table II.4(c)

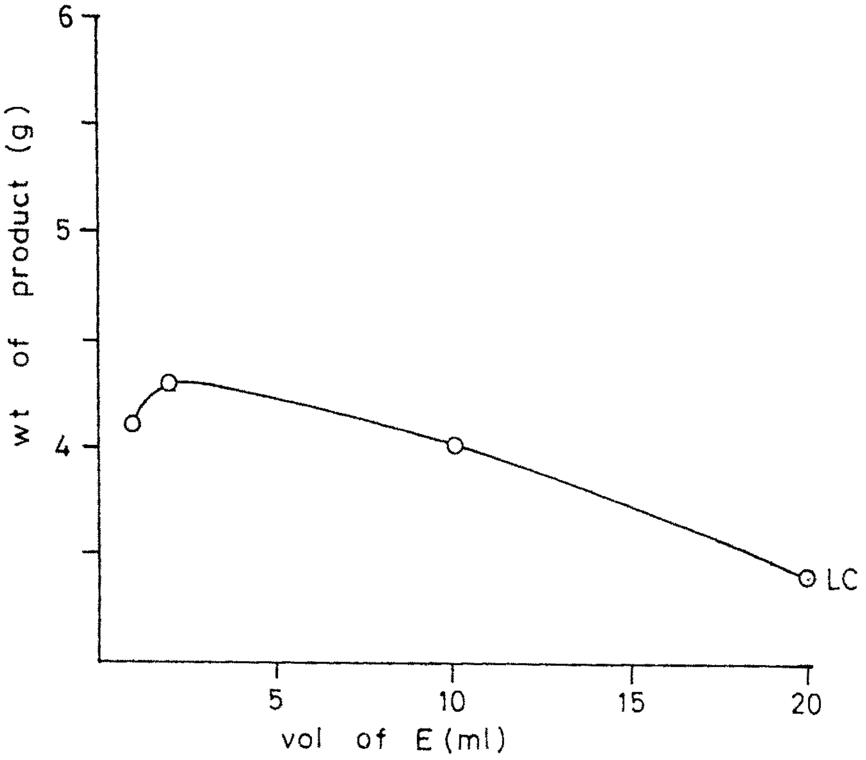


Fig III.7(b) data from table II 4(c)

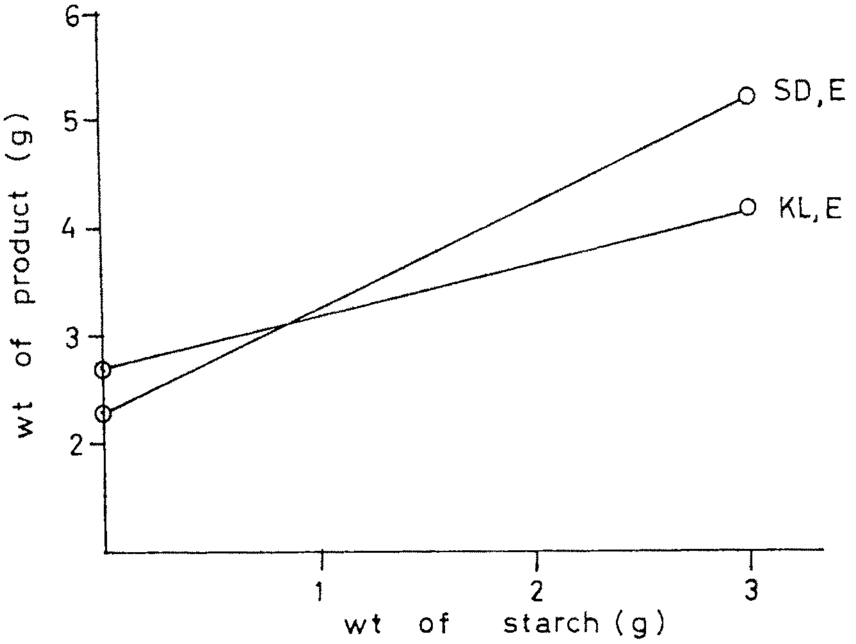


Fig III. 8 (a) data from table II.4(d)

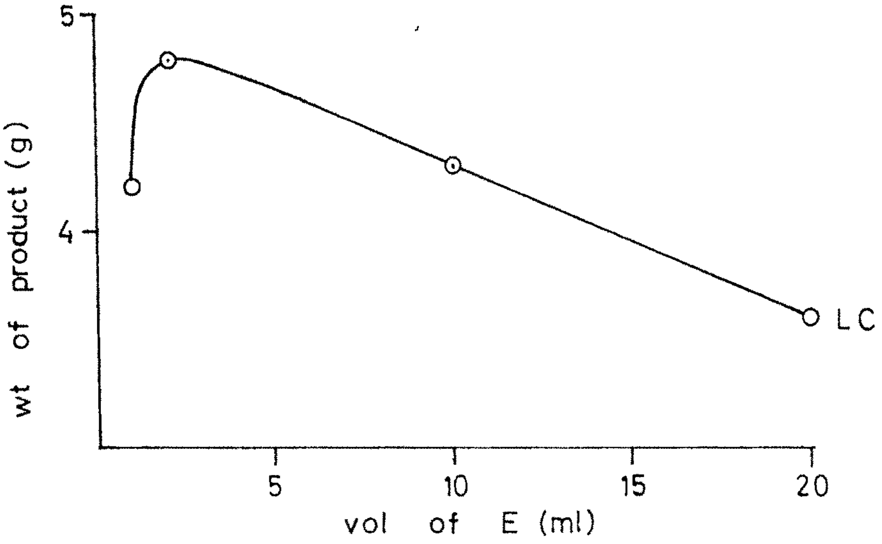


Fig III. 8 (b) data from table II 4(d)

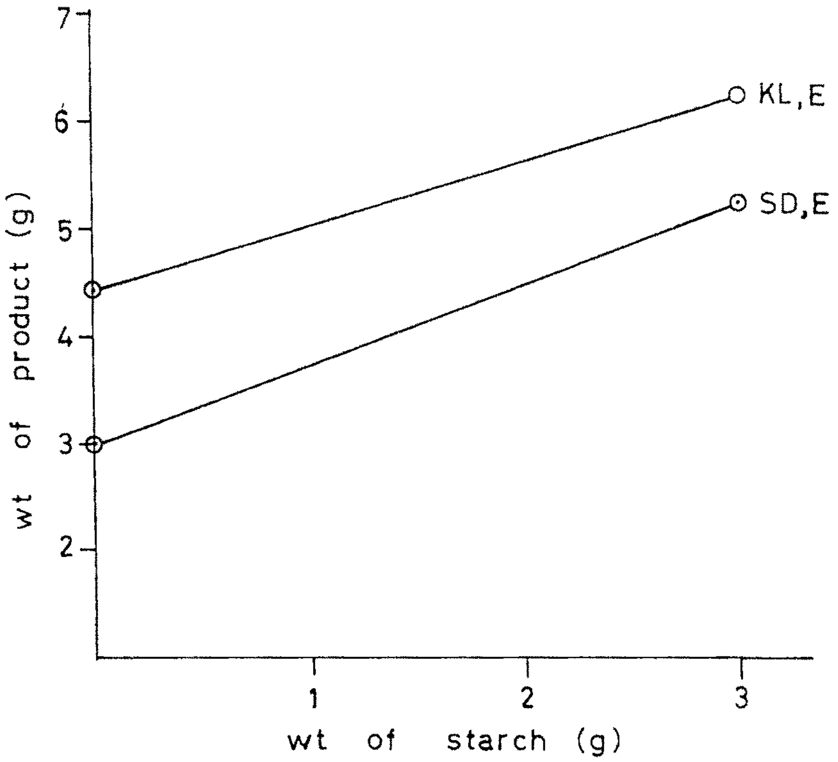


Fig III.9 data from table II 4(e)

3(c) Salicyl aldehyde

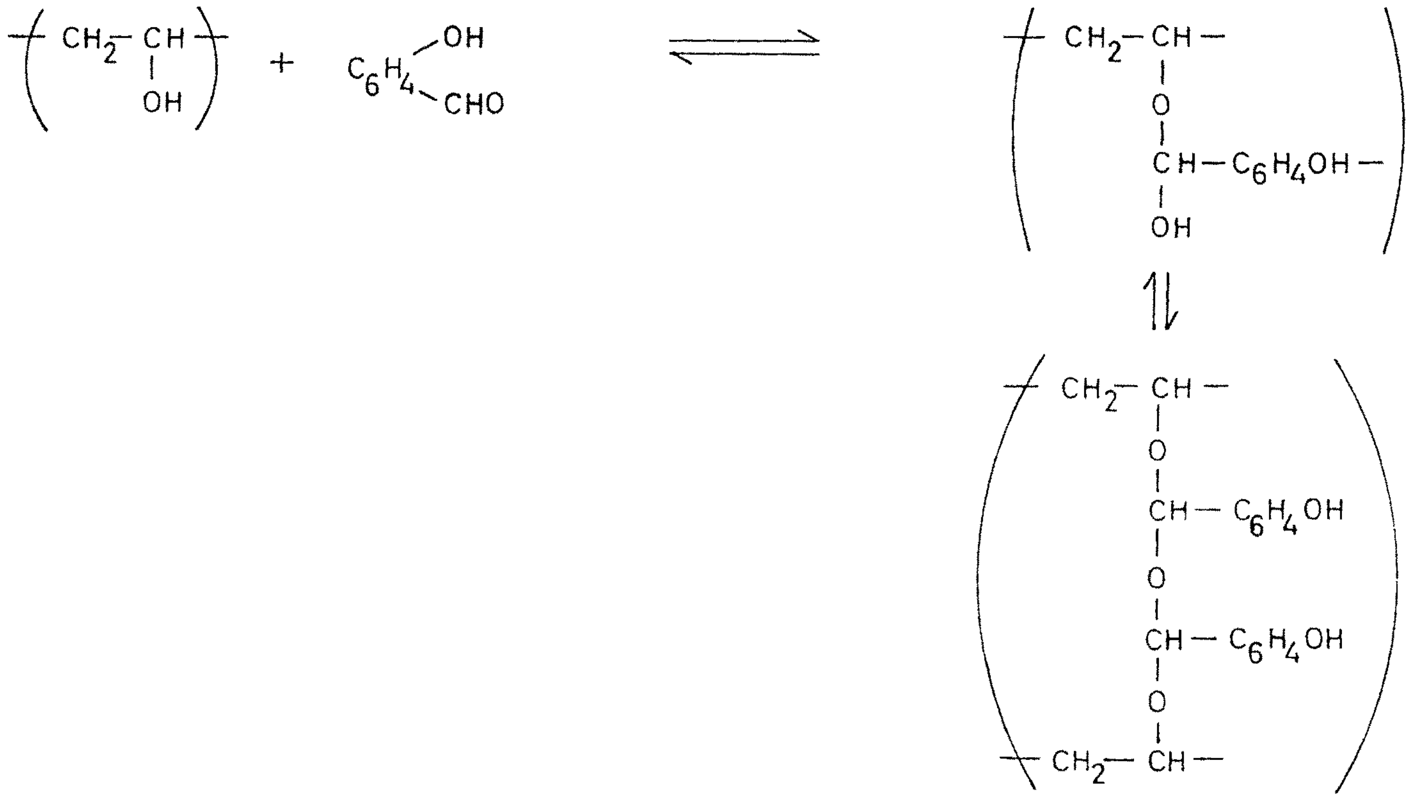
Salicyl aldehyde was used both as a condensing agent (144) and as a chelating agent. The condensation reaction is expected to yield hemi-formal type of the product which on curing would get transformed into formal type of the product (eq.III.4).

The yield of the product increases as the amount of salicyl aldehyde increases under alkali-acid condition (fig III.10). It is obserred that the yield in absence of water or alcohol is lower than in its presence and the yield in presence of water is generally lower than that in presence of alcohol. It is considered that the reaction would be in heterogeneous phases.

The addition of starch generally increases the yield of the product. It implies that starch may favour the reaction with salicyl aldehyde.

3(d) Chloral hydrate

Chloral hydrate has been used as a condensing agent. It is observed that increase in the amount of chloral hydrate increases the yield of the product (figs III.11 and 12). It is suggested that poly oxy-methylene type of reaction is also taking place (eq.III.5).



Eq. III . 4

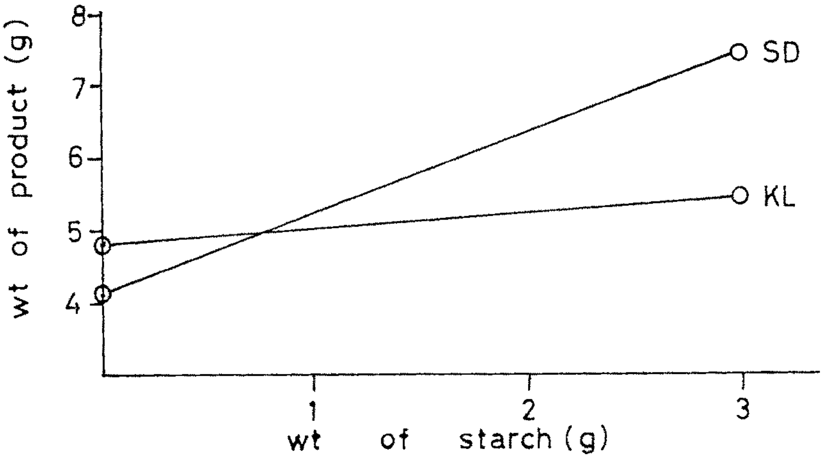


Fig III. 10(a) data from table II.4(g)

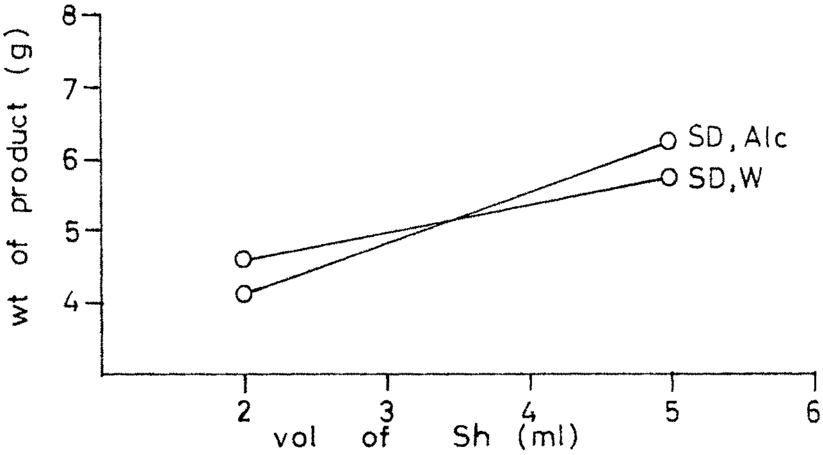


Fig III. 10(b) data from table II 4(g)

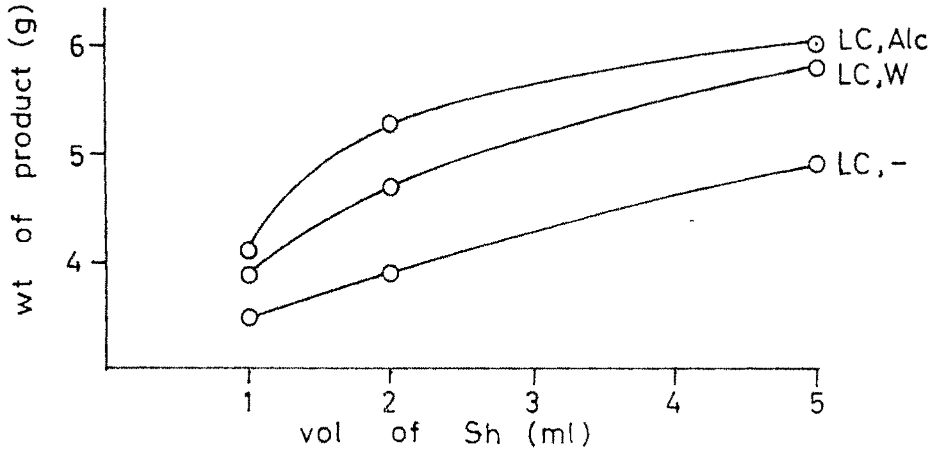


Fig III. 10(c) data from table II 4(g)

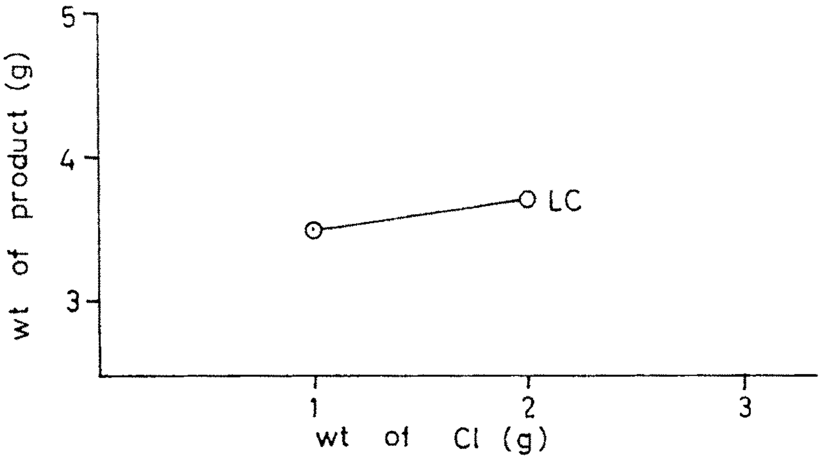


Fig III.11(a) data from table II 4(h)

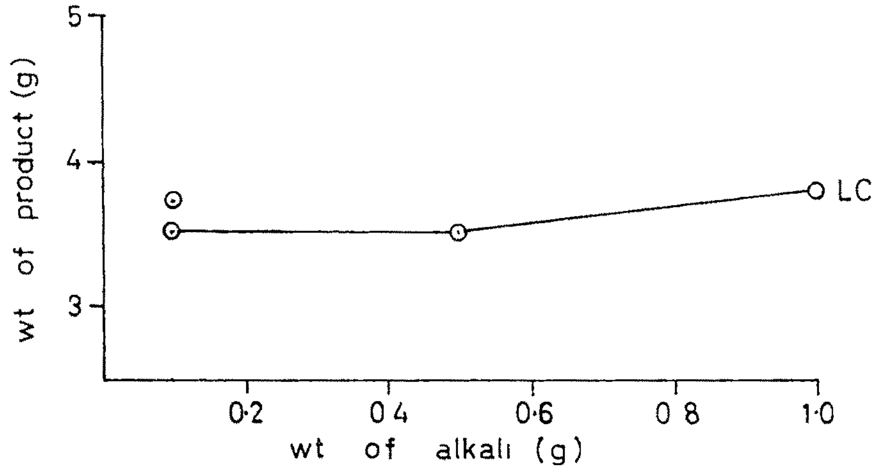


Fig III.11(b) data from table II 4(h)

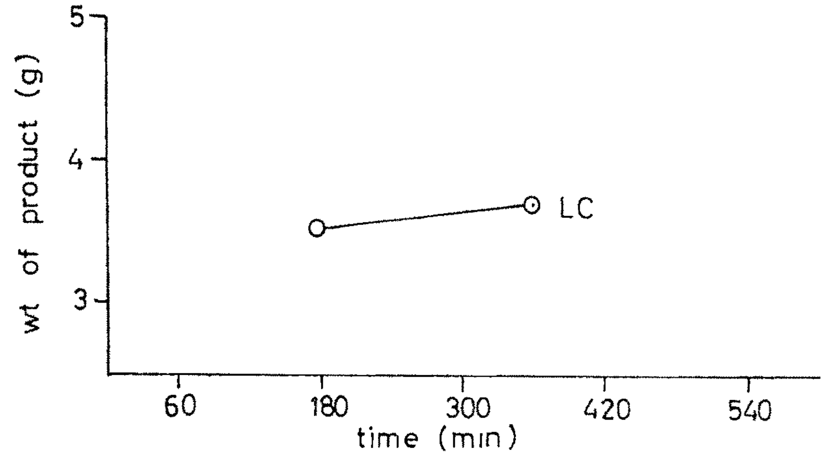


Fig III.11(c) data from table II 4(h)

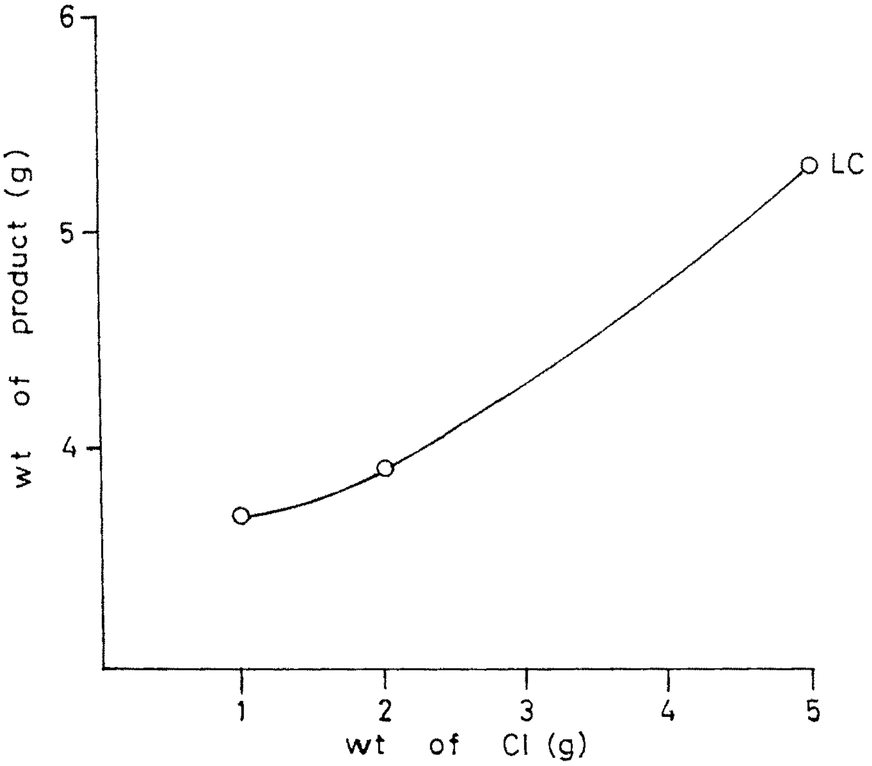


Fig **III.12(a)** data from table II.4(j)

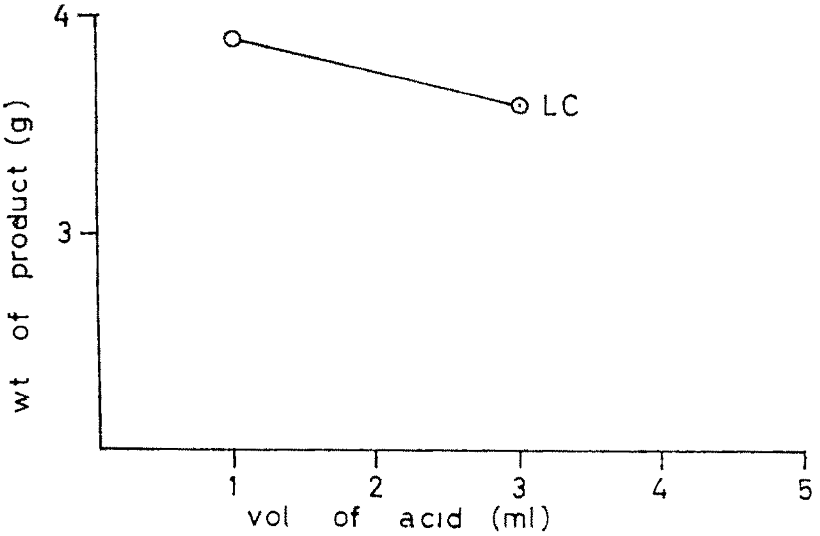
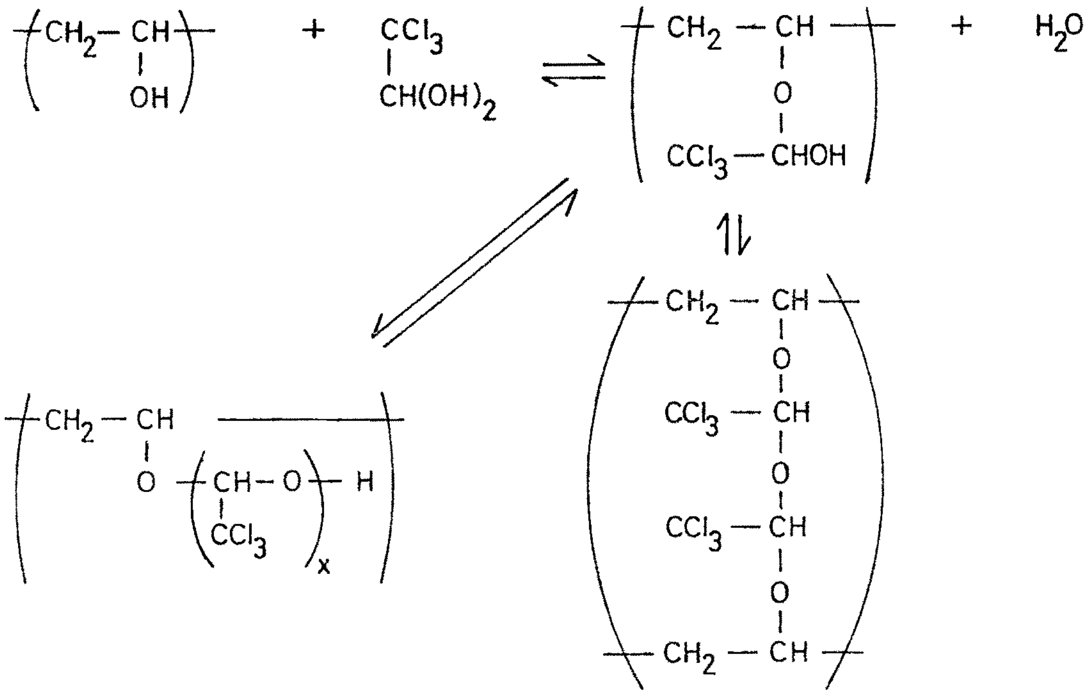


Fig **III.12(b)** data from table II.4(j)



Eq. III.5

The yield of the product increases some what with time and with the amount of alkali but decreases with the increase in the amount of acid. The acid treatment of the product obtained under alkaline conditions causes some deformalization.

All the products are coloured and are insoluble in various solvents but are affected slightly by acids and alkalis. Hence these products also do not seem to be suitable for exchange studies. Some studies were made on the weight loss in water, salt solution, etc. It was observed that weight loss is not neglible. Weight loss was higher in acidic solutions. Therefore it was decided to resinify some of these products with the aim of making them less soluble and more stable. These studies are considered next.

III.4 Chelating polyformals - Further resinification

4(a) Resorcinol

Poly vinyl alcohol was formalized and then further condensed with resorcinol (figs III.13(a) and 14 (a)). It has been observed that (i) the yield of the product increases with the increase in the amount of resorcinol, (ii) the addition of starch to the reaction system increases the yield of the product, (iii) the yield of the product in glycerine medium is higher than that in poly ethylene glycol medium.

4(b) 8-Hydroxy quinoline and resorcinol

Poly vinyl alcohol was formalized with formaldehyde, condensed with 8-hydroxy quinoline and further condensed with resorcinol. It has been observed (figs III.13(b) and 14(b))that the yield of the product increases with the increase in the amount of 8-hydroxy quinoline. Addition of starch to the reaction system also increases the yield of the product.

4(c) Ethyl aceto acetate and resorcinol

Poly vinyl alcohol was condensed with ethyl aceto acetate and then further condensed with resorcinol and formaldehyde (fig III.13(c) and 14(c)). It has been observed that the yield of the product increases with the increase in the amount of ethyl aceto acetate. Addition of starch also increases the yield of the product.

4(d) Chloral hydrate and resorcinol

Poly vinyl alcohol was condensed with chloral hydrate and then further condensed with resorcinol and formaldehyde (fig III.13(d) and 14(d)). It has been observed that (i) the addition of starch increases the yield of the product and (ii) increasing the amount of alkali increases the yield in presence of starch and decreases the yield in absence of starch.

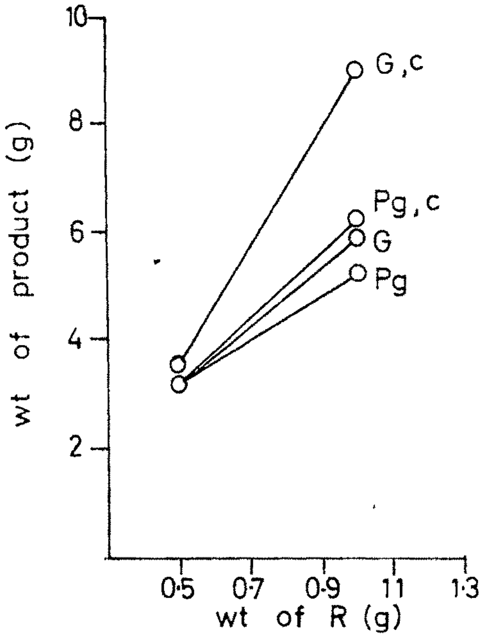


Fig III.13(a)

data from table II.6(a)

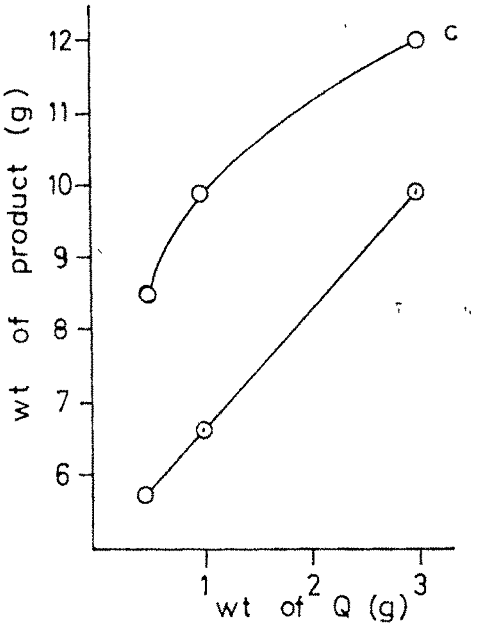


Fig III.13(b)

data from table II 6(b)

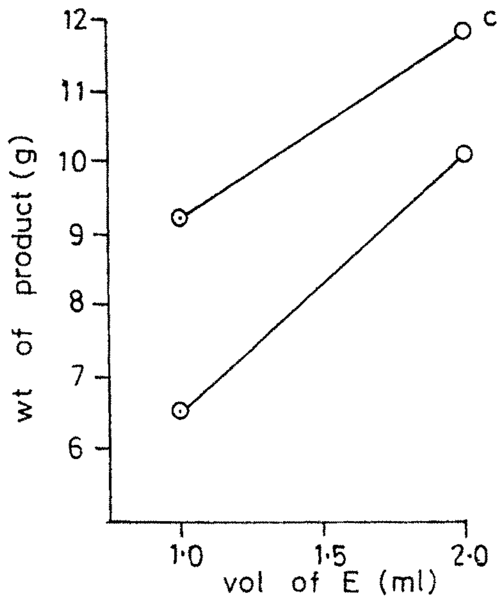


Fig III.13(c)

data from table II 6(c)

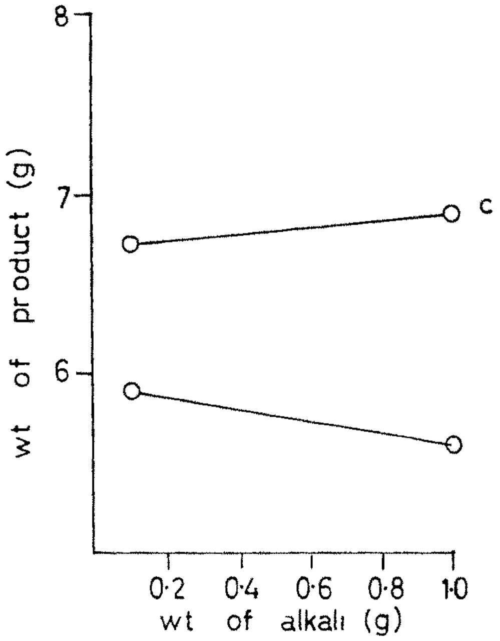


Fig III.13(d)

data from table II.6(d)

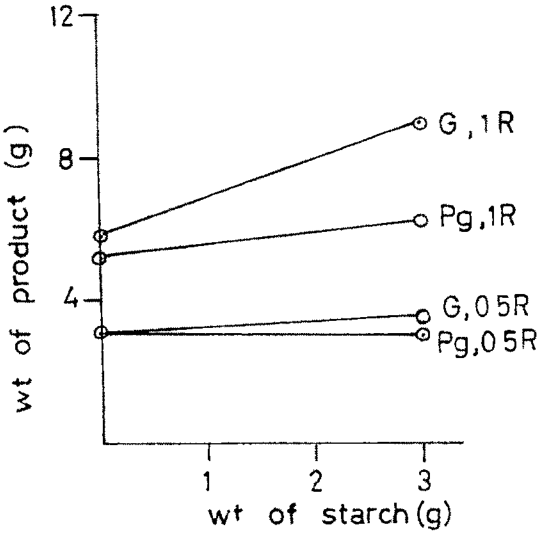


Fig III.14(a)
data from table II.6(a)

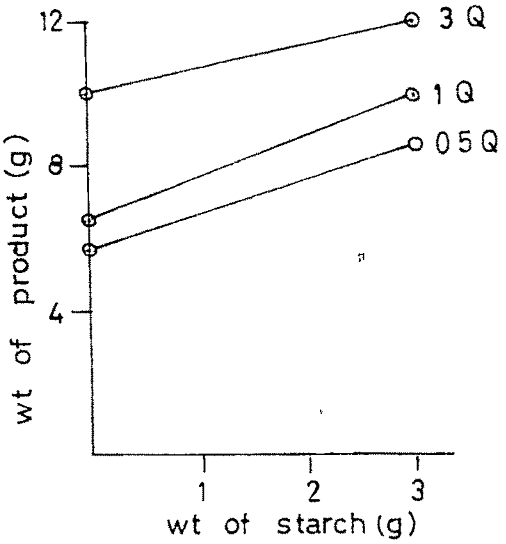


Fig III.14(b)
data from table II.6(b)

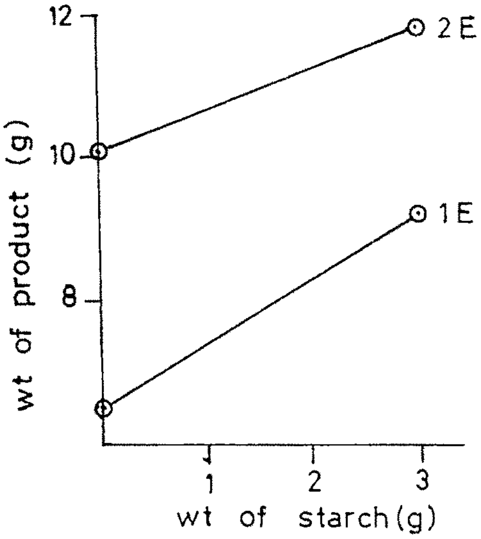


Fig III.14(c)
data from table II 6(c)

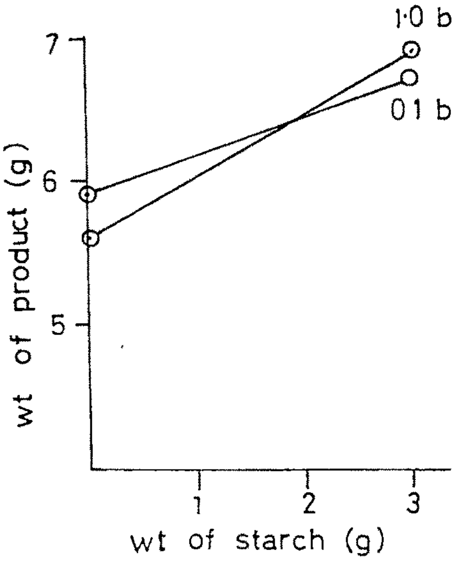


Fig III.14(d)
data from table II.6(d)

4(e) Colour and solubility of the products

It is seen that products considered in 4(a) above are reddish brown (or brown) in colour and insoluble in various solvents. The products obtained with 0.5g resorcinol are slightly affected by acids and alkalis but the products obtained with 1g resorcinol are insoluble in various solvents and are stable to the action of acid and alkali.

The products considered in 4(b) are red or orange in colour. They are insoluble in various solvents and are stable to the action of acid and alkali.

The products obtained with ethyl aceto acetate and resorcinol are reddish brown or black and are insoluble in various solvents, and are stable to 1N acid and alkali.

The products obtained with chloral hydrate and resorcinol are brown or reddish brown in colour and are insoluble in various solvents and are stable to 1N acid and alkali.

These products are now studied for their sorption and solubility in water.

4(f) Swelling and solubility

Water content of these products varies from 4% to 36%. The products obtained by condensation with ethyl aceto acetate or chloral hydrate have relatively higher water content than those obtained by condensation with formaldehyde alone.

Wt gain/g of the sample vs % conc. of NaCl in water is plotted in fig III.15, wt gain/g of the sample vs the amount of resorcinol used in the reaction is plotted in fig III.16 and wt loss of the sample/l of water or solution is plotted in fig III.17. Wt gain/g of the sample represents its degree of swelling in water. It has been observed that the degree of swelling of the sample generally decreases as the concentration of NaCl in solution increases and as the amount of resorcinol in the reaction increases. It can be suggested that increase in the amount of resorcinol in the reaction increases the resinification of the product and hence causes reduced swelling.

Wt loss of the sample/l can be related to the g-solubility of the sample. It has been observed that the samples which exhibited g-solubility in water have become insoluble in 1% salt solution (fig III.17). Thus the samples are salted out from

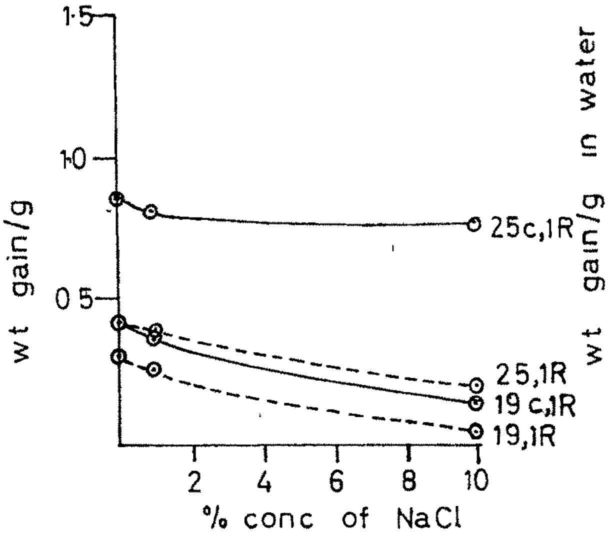


Fig III.15(a)
data from table II 9,10,11(a)

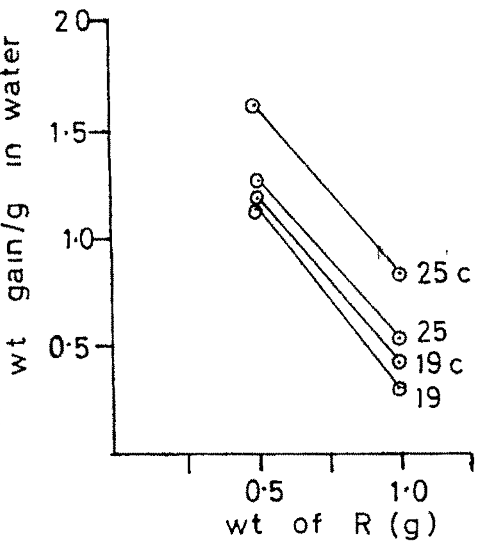


Fig III.16
data from table II.9,10,11(a)

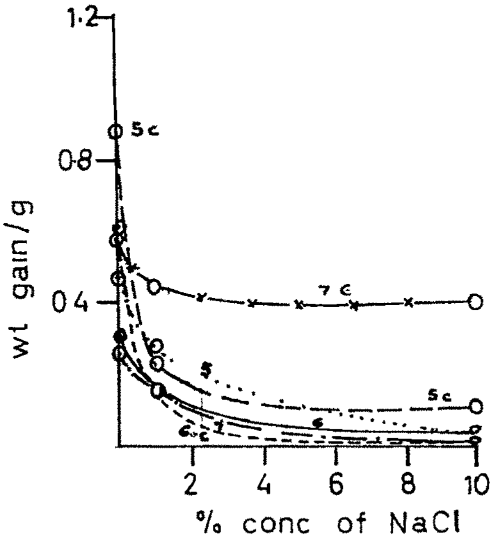


Fig III.15(b)
data from table II.9,10,11(b)

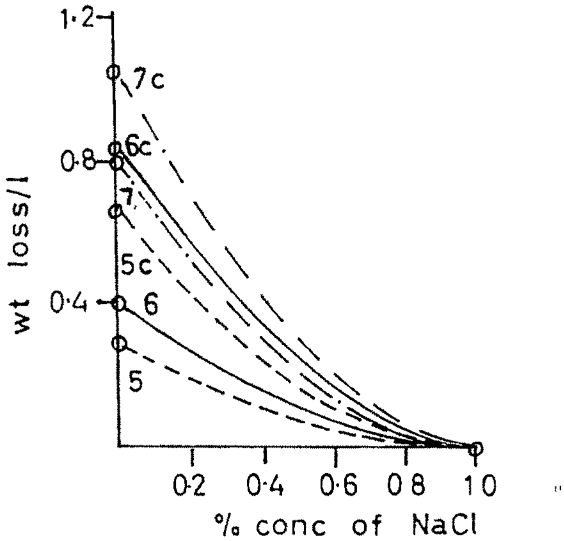


Fig III.17(a)
data from table II 9,10,11(b)

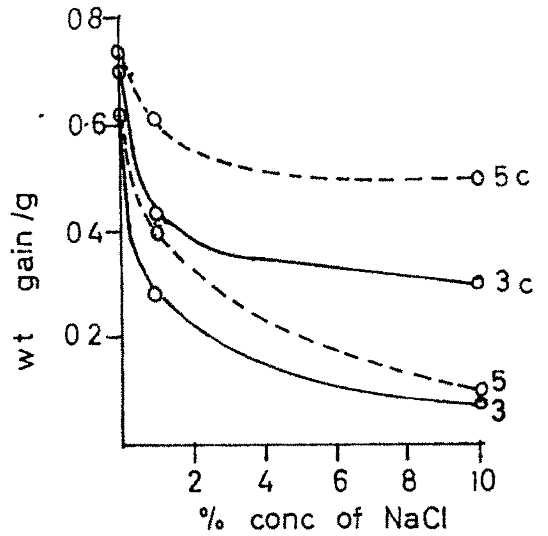


Fig III.15(c)
data from table II. 9,10,11(c)

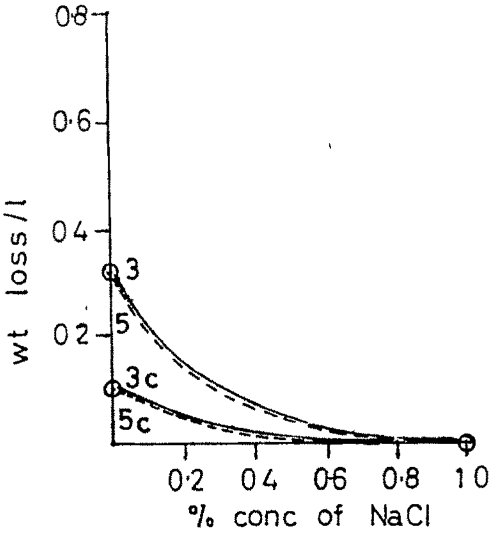


Fig III.17(b)
data from table II.9,10,11(c)

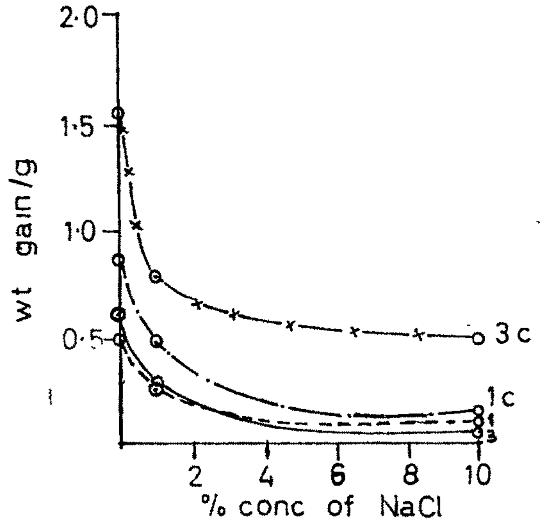


Fig III.15(d)
data from table II.9,10,11(d)

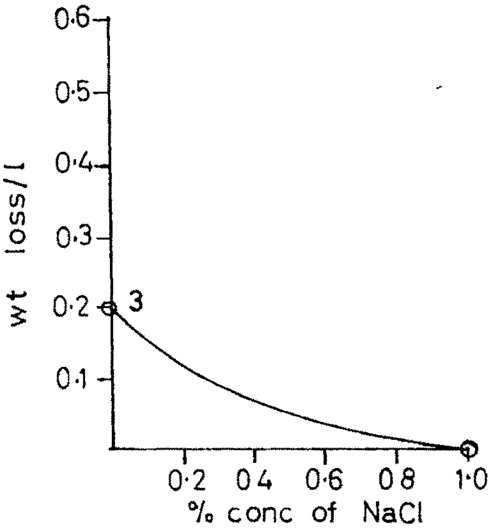
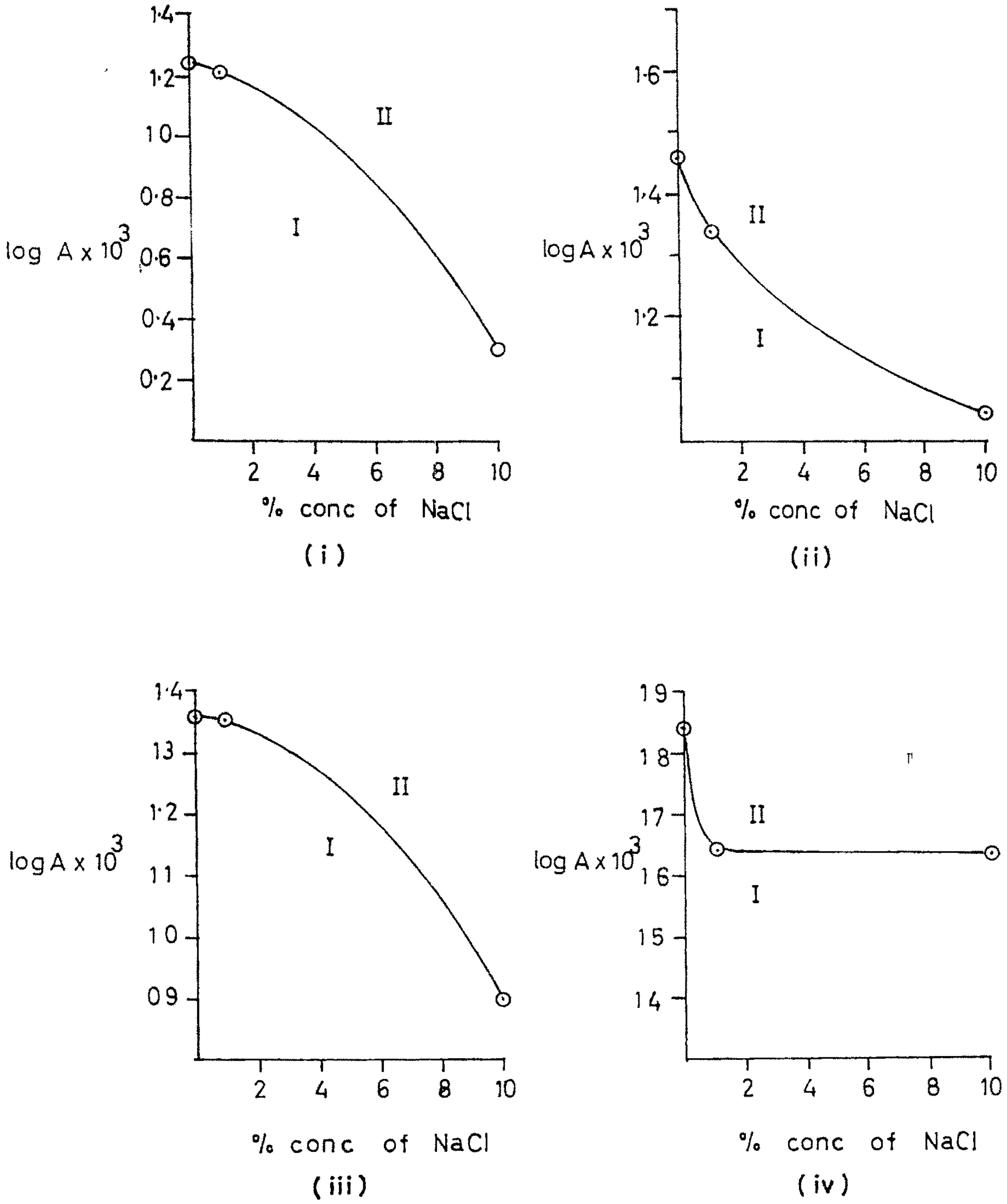


Fig III.17(c)
data from table II.9,10,11(d)

1% salt solution and the degree of salting out can be considered almost unity. It is considered that g-solubility and degree of swelling are inter-related i.e. decrease in solubility causes decrease in swelling.

Calculations have been made of the water (moles) (A) required to cause maximum swelling of 1g of the sample and water (moles) (B) required just to dissolve 1g of the sample. Plots of logA or logB versus % concentration of salt in solution has been presented in fig III.18. There are three regions I, II, and III separated by two lines- Region I can be termed as region of incomplete swelling, region III can be termed as region of complete solubilization and region II can be termed as region of equilibrium of swelling and solubilization. Region III is observed only in few cases. Hence in most cases only swelling is observed. Similar results were obtained for salt solutions at pH 10. These products were, therfore, used for the study of ion exchange of Cu(II), Ni(II) and Zn(II) ions.

An attempt is also made to corelate number of moles of water (A) required for maximum swelling of the product with its water content (moles) per g (q'). It is observed that the ratio of A to q/18 varies from 1.6 to 11.0 for water, 1 to 5.7 for 1% NaCl solution and 0.1 to 5.5 for 10% NaCl solution(table III.2)



(i)

(ii)

(iii)

(iv)

Fig III . 18 (a)

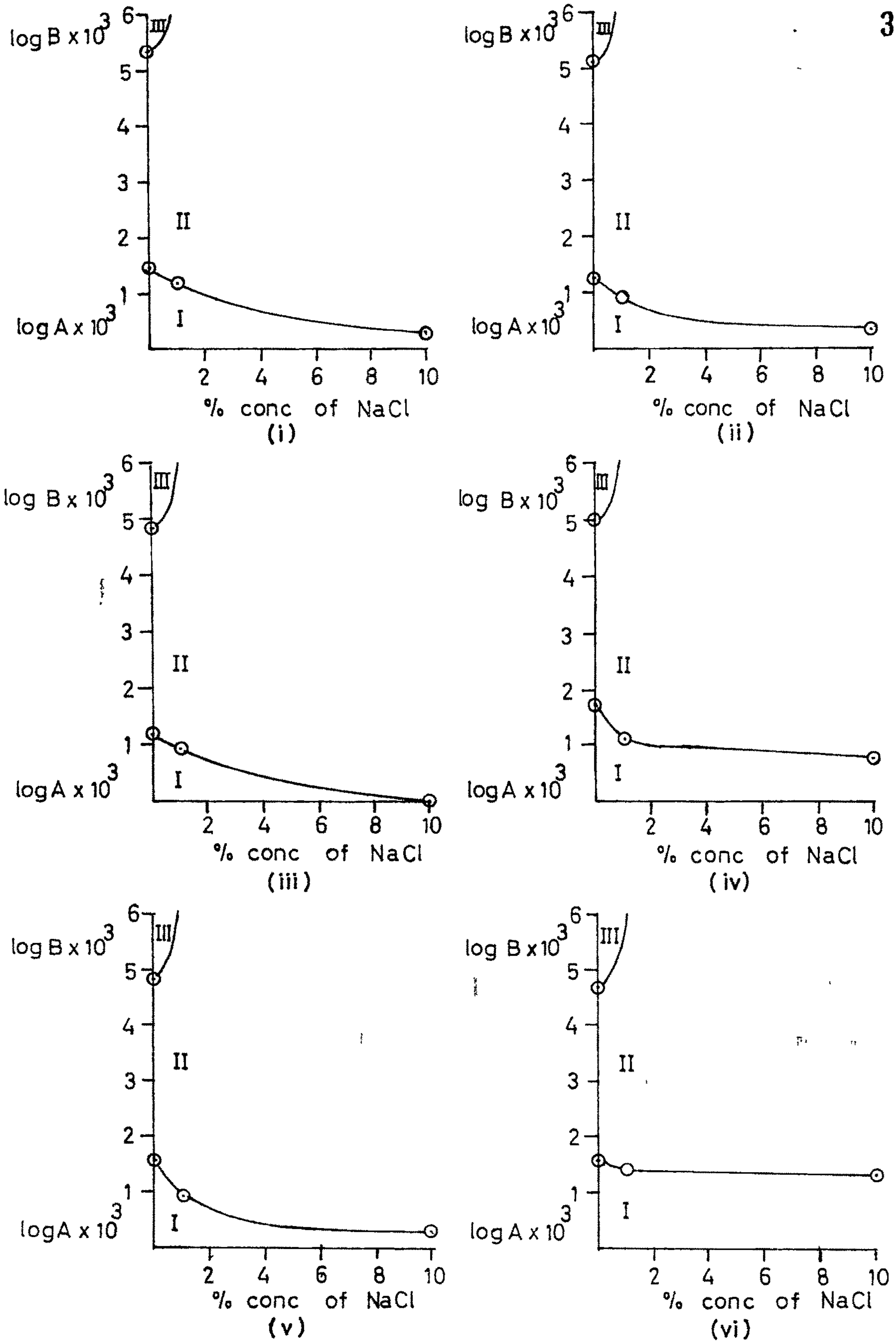

log B x 10^3
log A x 10^3
6
5
4
3
2
1
I
II
III
2
4
6
8
10
% conc of NaCl
(i)
(ii)
(iii)
(iv)
(v)
(vi)

Fig III.18(b)

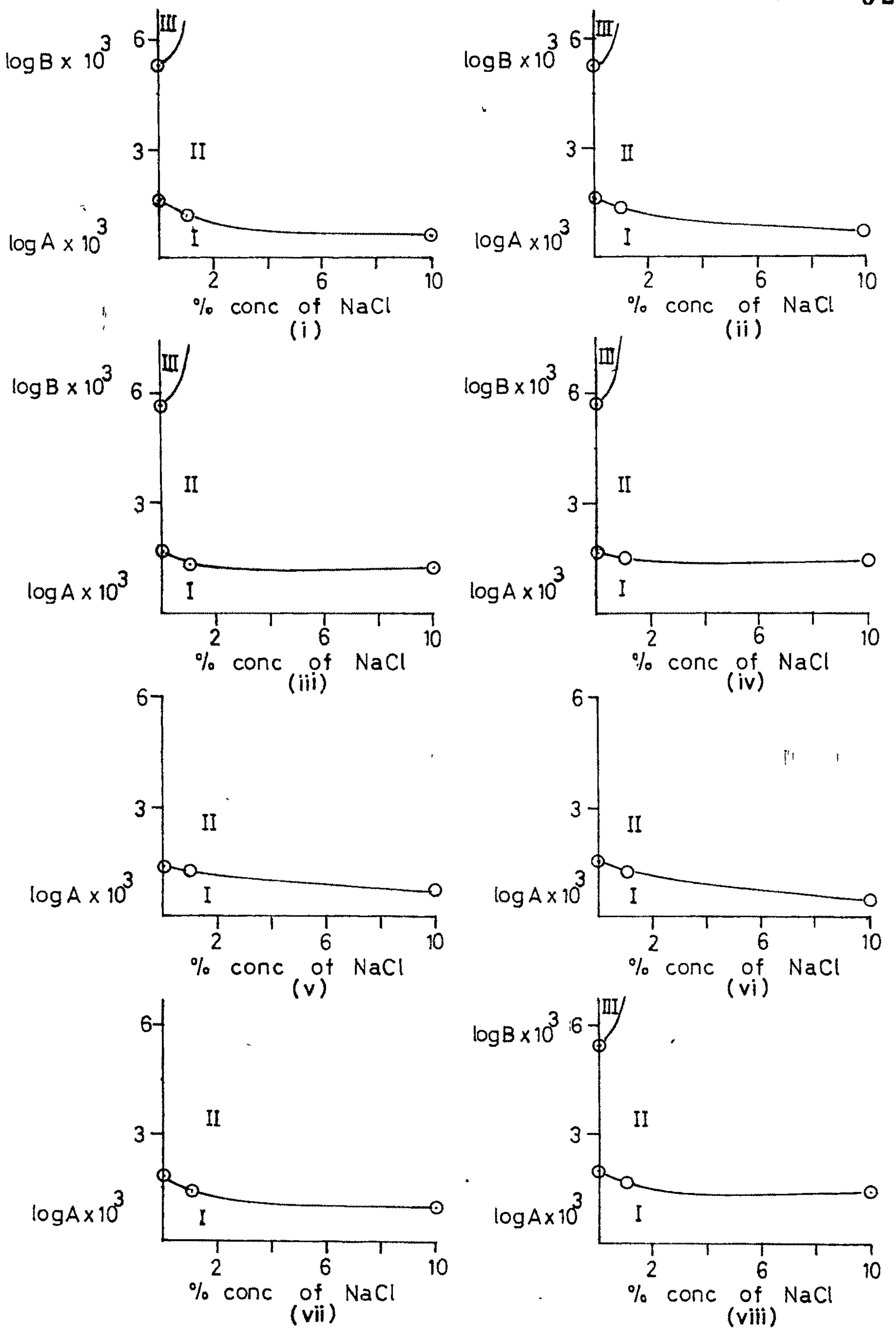

log B x 10^3
log A x 10^3
6
3
III
II
I
2
6
10
% conc of NaCl
(i)
(ii)
(iii)
(iv)
(v)
(vi)
(vii)
(viii)

Fig III.18(c)

Table III.2

No	Product	ratio A : 9/18		
		water	1% NaCl solution	10% NaCl solution
1	2	3	4	5
1	19KPFR	3.40	3.20	0.40
2	25KPFR	5.80	4.40	2.20
3	19KPFRc	2.30	2.30	0.80
4	25KPFRc	8.87	5.66	5.53
5	5KPFQR	3.90	2.25	0.30
6	6KPFQR	2.04	1.08	0.24
7	7KPFQR	1.69	1.01	0.11
8	5KPFQRc	6.65	1.66	0.83

Table III.2 (contd.)

1	2	3	4	5
9	6KPFQRc	4.57	1.11	0.28
10	7KPFQRc	4.57	3.32	3.05
11	3KPERF	2.91	1.29	0.34
12	5KPERF	4.71	3.05	0.69
13	3KPERFc	4.13	2.54	1.80
14	5KPERFc	4.34	3.50	2.96
15	1KPClRF	2.65	1.52	0.47
16	3KPClRF	5.73	2.95	0.49
17	1KPClRFc	4.64	2.65	0.85
18	3KPClRFc	11.05	5.66	3.60

Values less than one ih case of 10% NaCl solution indicates that the capacity of the product to contain water is reduced under those conditions. It is suggested that water molecules get preferentially attached to ions in concentrated salt solutions and these large solvated ions would not penetrate through the polymeric network.

4(g) Copper (II) chelates, Ni (II) chelates and Zn (II) chelates

Resins were prepared by cross-linking metal oxinates with furfural and rosorcinol and their distribution coefficients were studied by Bernhard and Grass (105). Chelate polymers of Cu (II), Ni(II) and Mn(II) with the resins of oxine with formaldehyde were prepared by Minato and Fujisawa (151). Tolmacher and Orlova (79) prepared resins of oxine with formaldehyde and resorcinol. OH groups in the polymer are very weakly acidic and the resins swelled more in basic than in neutral solutions because of the greater dissociation of OH groups at high pH, which leads to the electrostatic repulsion of the charged macromolecular particles and additional hydration. These resins absorb metal ions better at high pH because of their weakly acidic properties. Orlova, Tolmacher and Simonnko (152) observed that the adsorption of Cu(II) ions by oxine-resorcinol-formaldehyde resin was attributed to the complex formation between Cu(II) ions and oxine and followed a gel adsorption mechanism. Vernon and Eccles (108) prepared and compared various oxine-containing chelating ion exchangers and suggested that other factors were responsible for chelation in addition to the oxine groups present. Vernon (153) reported the preparation of oxine-resorcinol-formaldehyde resin having Cu exchange capacity of 3.2 m mol/g. Vernon and Nyo (114) correlated the reactant ratios, nature of cure, degree of cross-linking and hydrophilicity of the oxine based ion exchangers with their metal ion exchange capacity and kinetics of metal ion uptake. Jones and Nyssen (110) studied ion uptake by various phenolic and other resins and observed that the functional groups present and the nature of polymerization linkages are less important in determining the hydrophilic/hydrophobic character of the polymers than the extent of potential cross-linkage and the presence of extensive non-polar segments. Borrowman and Altringer (111) observed that tungsten is adsorbed from alkaline solutions by oxine-resorcinol-formaldehyde resin. Nakatsuka and Hanabusa (113) patented oxine-cresolformaldehyde resin capable of sorbing metal ions above pH 9. Donya and coworkers (154) prepared oxine-containing amino styrene polymers and studied their Cu ion exchange capacity. Thus oxine based condensation resins have been studied by various workers.

The present studies deal with Cu(II) ion, Ni(II) ion and Zn(II) ion uptake by the products. The products can be considered as (i) formaldehyde condensation resins (FR), (ii) oxine-added formaldehyde condensation resins (QFR), (iii) ethyl aceto acetate condensation resins (ER) and (iv) chloral condensation resins (ClR). They are prepared in presence or absence of starch (c). The metal ion uptake recorded (i.e. metal ion sorbed by resin at equilibrium) is maximum and hence can represent the ion exchange capacity (m mole/g). It is observed that in case of Cu(II) ion exchange capacity (i) the products prepared in presence of starch have, in general, higher capacity than those prepared in absence of starch indicating the effect of factors other than the complexing groups present on ion uptake, (ii) ClR products have lower capacity than the corresponding ER products, (iii) ER products have lower capacity than the corresponding FR products, (iv) QFR products have lower capacity than FR products indicating that addition of oxine does not increase the exchange capacity of the product, (v) the exchange capacity lies in the range of 0.68 - 2.33 for FR products, 0.21 - 0.51 for QFR products, 0.56 - 1.12 for ER products and 0.35 - 0.97 for ClR products, (vi) increase in the amount of oxine in the preparation does not increase the exchange capacity and (vii) increase in the amount of resorcinol in the preparation does not increase the exchange capacity. It is suggested that poly vinyl alcohol is the major complexing agent in the product and addition of increasing amounts of resorcinol or oxine lowers poly vinyl alcohol percentage and hence the exchange capacity is lowered.

It is observed that in case of Ni(II) ion exchange capacity (i) products prepared in presence of starch have lower exchange capacity than those prepared in absence of starch, (ii) ClR products have higher exchange capacity than the corresponding ER products, (iii) ClR products have higher exchange capacity than FR products, (iv) QFR products have lower exchange capacity than FR products, (v) the exchange capacity lies in the range of 0.21 - 1.66 for FR products, 0.51 - 0.77 for QFR products, 0.71 - 0.94 for ER products and 0.91 - 1.30 for ClR products,

(vi) increase in the amount of oxine in preparation does not increase the exchange capacity of the product and (vii) increase in the amount of resorcinol in the preparation increases the exchange capacity of the product. It is suggested that poly vinyl alcohol and resorcinol are major complexing agents.

It is observed that in case of Zn(II) ion exchange capacity (i) majority of the products prepared in presence of starch has higher exchange capacity than those prepared in absence of starch, (ii) ClR products have higher exchange capacity than the corresponding ER products, (iii) ER products have lower exchange capacity than the corresponding FR products, (iv) QFR products have lower exchange capacity than FR products, (v) the exchange capacity lies in the range of 0.58 - 1.86 for FR products, 0.31 - 0.81 for QFR products, 0.42 - 0.78 for ER products and 0.69 - 0.87 for ClR products, (vi) increase in the amount of oxine in the preparation in the presence of starch increases the exchange capacity of the product and (vii) increase in the amount of resorcinol in presence of starch decreases the exchange capacity of the products and increase in the amount of resorcinol in the preparation in absence of starch increases the exchange capacity of the product.

The degree of extraction of metal ion from solution (pH $\sim$10) by the product is evaluated as the ratio of m moles of ion sorbed by the product to the m moles of metal ion taken in solution for the same amount of the products. The values are presented in table III. 3. It is observed that (i) the values lie in the range of 0.018 - 0.100 for Cu(II) ions, 0.005 - 0.063 for Ni(II) ions and 0.011 - 0.033 for Zn(II) ions and (ii) the value increase in order

$$\text{Zn(II)} < \text{Ni(II)} < \text{Cu(II)}$$

for most of the products except 5KPFQR, 6KPFQR, 1KPClRF and 3KPClRF where the values increase in order

$$\text{Zn(II)} < \text{Cu(II)} < \text{Ni(II)}$$

for 19KPFR'c and 25KPFR'c where the values increase in order

$$\text{Ni(II)} < \text{Zn(II)} < \text{Cu(II)}$$

and for 7KPFQR where the values increase in order

$$\text{Cu(II)} < \text{Zn(II)} < \text{Ni(II)}$$

The majority of the sorbed species follow the expected stability order

$$\text{Ni} < \text{Cu} < \text{Zn}.$$

Table III.3

No	Product	degree of extraction x 10^2		
		Cu(II)	Ni(II)	Zn(II)
1	2	3	4	5
1	19KPFR	6.1	4.5	2.9
2	25KPFR	10.0	5.0	2.6
3	19KPFRc	7.0	2.9	2.6
4	25KPFRc	10.0	3.3	2.9
5	19KPFR'	6.7	3.4	1.2
6	25KPFR'	3.3	1.3	1.2
7	19KPFR'c	7.4	0.9	3.2
8	25KPFR'c	8.9	0.5	3.7
9	5KPFQR	3.0	3.3	1.8
10	6KPFQR	1.8	2.5	1.1

Table III.3 (contd.)

1	2	3	4	5
11	7KPFQR	2.2	3.0	2.6
12	5KPFQRc	4.4	3.7	1.4
13	6KPFQRc	3.4	2.5	1.8
14	7KPFQRc	4.4	3.3	2.9
15	3KPERF	4.4	3.7	2.6
16	5KPERF	4.8	4.5	1.8
17	3KPERFc	6.5	3.3	1.5
18	5KPERFc	9.2	3.4	2.1
19	1KPClRF	3.4	4.5	2.7
20	3KPClRF	3.1	6.3	2.6
21	1KPClRFc	6.1	4.1	2.9
22	3KPClRFc	8.2	4.6	2.7

III.6 Bis-phenol-A resins

Resins have been prepared by condensing bisphenol-A with formaldehyde in presence of other phenolic or amino compounds. Products are modified by treatment with epichlorhydrin. Resins are also prepared in toluene.

Weight of the product obtained is plotted against the weight of the phenolic or amino compound in fig III. 19 , and against the weight of the reactant in presence of epichlorlhydrin in fig III. 20 . It is observed that (i) higher yield is obtained in presence of starch than in absence of starch indicating the reaction of starch with formaldehyde, (ii) higher yield is obtained under basic conditions than under acidic conditions, implying higher reactivity of ionic species under basic conditions, (iii) addition of diethylene triamine increases the yield of the product indicating its participation with the reacting species and (iv) yield is higher when the reaction is carried out in toluene than when the corresponding reaction is carried out in water.

The products prepared in water are red, orange or brown and are insoluble in various solvents. They are stable to the action of 1N acid or alkali. The products

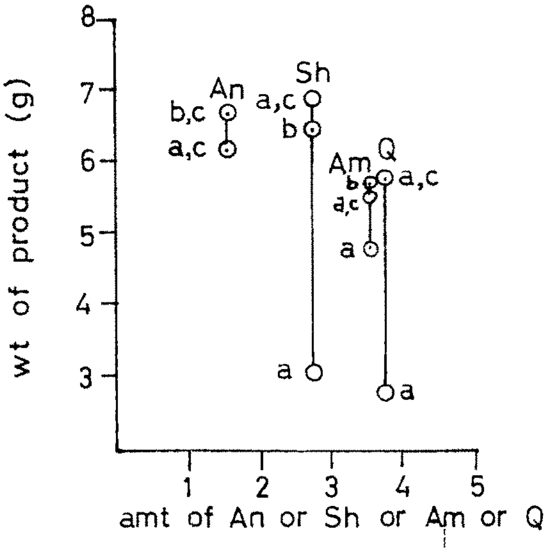


Fig III.19
data from table II.15(a,b,c)

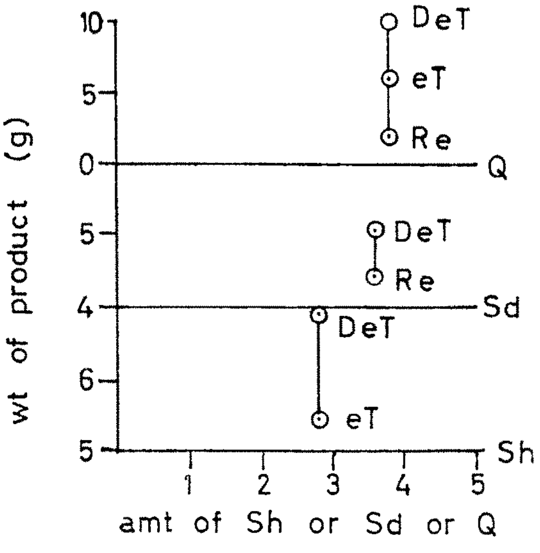


Fig III.20
data from table II 15 (f,g,h)

prepared in toluene are yellow, red or brown and are insoluble in various solvents. They are stable to the action of 1N acid or alkali.

The water content of these products lies in the range of 2.5 - 12.0%. It is observed that there is no weight loss/1 for any of these products in water. The degree of swelling of these products lies in the range of 0.13 - 1.61. All products except TBFQe have the degree of swelling in the range of 0.13 - 0.53. Oxine - based resins prepared in toluene have relatively higher degree of swelling than other products.

Calculations have been made of A ÷ q/18 for water and the values are presented in table III.4. It is observed that the values lie between 1.89 and 17.80. High values are observed for TBFQe (17.80) and BFSda (12.86).

Kamon and Saito (155) studied the curing of epoxy resins with acid hydrazides. Fock, Schedlitzki and Wacker (156) patented flexible products prepared from acrylic copolymers and bisphenol-A-epichlorhydrin copolymers. Domba (157) patented the copolymers from amino acids and epichlorhydrin. Laverty (158) polymerized N(salicylidene aniline) acrylamide in toluene and studied its chelates

Table III.4

No	Product	ratio A : g/18
		water
1	2	3
1	BFSha	2.86
2	BFSda	12.86
3	BF	3.57
4	BFSh	7.14
5	BFAm	2.26
6	BFAh	7.86
7	BFAn	3.59
8	BFRF	7.58
9	BFQRF	2.13

Table III.4 (contd.)

1	2	3
10	BFAmRF	1.89
11	BFQRFc	5.15
12	BFShRFc	4.87
13	BFSdRFc	4.44
14	BFAhRFc	5.76
15	BFAmRFc	5.15
16	BFAnRFc	6.97
17	BFSdRF	3.80
18	BFShe	3.64
19	BFQeRF	2.41

Table III.4 (contd.)

1	2	3
20	BFSdeRF	4.55
21	BFAmeRF	5.20
22	TBFe	2.50
23	TBFQe	17.80
24	TBFShe	4.85
25	TBFAne	4.72
26	TBFDe	2.78
27	TBFQDe	4.33
28	TBFShDe	4.87
29	TBFSdDe	2.98

with metal ions. Vernon and Eccles (159) prepared condensation resins from salicylic acid and p-hydroxy benzoic acid and found that salicylic acid exchanger had a higher selectivity for Fe(III) than the corresponding p-hydroxy benzoic acid exchanger. 4-Chlorosalicylic acid polymers were prepared and were found to exhibit polyelectrolyte behaviour (160). Tercopolymers were prepared by condensing salicylic acid and thiourea with trioxane and their ion uptake was studied (161). Similarly salicylic acid-urea-formaldehyde copolymer was prepared and its metal chelates were studied (162). A chelating resin cantaining nitroso-resorcinol was prepared and its metal ion sorption behavior was examined (163).

In the present studies Cu(II), Ni(II) and Zn(II) ion uptake by these products has been investigated. The products may be considered as (i) bisphenol-A-formaldehyde-amino or phenolic compounds condensation resins (BF), (ii) bisphenol-A-amino or phenolic compound-resorcinol-formaldehyde condensation resins (BFR), (iii) bisphenol-A-phenolic compound-formaldehyde-epichlorhydrin epoxy resins (BFe). and (iv) bisphenol-A-amino or phenolic compound-formaldehyde-epichlorhydrin or diethylene triamine (toluene medium) condensation resins (TBF). Ion uptake represents the exchange capacity of the products. It is observed that in case of Cu(II) ion exchange capacity (i) the exchange capacity lies in the range of 0.21-1.53 for BF products, 0.85-1.54 for BFR products, 0.31-1.81 for BFe products and 0.11-0.64 for TBF products, (ii) addition of resorcinol in the preparation increases the exchange capacity of the product indicating the additional exchange sites provided by resorcinol, (iii) addition of starch in the preparation lowers the exchange capacity of the product, (iv) addition of epichlorhydrin in the preparation increases the exchange capacity, (v) product obtained from the reaction in toluene medium has lower exchange capacity than the corresponding preparation in water and (vi) addition of diethylene triamine in the preparation increases the exchange capacity of the product.

It is observed in case of Ni(II) ion uptake that (i) the exchange capacity lies in the range of 0.39-1.96 for BF products, 1.23-2.74 for BFR products, 0.40-2.11 for BFe products and o.00 to 1.06 for TBFe products, (ii) no exchange is observed for TBFShDe and TBFQDe products, (iii) BFSdRF has a relatively high value (2.74) of exchange capacity (iv) addition of resorcinol in the preparation increases the exchange capacity of the product, (v) addition of epichlorhydrin in the preparation increases the exchange capacity of the product, (vi) product obtained from the reaction in toluene medium has lower value of exchange capacity than the corresponding one from aqueous medium, (vii) addition of ethylene triamine in the preparation considerably lowers the exchange capacity of the product and (viii) Amino and hydroxy derivatives of the same aromatic system have the same exchange capacity of their resin products.

It is observed in the case of Zn(ii) ion exchange that (i) the values of exchange capacity lie in the range of 0.40-2.04 for BF products, 1.46-2.35 for BFR products, 0.61 -2.35 for BFe products and 0.21-1.06 for TBF products, (ii) addition of resorcinol in the preparation increases the exchange capacity of the product, (iii) addition of starch in the preparation lowers the exchange capacity of the product, (iv) product obtained from the reaction in toluene medium has lower exchange capacity than the corresponding preparation in water and (v) resin containing amino aromatic compound has higher exchange capacity than the resin containing the corresponding phenolic compound.

The degree of extraction of metal ion from solution (pH $\sim$10) by the product is evaluated and the values are presented in table III.5. It is observed that (i) the values lie in the range of 0.4-6.8 for Cu(II) ions, 0.00-4.3 for Ni(II) ions and 0.4-4.6 for Zn(II) ions and (ii) the values increases in order.

$Ni \leqslant Zn \leqslant Cu$

for most of the products except BFSha, BFSda, BFSh, BFSdRF and BFSdeRF where the values increase in order

$Zn < Ni < Cu$,

BFQeRF where the values increase in order

$Zn < Cu < Ni$

and TBFQe where the values increase in order

$Cu < Ni < Zn$

III.7 Chelating polymers (acrylic and xanthate Resins)

Acrylamide reacts with formaldehyde forming methylol derivatives. These would react with other amino compounds forming resinous network. Amino compounds used in the present studies are glycine, anthranilic acid, p-amino benzoic acid and m-amino phenol. The products obtained are brown, yellow or white in colour and are insoluble in all solvents and stable to 1N acid and alkali.

Table III.5

No	Product	degree of extraction		
		Cu(II)	Ni(II)	Zn(II)
1	2	3	4	5
1	BFSha	0.012	0.009	0.008
2	BFSda	0.060	0.043	0.034
3	BF	0.008	0.009	0.008
4	BFSh	0.012	0.009	0.008
5	BFAm	0.048	0.030	0.042
6	BFAh	0.044	0.030	0.034
7	BFAn	0.044	0.031	0.034
8	BFRF	0.044	0.043	0.042
9	BFQRF	0.052	0.030	0.042

Table III.5 (contd.)

1	2	3	4	5
10	BFAmRF	0.056	0.043	0.046
11	BFQRFc	0.032	0.027	0.032
12	BFShRFc	0.032	0.023	0.028
13	BFSdRFc	0.040	0.027	0.032
14	BFAhRFc	0.036	0.027	0.032
15	BFAmRFc	0.040	0.027	0.036
16	BFAnRFc	0.036	0.023	0.032
17	BFSdRF	0.056	0.056	0.042
18	BFShe	0.012	0.009	0.013
19	BFQeRF	0.040	0.043	0.034

Table III.5 (contd.)

1	2	3	4	5
20	BFSdeRF	0.068	0.043	0.046
21	BFAmeRF	0.061	0.043	0.046
22	TBFe	0.004	0.004	0.004
23	TBFQe	0.004	0.008	0.008
24	TBFShe	0.004	0.004	0.004
25	TBFAhe	0.022	0.020	0.020
26	TBFDe	0.004	0.004	0.004
27	TBFQDe	0.008	0.000	0.004
28	TBFShDe	0.008	0.000	0.004
29	TBFSdDe	0.011	0.004	0.008

Xanthate resin is prepared from m-amino phenol, formaldehyde and carbon disulphide. The product is black in colour and insoluble in various solvents and stable to 1N acid and alkali.

The water content of these products varies between 7.5 and 10.0%. The degree of swelling of these products lies in the range of 0.13 -2.65. Relatively high value is obtained for AFG1 (2.65).

The ratio A: q/18 has been calculated for these products (table III.6). The values lies in the range of 1.4 - 26.5. Very high sorption of water is observed for AFG1. It can be a good sorbent meterial.

The ion exchange capacity of these products lies in the range of 0.77 - 1.32 for Cu(II) ion, 0.44 - 0.89 for Ni(II) ion and 0.86 - 1.54 for Zn(II) ion. In the case of acrylic and xanthate resin the capacity is increasing in order.

$\mathrm{Ni} < \mathrm{Cu} \leq \mathrm{Zn}$

The degree of extraction of Cu(II), Ni(II) and Zn(II) ions by these products has been calculated. The values lie in the range of 2.8 - 4.8% for Cu(II) ions, 0.9 - 1.4% for Ni(II) ions and 1.6 - 2.9% for Zn(II) ions (table III. 7).

Table III.6

No	Product	ratio A: q/18
		water
1	2	3
1	AFGl	26.50
2	AFAd	3.33
3	AFAm	6.67
4	AFAp	5.70
5	ApFX	1.44

Tatle III.7

No	Product	degree of extraction x 10^2		
		Cu(II)	Ni(II)	(Zn(II)
1	2	3	4	5
1	AFGl	0.028	0.014	0.016
2	AFAd	0.028	0.014	0.021
3	AFAm	0.032	0.014	0.016
4	AFAp	0.036	0.019	0.025
5	ApFX	0.048	0.009	0.029

III.8 Chelating membranes

Various chelating resins containing formal and epoxy linkages have been presented. These resins were obtained in particle form and were studied in particle form. During the preparation of some of these products it was observed that they can be prepared in film or membrane form and if necessary may be plasticized by polyols. The membranes were prepared by casting without using matrix or support membrane. These include the membranes obtained from the reaction of (i) poly vinyl alcohol, resorcinol and formaldehyde (MPFR), (ii) poly vinyl alcohol, formaldehyde, oxine and resorcinol (MPFQR), (iii) poly vinyl alcohol, ethyl aceto acetate, resorcinol and formaldehyde (MPERF), (iv) poly vinyl alcohol, chloral, resorcinol and formaldehyde (MPClRF), (v) poly vinyl alcohol, formaldehyde, salicylic acid and resorcinol (MPFSdR), (vi) poly vinyl alcohol, formaldehyde, salicylic acid, oxine and resorcinol (MPFSdQR), (vii) poly vinyl alcohol, ethyl aceto acetate, salicylic acid, formaldehyde and resorcinol (MPESdRF), (viii) poly vinyl alcohol, chloral, salicylic acid, formaldehyde and resorcinol (MPClSdRF), (ix) poly vinyl alcohol, formaldehyde, salicylic acid and melamine (MPFSdm),

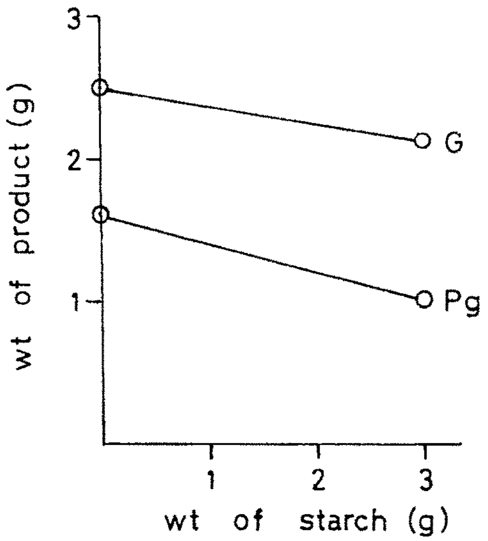


Fig III.21(a)
data from table II.29(a)

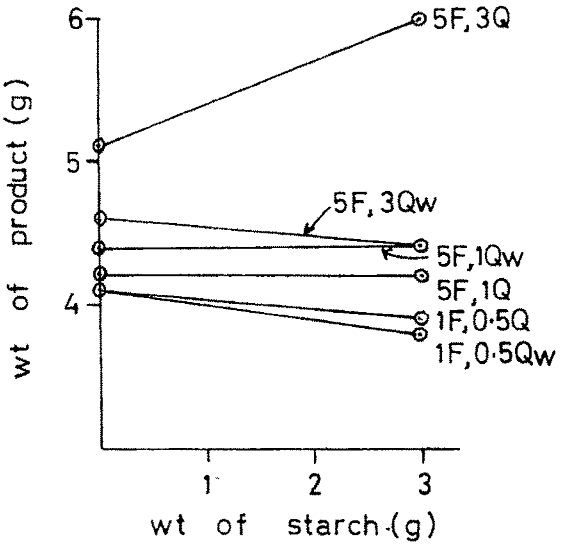


Fig III.21(b)
data from table II.29(b)

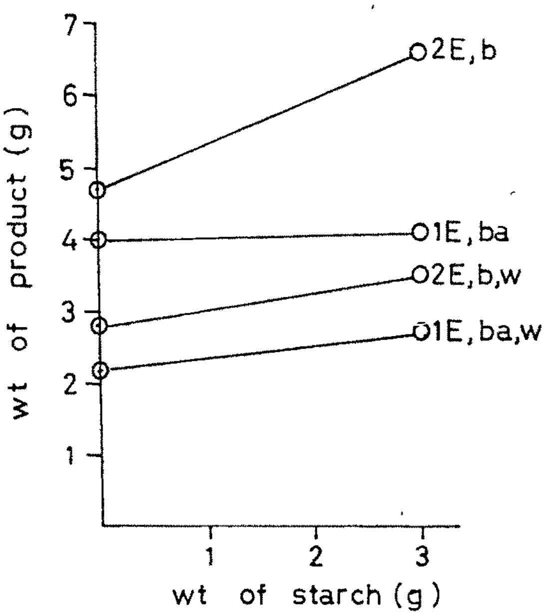


Fig III.21(c)
data from table II.29(c)

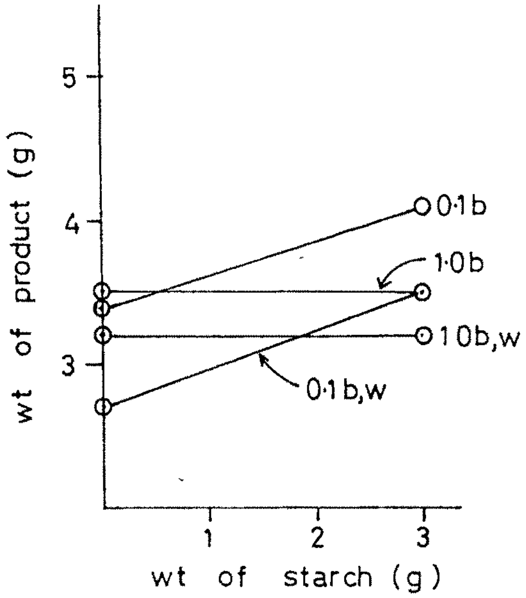


Fig III 21(d)
data from table II.29(d)

for MPClRF, 0.68 - 2.13 for MPXSdR where X=F,E or Cl, 0.64 - 1.04 for MPFSdm and MPFSdQm and 0.84 - 2.16 for MPXSdmB' where X=E or Cl. It is noted that relatively large values for % sorption are observed for M1KPClSdRFc (2.13) and M1KPESdmB'c (2.16).

Calculations have been made for the ratio $A \div q/18$ (table III.8). The values lie in the range of 5.77 - 48.24. Thus the amount of water sorbed by the product is much greater than the water content. Many of the membranes are considered to be good sorbents for water.

Intermolecular cross-linking was achieved by the reaction of formaldehyde, hydroxy acetaldehyde and chloro acetaldehyde with poly vinyl alcohol but not by the reaction of acetaldehyde, benzaldehyde, etc (164) and the degree of swelling of formaldehyde poly vinyl alcohol was correlated with cross -linking (165). Transparent water-resistant films were prepared by the reaction of formaldehyde with starch and acetalized poly vinyl alcohol (166). Formalized poly vinyl alcohol membranes have been studied for water vapour permeability (167). Porous material was obtained by the reaction of formaldehyde with starch and poly vinyl alcohol (168). Increasing pKc of aromatic sulphonic acid catalysts decreased the degree of formation

Table III 8

No	Product	ratio A: q/18
		water
1	2	3
1	M19KPFRw	11.00
2	M25KPFRw	8.96
3	M19KPFRcw	20.00
4	M25KPFRcw	11.83
5	M5KPFQR	5.94
6	M6KPFQR	5.77
7	M7KPFQR	12.90
8	M5KPFQRc	1.50
9	M6KPFQRc	12.59
10	M7KPFQRc	17.83

Table III. 8 (contd.)

1	2	3
11	M5KPFQRw	10.38
12	M6KPFQRw	12.17
13	M7KPFQRw	10.80
14	M5KPFQRcw	27.14
15	M6KPFQRcw	30.83
16	M7KPFQRcw	24.29
17	M3KPERF	11.82
18	M5KPERF	7.78
19	M3KPERFc	48.24
20	M5KPERFc	44.62
21	M3KPERFw	10.69
22	M5KPERFw	16.96

Table III. 8 (contd.)

1	2	3
23	M3KPERFcw	42.50
24	M5KPERFcw	41.54
25	M1KPClRF	15.56
26	M3KPClRF	25.46
27	M1KPClRFc	35.00
28	M3KPClRFc	38.46
29	M1KPClRFw	30.91
30	M3KPClRFw	11.71
31	M1KPClRFcw	45.45
32	M3KPClRFcw	31.76

of poly vinyl alcohol with formaldehyde, acetaldehyde, etc (169). Solubilization of the polymer was inhibited by adding sufficient salt to the aqueous solution of poly vinyl alcohol and treating with aldehyde (170). Poly vinyl alcohol film with optimum water resistance and satisfactory optical properties were prepared by the reaction of aldehyde with poly vinyl alcohol (171). Starch-poly vinyl alcohol films were studied for plasticization by glycerol, sorbitol, etc (172-173).

These membranes contain complexing and chelating groups. Their ion exchange capacity for Cu(II), Ni(II), and Zn(II) ions has been studied. Some of the values are plotted in figIII.22.It is observed that the products (MPFR) prepared in presence of starch have a higher exchange capacity for Cu(II), Ni(II) and Zn(II) ions than those prepared in absence of starch. and those prepared in presence of poly ethylene glycol have higher capacity than those prepared in presence glycerol, (ii) the exchange capacity of the products prepared in absence of starch increases generally in order

Zn < Ni < Cu

(iii) the exchange capacity of the products prepared in presence of starch increases generally in order

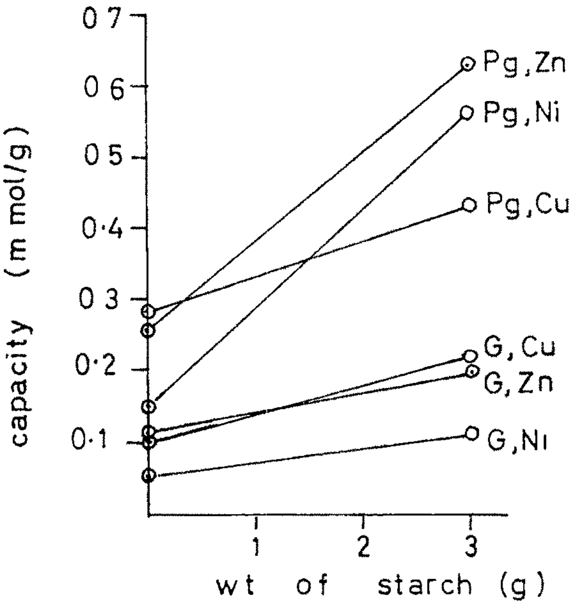


Fig III.22(a)
data from table II 33 34 35-(a)

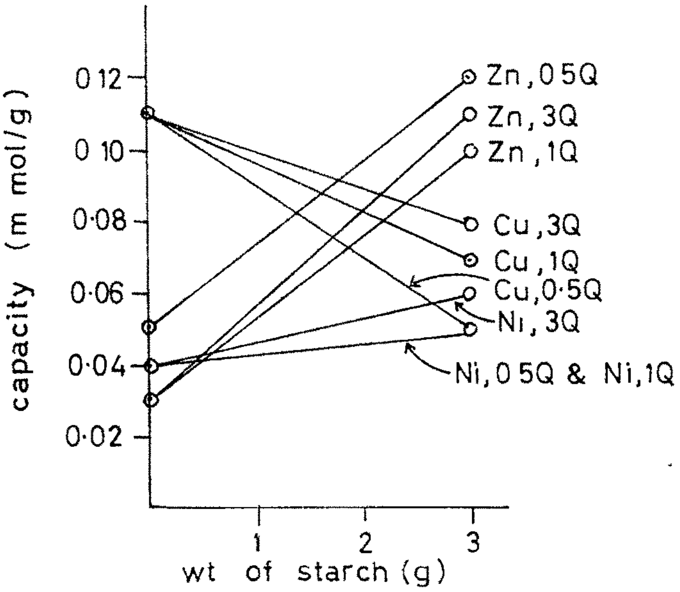


Fig III.22(b)
data from table II 33,34,35-(b)

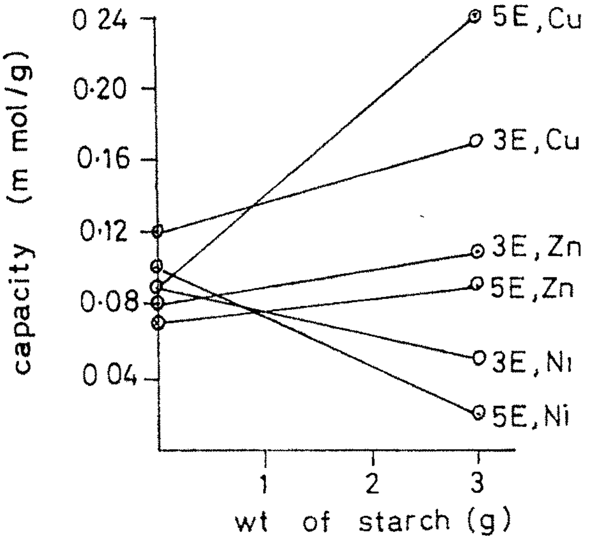


Fig III.22(c)
data from table II 33,34,35-(c)

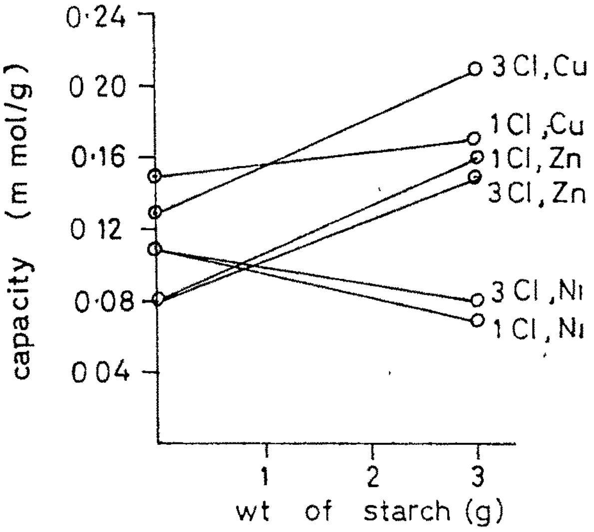


Fig III.22(d)
data from table II 33,34,35-(d)

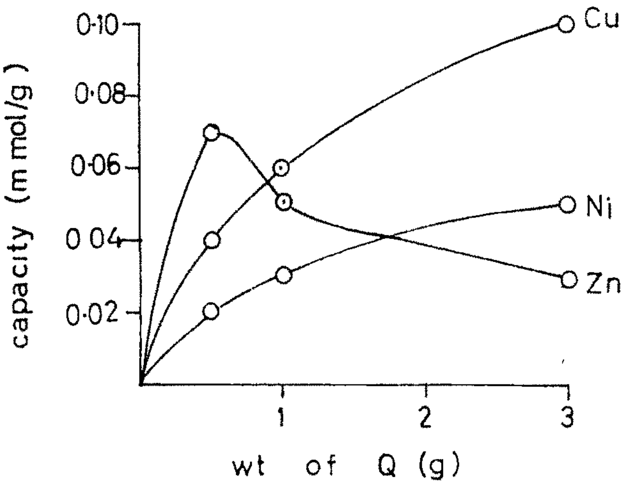


Fig III.22(e)
data from table II 33,34,35-(f)

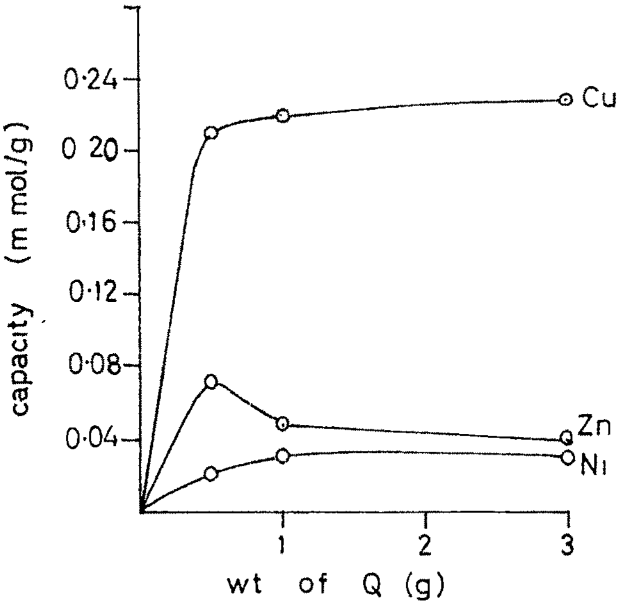


Fig III.22(f)
data from table II 33,34,35-(k)

Ni < Zn < Cu

(iv) increasing the amount of oxine in the preparation increases the exchange capacity of the product for Cu(II) and Ni(II) ions, but not for Zn(II) ions and (v) products prepared in presence of melamine have higher exchange capacity in general than the corresponding products prepared in presence of resorcinol.

The degree of extraction of Cu(II), Ni(II) and Zn(II) ions from their solutions by these membranes has been evaluated and the values are presented in table III.9. It is observed that upto 18% extraction is achieved for Cu(II) ions, 5% for Ni(II) ions and 6% for Zn(II) ions.

III.9 General

(i) Three different grades of poly vinyl alcohol differing in their degree of polymerization and % hydrolysis were used in these investigations. Their tacticity was not determined.

(ii) Poly vinyl alcohol was formalized with formaldehyde, chloral, ethyl aceto acetate, etc by precipitation method. Media used for the reaction were water, aqueous glycerine, glycerine and polyethylene glycol.

Table III.9

No	Product	degree of extraction x 10^2		
		Cu(II)	Ni(II)	Zn(II)
1	2	3	4	5
1	M19KPFRw	0.051	0.015	0.025
2	M25KPFRw	0.074	0.024	0.033
3	M19KPFRcw	0.107	0.025	0.031
4	M25KPFRcw	0.070	0.041	0.043
5	M5KPFQR	0.087	0.016	0.020
6	M6KPFQR	0.089	0.017	0.013
7	M7KPFQR	0.092	0.020	0.015
8	M5KPFQRc	0.038	0.022	0.048
9	M6KPFQRc	0.055	0.022	0.041
10	M7KPFQRc	0.073	0.029	0.049
11	M5KPFQRw	0.025	0.019	0.035

Table III.9 (Contd.)

1	2	3	4	5
12	M6KPFQRw	0.027	0.016	0.021
13	M7KPFQRw	0.030	0.022	0.043
14	M5KPFQRcw	0.118	0.050	0.043
15	M6KPFQRcw	0.160	0.047	0.056
16	M7KPFQRcw	0.168	0.035	0.049
17	M3KPERF	0.105	0.041	0.038
18	M5KPERF	0.066	0.039	0.027
19	M3KPERFc	0.173	0.024	0.046
20	M5KPERFc	0.180	0.008	0.033
21	M3KPERFw	0.063	0.020	0.037
22	M5KPERFw	0.084	0.019	0.034
23	M3KPERFcw	0.129	0.033	0.048
24	M5KPERFcw	0.080	0.029	0.043

Table III.9 (contd.)

1	2	3	4	5
25	M1KPC1RF	0.099	0.038	0.028
26	M3KPC1RF	0.090	0.039	0.029
27	M1KPC1RFc	0.124	0.028	0.057
28	M3KPC1RFc	0.133	0.029	0.049
29	M1KPC1RFw	0.080	0.019	0.036
30	M3KPC1RFw	0.065	0.019	0.030
31	M1KPC1RFcw	0.095	0.037	0.047
32	M3KPC1RFcw	0.076	0.029	0.035
33	M1KPFSdRc	0.073	0.000	0.010
34	M2KPFSdRc	0.054	0.000	0.000
35	M1KPFSdQRc	0.032	0.009	0.025
36	M2KPFSdQRc	0.048	0.014	0.019
37	M3KPFSdQRc	0.081	0.023	0.011

Table III.9 (contd.)

1	2	3	4	5
38	M1KPESdRFc	0.067	0.000	0.010
39	M1KPESdRFc	0.043	0.036	0.035
40	M1KPClSdRFc	0.025	0.000	0.008
41	M2KPClSdRFc	0.089	0.010	0.008
42	M1KPFSdmc	0.197	0.010	0.015
43	M2KPFSdmc	0.110	0.022	0.012
44	M1KPFSdQmc	0.137	0.008	0.021
45	M2KPFSdQmc	0.149	0.012	0.016
46	M3KPFSdQmc	0.139	0.010	0.011
47	M1KPESdmB'c	0.065	0.005	0.009
48	M2KPESdmB"c	0.063	0.021	0.020
49	M1KPClSdmB'c	0.067	0.010	0.008
50	M2KPClSdmB'c	0.086	0.015	0.008

(iii) Poly vinyl alcohol can undergo intra molecular or inter molecular formalization. Cross-linking resulting from inter molecular formalization leads to the formation of a gel.

(iv) Higher yield of the product observed in presence of glycerine may be attributed to the side reaction involving glycerine and formaldehyde.

(v) Increase in the amount of aldehyde used as condensing agent increases the yield of the product. It may be attributed to the formation of poly methylenes in the rings and cross-links.

(vi) As anticipated, increase, in the amount of water decreases the yield of the formalated product.

(vii) The formal bond in these formalated poly vinyl alcohol products is susceptible to the action of acids and alkalis.

(viii) Chelating polyformals were prepared by condensing poly vinyl alcohol with (a) formaldehyde and 8-hydroxy quiholine, (b) ethyl aceto acetate, (c) salicyl aldehyde and (d) chloral hydrate, These products were slightly affected by acids and alkalis.

(ix) Chelating polyformals were further resinified by condensing with resorcinol and formaldehyde. Addition of starch in the reaction system increased the yield of the product. Literature survey shows that products obtained by the reaction of starch with formaldehyde have been patented (174 - 177) and used as size for paper, fabrics etc. The cross-linked products were partially depolymerized and their viscosity was studied. Higher yield obtained in presence of starch in these preparations may be attributed to the formalized starch getting into the reaction product through cross-linking.

(x) Higher yield obtained in presence of glycerine can be attributed to the formation of mixed methylidine glycerols and their getting into the reaction products through cross-linking (178).

(xi) Chelating poly formals obtained after resinification are relatively insoluble in water. Those of the products which exhibit solubility in water become insoluble in 1% salt solution. The polymeric products are considered salted out by the saline solution.

(xii) The degree of swelling of these resinified chelating polyformals decreases as the concentration of salt in solution increases and as the amount of resorcinol in the preparation increases. It is considered that salting-out effect also affects the degree of swelling.

(xiii) Calculations have been made of the moles of water (A) required to cause maximum swelling of 1g of the product and the number of moles of water (B) required just to dissolve 1g of the product. These values give an idea of swelling in relation to solubility.

(xiv) Ion exchange capacity of these resinified chelating polyformals for Cu(II), Ni(II) and Zn(II) ions has been determined. It is generally observed that products prepared in presence of starch have higher exchange capacity than the corresponding products prepared in absence of starch for Cu(II) ions and Zn(II) ions, indicating the effect of factors other than the complexing groups present, on ion uptake (108). It is also observed that products obtained using chloral amino or phenolic compounds. Xanthate resin has been prepared by the reaction of m-amino phenol with carbon disulphide and formaldehyde. High degree of swelling is observed for some of these resins.

(xix) Ion exchange capacity of these resins for Cu(II), Ni(II) and Zn(II) ions has been determined. The value is increasing in order

$$Ni < Cu \leqslant Zn.$$

The degree of extraction of these metal ions has been evaluated. 1-5% of the metal is extracted by these resins.

(xx) Chelating membranes have been prepared by the preparatory methods suggested above and casting the products without support or reinforcement. Some of these membranes have relatively large values of the degree of swelling.

(xxi) Ion exchange capacity of these membranes for Cu(II), Ni(II) and Zn(II) ions has been evaluated. The exchange capacity of the products prepared in absense of starch increases in order

Ni < Zn < Cu

The exchange capacity of the products prepared in presence of melamine is higher than that of the corresponding products prepared in presence of resorcinol. Cu(II) ions can be extracted upto 18% from the solution by the membranes.