III.

RESULTS

AND

DISCUSSION

III. RESULTS AND DISCUSSION.

III.1 POLY(VINYL ALCOHOL) :-

Poly(vinyl alcohol) has been used by us as a starting meterial for our 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 poly(vinyl alcohol). Their classification is based on (i) percent hydrolysis and (ii) degree of polymerization. They fall into (i) fully hydrolysed group having about 98 % hydrolysis and (ii) partly hydrolysed group with (a) 87-89 % hydrolysis or (b) 78-80 % hydrolysis. In terms of degree of polymerization (DP), the major groups are (i) low viscosity group with DP of 600 , (ii) medium viscosity group with DP of 1700 and (iii) high viscosity group with DP of 2400, with subgroups having DP of 1000, 2800 and 3200.

We used two makes of poly(vinyl alcohol). The characteristics of Koch - Light make (K grade) and SD chem make (S grade) are

	K grade	S grade
% hydrolysis	97	80
degree of polymerization	1640	2840

Stereoregular forms of poly(vinyl alcohol) are shown in Fig. III.1

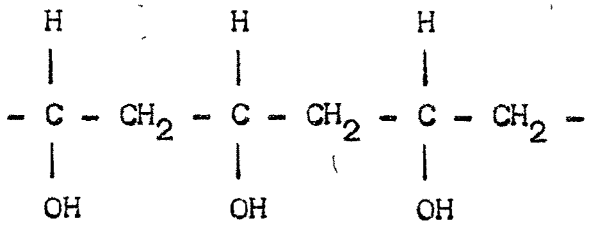
Stereoregularity of poly(vinyl alcohol) depends on the method of preparation. Poly(vinyl triflurocetate), on hydrolysis, was found to yield syndiotactic poly(vinyl alcohol) with low 1,2 gycol content (94, 95). Ionic polymerization of vinyl ethers (96) produced isotactic poly(vinyl ethers) and polymerization of divinyloxy compounds yielded mixed products (97, 98).

The crystallinity of poly(vinyl) 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 (99, 100).

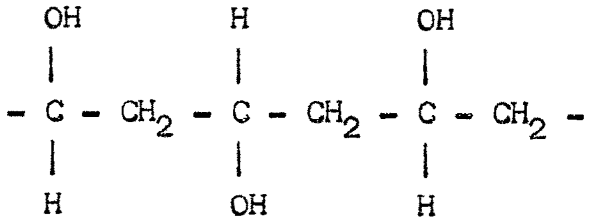
Poly(vinyl alcohol) gives characteristic colour reaction with iodine, depending on its tacticity, degree of polymerization, etc (101, 102). The colouration is related to alcohol-iodine complex and has an absorption maximum at 620 nm. The intensity decreases with the increase in both 1, 2 glycol content and isotactivity and is almost zero when isotacticity exceeds 70 % .

III.2 POLY(VINYL ESTERS) :-

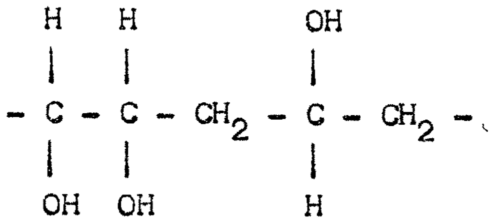
Studies on poly(vinyl esters) were made with a wide and varied interest such as theoretical explorations, industrial applications based on their adhesive properties,



Isotactic



Syndiotactic



heterotactic

Fig. III.1
Stereoregularity of poly(vinyl alcohol).

mechanical properties, optical properties, sorption properties, etc.

Poly(vinyl trifluro acetate) yielded, on hydrolysis, syndiotactic poly(vinyl alcohol) with low 1, 2 glycol content (94, 95). The crystallinity of poly(vinyl formate) is sensitive to differences in tacticity (99, 100).

Poly(vinyl pelentanoate) was prepared and studied as an anticoagulant of blood(103).

Branched poly(vinyl acetate) exhibited decrease in solubility with increase in frequency of branching (104).

The maximum degree of esterification of poly(vinyl stearate) was 80 % (105). The Schotten - Baumann reaction between poly(vinyl alcohol) and alkenyl cyclopropane carbonyl chloride was of the first order and the degree of esterification of the product depended on temperature (106).

Freez-resistant dispersions were made by emulsion polymerization of vinyl esters of monocarboxylic acids(107).

Cross-linked poly(vinyl acetate) exhibited increase in mechanical and thermal stability with increase in the number of bridge bonds (108).

Poly(vinyl sulphonate) resin showed the absorption of Na^+ equivalent to 0.0038 mole NaOH (109).

Poly(vinyl sulphates) with varying emulsifying capacities were prepared (110).

Water - soluble mono-esters of poly(vinyl alcohol) with di and tribasic acids were prepared and used as dispersing agents for silver - halides (61).

Solubility of cross-linked poly(vinyl esters) was studied by Waclaw (111).

The speed of esterification poly(vinyl alcohol) with chloracetyl chloride increased with pH of the solvent (112).

Poly(vinyl cinnamate) and poly(vinyl p-nitro benzoate) were prepared and used as photocopier layers(73).

Takahashi et al (113) observed that poly(sodium vinyl sulphate) had a degree of esterification of 0.7 . Kornova et al (114) prepared poly(vinyl sulphonate) with 50 % esterification. Dahl and Reid (115) prepared poly (vinyl dihydrogen phosphate) with about 66 % esterification. Poly(vinyl hydrogen sulphate) with 100 % esterification is also reported (116). Kornova et al (114) observed that changes in mole ratios of the reactants did not affect the degree of esterification, whereas Jantas and Polowinski (117) observed that degree of esterification increased with increasing concentration of acid chloride.

Kararay Co.(118-123) patented the preparation of

The products obtained from K-grade poly(vinyl alcohol) are, in general, insoluble in various solvents (K-P-SBA, K-P-AAA and K-P-HBA have slight solubility in dimethyl formamide); however, the products obtained from S-grade poly(vinyl) are soluble in dimethyl formamide but insoluble in other solvents. The solubility of products from S-grade poly(vinyl alcohol) in 3N HCl and 3N NaOH is as follows :

Soluble in 3N HCl :	S-P-FMA, S-P-ACA, S-P-ABA
Partly Soluble in 3N HCl:	S-P-SBA, S-P-ADA, S-P-ABA
Insoluble in 3N HCl :	S-P-TPA, S-P-SAA, S-P-IPTA, S-P-AAA, S-P-HBA.
Soluble in 3N NaOH :	S-P-FMA, S-P-ACA, S-P-ADA, S-P-ABA.
Partly Soluble in 3N NaOH :	S-P-SBA, S-P-ANA, S-P-HBA
Insoluble in 3N NaOH :	S-P-TPA, S-P-ACA, S-P-IPTA, S-P-AAA.

Because of the solubility and hydrolytic tendencies of many of the products from S-grade poly(vinyl alcohol) in solution of acid or alkali, their further studies were discontinued.

Regarding the thermal behaviour, the products from S-grade poly(vinyl alcohol) do not melt upto 300°C, whereas the products obtained from K-grade poly(vinyl alcohol) either melt or decompose as indicated below :

poly(vinyl maleates) with varying degree of esterification, solubility and swelling.

The products with varying degree of esterification are termed as poly(vinyl alcohol) esters and brifly as alcohol esters. These were prepared and studied as presented below.

III.3 POLY(VINYL ALCOHOL) ESTERS :-

Poly(vinyl alcohol) esters have been prepared by partial esterification of poly(vinyl alcohol) using different acid chlorides (Table II.1) (or acid/acid anhydride) in varying propertions. Pyridine and DMF were used in case of K-grade poly(vinyl alcohol) and aqueous sodium carbonate and chloroform were used in case of S-grade poly (vinyl alcohol). The results have been presented in Table II.3 and II.4 . Their colour, solubility and thermal behaviour have been presented in Tables II.5 and II.6 . All the products obtained from K-grade poly(vinyl alcohol) are brown or black in colour in general ; however, the products obtained from S-grade poly(vinyl alcohol) have different colours as indicated below :

White : S-P-TPA, S-P-SAA, S-P-IPTA, S-P-HBA.
Orange : S-P-ANA, S-P-ABA* .
Brown or Black : S-P-SBA, S-P-FMA, S-P-ACA, S-P-ADA, S-P-AAA.

[* Yellowish green : S-P-ABA(1)].

melt : K-P-SBA, K-P-FMA, K-P-ACA, K-P-ADA, K-P-ANA, K-P-AAA, K-P-HBA, K-P-SAA, K-P-TCAA, K-P-TMAN.

decompose : K-P-IPA, K-P-IPTA, K-P-ABA.

In case of every series of products showing melting behaviour, melting point increases with increase in the proportion of poly(vinyl alcohol) as shown in Fig. III.2 .

If we plot m.pt. versus ratio of equivalent fraction of poly(vinyl alcohol) to that of acid chloride used in the experiment. (Fig. III.2(a)), we get curves, extrapolation of which can give us an idea about the m.pt. of poly(vinyl ester). However better extrapolation would be expected if the rates of equivalent fraction of poly (vinyl alcohol) to that of ester observed in the product is used for plots. Hence we ploted m.pt. versus x (determined as shown later and presented in table III.1) (Fig. III.2(b)). These curves give us probable values of m.pt. of the poly (vinyl esters) by extrapolating the curves to x =o and these are presented below.

1. K-Poly(vinyl fumarate) .... 165°
2. K-Poly(vinyl acrylate) .... 115°
3. K-Poly(vinyl salicylate) .... 20°
4. K-Poly(vinyl adipate) .... 100°
5. K-Poly(vinyl glycinate) .... 140°
6. K-Poly(vinyl-p-hydroxy benzoate).. 40°

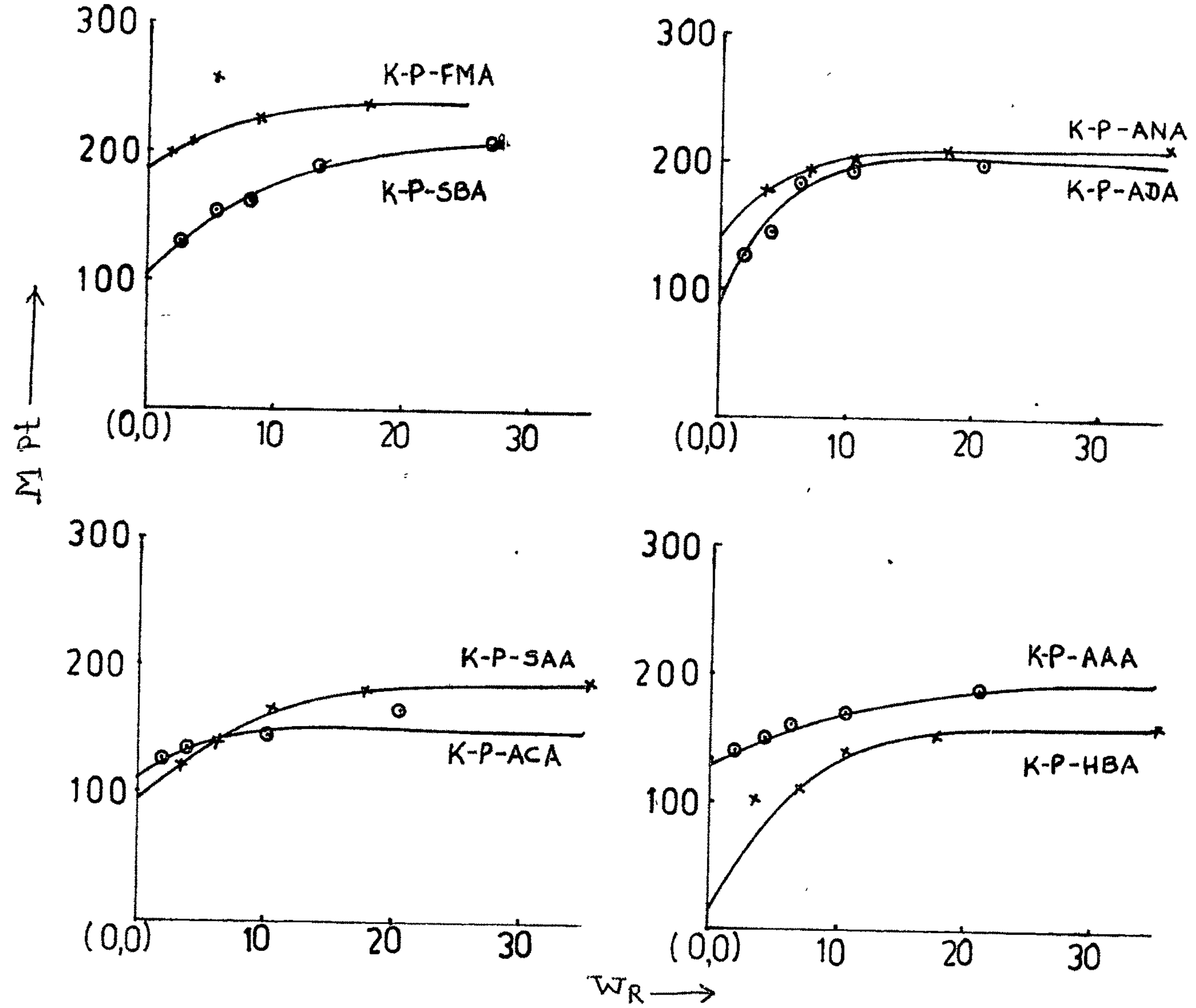


Fig III. 2(a) M.Pt. vs Ratio (W_R) of eq fraction of PVA to that of acid chloride

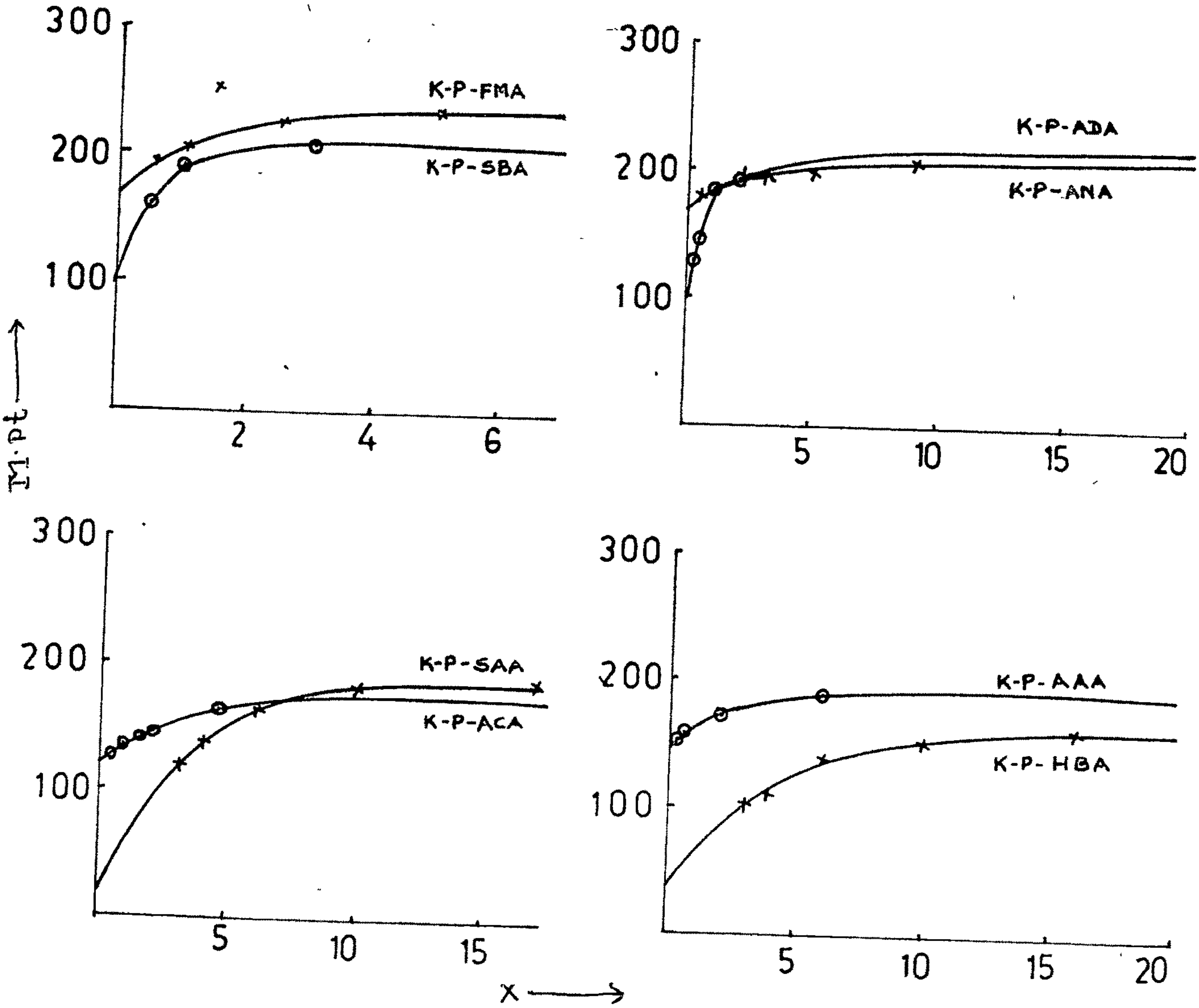


Fig. III.2(b) M.Pt. vs X

7. K-Poly(vinyl sebacate) .... 100^{o}

8. K-Poly(vinyl anthrancilate).... 165^{o}.

It may be noted here that poly(vinyl stearate) melts at 52^{o}C.

The products obtained from K-grade poly(vinyl alcohol) have been analysed and the results of analysis (%C, %H, and %N) of the products have been presented in Table II.7. The products can be generally represented as $(EA_xQ_y)_n$ where E represents the ester unit. A represents vinyl alcohol unit (i.e. monomer unit of poly(vinyl alcohol)), Q represents water molecule and x, y and n are numbers indicating (i) the number of vinyl alcohol units, number of water molecules and degree of polymerization respectively. (In two cases, the products may have the structure $(ED_{.5}Q_y)_n$ where D represents the additional acid component present in the product molecule). The values of x and y are presented in Table (III.1). Two trends have been observed in the values e.g. with Z = 10 (Z is wt proportion of Poly(vinyl alcohol) to acid chloride used) the values of x lie in the range of i) 3 to 5 or (ii) 16 to 20. As the ratio of wt of poly (vinyl alcohol) to that of acid chloride decreases, the values of x decreases and in a couple of cases, excess acid unit gets into the ester molecule. Thus, with the dibasic acid (SBA), one acid unit gets esterified with poly(vinyl alcohol) and the other acid unit remains unreacted, and with glycine, one acid molecule gets esterified with poly(vinyl alcohol) and

Table III.1

No.	Product	Z = 1		2		3		5		10	
		x	y	x	y	x	y	x	y	x	y
1	2	3	4	5	6	7	8	9	10	11	12
1	K-P-SBA(Z)	*	2.5		2.0	0.5	2.0	1.0	2.5	3.07	2.5
2	K-P-TPA(Z)	0.25	1.0	0.5	1.5	1.0	1.5	2.0	2.0	4.0	2.5
3	K-P-FMA(Z)	0.5	0.5	1.0	0.5	1.5	2.0	2.5	2.0	5.0	1.5
4	K-P-ACA(Z)	0.5		1.0	0.25	1.5	0.25	2.0	0.5	4.5	1.0
5	K-P-SAA(Z)	3.0	0.5	4.0	0.5	6.0	0.5	10.0	1.0	17.0	0.5
6	K-P-IPTA(Z)	0.25	1.0	0.5	1.5	1.0	1.5	2.0	2.0	4.0	3.0
7	K-P-ADA(Z)	0.25	1.0	0.5	1.0	1.0	1.0	2.0	1.5	3.0	2.0

* Contains $D_{.5}$ unit.

Contd...

Table III.1 Contd...

1	2	3	4	5	6	7	8	9	10	11	12
8	K-P-ANA(Z)	0.5	0.5	2.0	0.5	5.0	1.0	9.0	1.0	20.0	2.0
9	K-P-AAA(Z)	*	0.5	0.25	0.5	0.5	0.5	2.0	0.5	6.0	0.5
10	K-P-4ABA(Z)	0.5	0.5	3.5	0.5	5.0	1.0	9.0	1.0	20.0	2.0
11	K-P-4HBA(Z)	3.0	1.5	4.0	2.0	6.0	2.0	10.0	3.0	16.0	4.0

* contains $D_{.5}$ unit

1	2	Z = 1/3		1/2	
		x 3	y 4	x 5	y 6
12	(a)K-P-TCAA(Z)		0.5		
	(b)K-P-TMAN(Z)			0.25	0.5

the other acid molecule may form the amide with the esterified glycine.

The ester group per g of alcohol-ester(meq/g) is calculated on the basis of the formula and corresponds with the value of A.V.H. obtained experimentally as shown in Table III.2. The two sets of values show close agreement. Similarly, water content per g of the alcohol-ester calculated theoretically on the basis of the formula corresponds with water content per g of the alcohol-ester (q) obtained experimentally as shown in Table III.2 . Close agreement between two sets of values has been observed. Thus all the data obtained from C, H, and N analysis, ester content and water content of the alcohol - ester molecular units favour and confirm the formulae suggested for these products.

Having suggested the formulae, we consider some correlations. Knowing the weight ratio (z) of vinyl alcohol to acid chloride used in the experiment, ratio (W_R) of equivalent fraction of vinyl alcohol to acid chloride used in the experiment has been calculated. Considering that all the chloride used has been available for esterification of poly(vinyl alcohol), the equivalent weight per ester group (W_V) has been evaluated. Hence ester group per g of alcohole- ester (E_V) has been suggested. These values are presented in Table III.3. These values are correlated with some values that can be calculated from the knowledge

Table III.2(a)

No.	Product	Ester Group per g (formula basis) (meq/g) (E_F)	Ester group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq.)	Water content per g (g/g) (q)
1	K-P-SBA(1)	6.74	6.9	0.202	0.202
2	K-P-SBA(2)	6.13	6.2	0.221	0.211
3	K-P-SBA(3)	5.40	5.6	0.195	0.183
4	K-P-SBA(5)	4.63	4.8	0.208	0.224
5	K-P-SBA(10)	3.29	3.2	0.148	0.152

Table III.2(b)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq.)	Water content per g (g/g) (q)
1	K-P-TPA(1)	7.87	8.0	0.142	0.120
2	K-P-TPA(2)	6.33	6.3	0.171	0.150
3	K-P-TPA(3)	5.56	5.6	0.150	0.130
4	K-P-TPA(5)	4.29	4.5	0.155	0.140
5	K-P-TPA(10)	3.03	2.9	0.136	0.110

Table III.2(c)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq.)	Water content per g (g/g) (q)
1	K-P-FMA(1)	8.70	9.0	0.078	0.070
2	K-P-FMA(2)	7.30	7.1	0.066	0.060
3	K-P-FMA(3)	5.38	5.6	0.194	0.160
4	K-P-FMA(5)	4.39	4.6	0.158	0.130
5	K-P-FMA(10)	3.02	3.1	0.082	0.080

Table III.2(d)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq.)	Water content per g (g/g) (q)
1	K-P-ACA(1)	9.71	9.3	0.000	0.008
2	K-P-ACA(2)	6.83	6.6	0.031	0.030
3	K-P-ACA(3)	5.93	5.8	0.027	0.020
4	K-P-ACA(5)	5.13	5.1	0.046	0.040
5	K-P-ACA(10)	3.18	3.1	0.057	0.050

Table III.2 (e)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Grpup per g By hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Weq)	Water content per g (g/g) (g)
1.	K-P-SAA(1)	3.28	3.0	0.030	0.030
2.	K-P-SAA(2)	2.86	2.6	0.026	0.020
3.	K-P-SAA(3)	2.29	2.3	0.021	0.020
4.	K-P-SAA(5)	1.61	1.5	0.029	0.030
5.	K-P-SAA(10)	1.09	1.1	0.009	0.010

Table III.2(f)

No.	Product	Ester group per g (Formula basis) (meq/g) (E_F)	Ester group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Weq)	Water Content per g (g/g) (q)
1	K-P-IPTA(1)	7.87	8.0	0.142	0.125
2	K-P-IPTA(2)	6.33	6.4	0.171	0.155
3	K-P-IPTA(3)	5.56	5.6	0.150	0.130
4	K-P-IPTA(5)	4.29	4.6	0.154	0.135
5	K-P-IPTA(10)	2.95	2.9	0.159	0.155

Table III.2(g)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq.)	Water content per g (g/g) (q)
1	K-P-ADA(1)	7.81	8.1	0.168	0.110
2	K-P-ADA(2)	7.19	7.2	0.129	0.115
3	K-P-ADA(3)	6.21	5.7	0.098	0.085
4	K-P-ADA(5)	4.67	4.5	0.161	0.145
5	K-P-ADA(10)	3.75	3.3	0.120	0.105

Table III.2(h)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Group per g by hydralysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq)	Water content per g (g/g) (g)
1	K-P-ANA(1)	5.15	4.8	0.046	0.040
2	K-P-ANA(2)	3.85	3.6	0.035	0.030
3	K-P-ANA(3)	2.49	2.6	0.045	0.040
4	K-P-ANA(5)	1.73	1.9	0.031	0.030
5	K-P-ANA(10)	0.93	1.1	0.033	0.030

Table III.2(j)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq)	Water content per g (g/g) (q)
1	K-P-AAA(1)	9.90	10.6	0.059	0.056
2	K-P-AAA(2)	8.26	8.1	0.074	0.070
3	K-P-AAA(3)	7.58	7.4	0.068	0.060
4	K-P-AAA(5)	5.43	5.0	0.049	0.040
5	K-P-AAA(10)	2.79	2.9	0.025	0.020

Table III.2(k)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq)	Water content per g (g/g) (q)
1	K-P-4ABA(1)	5.52	5.3	0.099	0.050
2	K-P-4ABA(2)	3.06	2.8	0.028	0.020
3	K-P-4ABA(3)	2.49	2.4	0.045	0.040
4	K-P-4ABA(5)	1.73	1.9	0.031	0.030
5	K-P-4ABA(10)	0.93	1.1	0.033	0.030

Table III.2(1)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Group per g by hydrolysis (meq/g) (A.V.H.)m	Water content per g (formula basis) (g/g) (Waq)	Water content per g (g/g) (q)
1	K-P-4HBA(1)	3.09	3.0	0.084	0.090
2	K-P-4HBA(2)	2.66	2.6	0.096	0.090
3	K-P-4HBA(3)	2.15	2.1	0.078	0.080
4	K-P-4HBA(5)	1.52	1.4	0.082	0.080
5	K-P-4HBA(10)	1.06	1.1	0.077	0.070

Table III.2(m)

No.	Product	Ester Group per g (Formula basis) (meq/g) (E_F)	Ester Group per g by hydrolysis (meq/g) (A.V.H.)	Water content per g (formula basis) (g/g) (Waq.)	Water content per g (g/g) (q)
1	K-P-TCAA(1/3)	5.05	5.2	0.045	0.033
2	K-P-TMAN(1/2)	7.88	8.0	0.071	0.062

Table III.3(a)

No.	Product	Weight proportion of PVA to acid chloride used (Z)	eq.fra.proportion of VA to acid chloride used (W_R)	eq.wt.per ester group (used wt. basis) (W_V)	ester group/g (meq/g) (used wt. basis) (E_V)
1	K-P-SBA(1)	1:1	2,72	202.50	4.93
2	K-P-SBA(2)	2:1	5.43	321.92	3.11
3	K-P-SBA(3)	3:1	8.15	441.60	2.26
4	K-P-SBA(5)	5:1	13.58	680.52	1.47
5	K-P-SBA(10)	10:1	27.16	1278.00	0.78

Table III.3(b)

No.	Product	Weight proportion of PVA to acid chloride used (Z)	eq.fra.proportion of VA to acid chloride used (W_R)	eq.wt.per ester group (used wt. basis) (W_V)	ester group (meq/g) (used wt. basis) (E_V)
1	K-P-TPA(1)	1:1	2.31	166.78	6.00
2	K-P-TPA(2)	2:1	4.61	267.98	3.73
3	K-P-TPA(3)	3:1	6.92	369.62	2.71
4	K-P-TPA(5)	5:1	11.53	572.46	1.75
5	K-P-TPA(10)	10:1	23.07	1080.22	0.93

Table III.3(c)

No.	Product	Weight proportion of PVA to acid chloride used (Z)	eq.fra.porportion of VA to acid chloride used (W_R)	eq.wt.per ester group (used wt. basis) (W_V)	ester group (meq/g) (used wt. basis) (E_V)
1	K-P-FMA(1)	1:1	1.74	116.56	8.58
2	K-P-FMA(2)	2:1	3.48	193.12	5.18
3	K-P-FMA(3)	3:1	5.22	269.68	3.71
4	K-P-FMA(5)	5:1	8.69	422.36	2.37
5	K-P-FMA(10)	10:1	17.39	805.16	1.24

Table III.3(d)

No.	Product	Weight proportion of PVA to acid chloride used (Z)	eq. fva. proportion of VA to acid chloride used (W_R)	eq. wt. per ester group (used wt. basis) (W_V)	ester group/g (meq/g) (used wt. basis) (E_V)
1	K-P-ACA(1)	1:1	2.06	144.64	6.92
2	K-P-ACA(2)	2:1	4.11	234.84	4.26
3	K-P-ACA(3)	3:1	6.17	325.48	3.07
4	K-P-ACA(5)	5:1	10.28	506.32	1.98
5	K-P-ACA(10)	10:1	20.57	959.08	1.04

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Table III.3(e)

No.	Product	Weight proportion of PVA to acid Chloride used (Z)	eq. fra. proportion of VA to acid chloride used (W_R)	eq.wt. per ester group (used wt. basis) (W_V)	ester group/g (meq/g) (used wt. basis) (E_V)
1	K-P-SAA(1)	1:1	3.56	276.64	3.61
2	K-P-SAA(2)	2:1	7.11	432.84	2.31
3	K-P-SAA(3)	3:1	10.67	589.48	1.70
4	K-P-SAA(5)	5:1	17.78	902.32	1.11
5	K-P-SAA(10)	10:1	35.57	1685.08	0.59

Table III.3(f)

No.	Product	Weight proportion of PVA to acid chloride used (Z)	Eq.fra.proportion of VA to acid chloride used (W_R)	eq.wt. per ester group (used wt. basis) (W_V)	ester group/g (meq/g) (used wt. basis) (E_V)
1	K-P-IPTA(1)	1:1	2.31	166.78	6.00
2	K-P-IPTA(2)	2:1	4.61	267.98	3.73
3	K-P-IPTA(3)	3:1	6.92	369.62	2.71
4	K-P-IPTA(5)	5:1	11.53	572.46	1.75
5	K-P-IPTA(10)	10:1	23.07	1080.22	0.93

Table III.3(g)

No.	Product	W eight Proportion of PVA to acid chloride used (Z)	eq.fva. proportion of VA to acid chloride used (W_R)	eq.wt.per-ester group (used wt. basis) (W_V)	ester group/g (meq/g) (used wt basis) (E_V)
1.	K-P-ADA (1)	1.1	2.08	146.52	6.83
2.	K-P-ADA (2)	2.1	4.16	238.04	4.20
3.	K-P-ADA (3)	3.1	6.24	329.56	3.03
4.	K-P-ADA (5)	5.1	10.40	512.50	1.95
5.	K-P-ADA (10)	10.1	20.80	970.00	1.03

Table III.3(h)

No.	Product	Weight proportion of PVA to acid chloride used (Z)	eq.fr. proportion of VA to acid chloride used (W_R)	eq.wt.per ester group (used wt. basis) (W_V)	ester group/g (meq/g) (used wt. basis) (E_V)
1	K-P-ANA(1)	1:1	3.53	275.50	3.63
2	K-P-ANA(2)	2:1	7.07	431.08	2.32
3	K-P-ANA(3)	3:1	10.60	586.50	1.71
4	K-P-ANA(5)	5:1	17.67	897.48	1.11
5	K-P-ANA(10)	10:1	35.34	1675.00	0.60

Table III.3(j)

No.	Product	weight proportion of PVA to acid chloride used (Z)	eq.wt.proportion of VA to acid chloride used (W_R)	eq.wt.per ester group (used wt. basis) (W_V)	ester group/g (meq/g)(Used wt. basis) (E_V)
1	K-P-AAA(1)	1:1	2.13	150.50	6.64
2	K-P-AAA(2)	2:1	4.25	244.00	4.10
3	K-P-AAA(3)	3:1	6.38	337.50	2.96
4	K-P-AAA(5)	5:1	10.63	524.72	1.91
5	K-P-AAA(10)	10:1	21.25	992.00	1.01

Table III.3(k)

No.	Product	weight proportion of PVA to acid chloride used (Z)	eq.fra.proportion of VA to acid chloride used (W_R)	eq.wt.per ester group (used wt. basis) (W_V)	ester group/g (meq/g)(used wt. basis) (E_V)
1	K-P-4ABA(1)	1:1	3.50	274.50	3.64
2	K-P-4ABA(2)	2:1	7.07	430.00	2.33
3	K-P-4ABA(3)	3:1	10.60	585.50	1.71
4	K-P-4ABA(5)	5:1	17.67	896.48	1.12
5	K-P-4ABA(10)	10:1	35.34	1675.00	0.60

Table III.3(1)

No.	Product	weight proportion of PVA to acid chloride used (Z)	eq.~~fva~~.proportion of VA to acid chloride used (W_R)	eq.wt.per ester group(used wt. basis) (W_V)	ester group/g (meq/g)(used wt. basis) (E_V)
1	K-P-4HBA(1)	1:1	3.56	276.64	3.61
2	K-P-4HBA(2)	2:1	7.11	432.84	2.31
3	K-P-4HBA(3)	3:1	10.67	589.48	1.70
4	K-P-4HBA(5)	5:1	17.78	904.32	1.11
5	K-P-4HBA(10)	10:1	35.57	1685.08	0.59

Table III.3(m)

No.	Product	weight proportion of PVA to acid (or acid anhydride used) (Z)	eq.wt.proportion of VA to acid (or acid anhydride used) (W_R)	eq.wt.per ester group (used wt. basis) (W_V)	ester group/g (meq/g)(used wt. basis) (E_V)
1	K-P-TCAA(1/3)	1:3	1.23	199.62	5.01
2	K-P-TMAN(1/2	1:2	2.18	158.67	6.29

of the formulae. Thus the ratios $\frac{W_R}{(1 + x)/(1 + D)}$ and

$\frac{W_v}{W_{F(a)}}$ are calculated and presented in Table III.4

($W_{F(a)}$ represents the formula weight of the product in the anhydrous form).

We observe that the values of $\frac{W_R}{(1 + x)/(1 + D)}$ increases with increasing values of W_R in general ; however, the values increase in steps in case of K-P-SBA(z), the values decrease in steps in case of K-P-ANA(z) and K-P-ABA(z) and the values show a maximum half way in the series in case of K-P-AAA(z). Similarly, we observe that the values of $\frac{W_v}{W_{F(a)}}$ increase with increasing values of W_v in general except in case of K-P-ANA(z) and K-P-(AAA(z) wherein the values reach a maximum and then decrease. Some of these results are shown graphically e.g. W_R versus (1 + x)/(1 + D) in Fig. III.3 and W_v versus $W_{F(a)}$ in Fig. III.4 .

All the plots are st.lines with definite slopes and intercepts. These results indicate linear relations between (i) W_R and (1 + x)/(1 + D) and (ii) W_v and $W_{F(a)}$.

Table III.4(a)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-SBA(1)	4.08	1.14
2	K-P-SBA(2)	5.43	1.98
3	K-P-SBA(3)	5.43	2.98
4	K-P-SBA(5)	6.79	4.00
5	K-P-SBA(10)	6.79	4.87

Table III.4(b)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-TPA(1)	1.85	1.39
2	K-P-TPA(2)	3.07	2.05
3	K-P-TPA(3)	3.46	2.42
4	K-P-TPA(5)	3.84	2.91
5	K-P-TPA(10)	4.61	3.79

Table III.4(c)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-FMA(1)	1.16	1.10
2	K-P-FMA(2)	1.74	1.51
3	K-P-FMA(3)	2.09	1.80
4	K-P-FMA(5)	2.48	2.20
5	K-P-FMA(10)	2.90	2.65

Table III.4(d)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-ACA(1)	1.37	1.20
2	K-P-ACA(2)	2.06	1.65
3	K-P-ACA(3)	2.47	1.98
4	K-P-ACA(5)	3.43	2.72
5	K-P-ACA(10)	3.74	3.24

Table III.4(e)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-SAA(1)	0.89	0.93
2	K-P-SAA(2)	1.42	1.27
3	K-P-SAA(3)	1.52	1.38
4	K-P-SAA(5)	1.62	1.49
5	K-P-SAA(10)	1.98	1.82

Table III.4(f)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-IPTA(1)	1.85	1.53
2	K-P-IPTA(2)	3.07	2.04
3	K-P-IPTA(3)	3.46	2.42
4	K-P-IPTA(5)	3.84	2.91
5	K-P-IPTA(10)	4.61	3.79

Table III.4(g)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-ADA(1)	1.66	1.33
2	K-P-ADA(2)	2.77	1.97
3	K-P-ADA(3)	3.12	2.30
4	K-P-ADA(5)	3.47	2.74
5	K-P-ADA(10)	5.20	4.19

Table III.4(h)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_A}{W_{F(a)}}$
1.	K-P-ANA(1)	2.35	1.49
2.	K-P-ANA(2)	2.36	1.72
3.	K-P-ANA(3)	1.77	1.53
4.	K-P-ANA(5)	1.77	1.61
5.	K-P-ANA(10)	1.68	1.59

Table III.4(j)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-AAA(1)	3.19	1.16
2	K-P-AAA(2)	3.40	2.18
3	K-P-AAA(3)	4.25	3.07
4	K-P-AAA(5)	3.54	3.43
5	K-P-AAA(10)	3.04	2.72

Table III.4(k)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-4ABA(1)	2.35	1.49
2	K-P-4ABA(2)	2.35	1.36
3	K-P-4ABA(3)	1.77	1.53
4	K-P-4ABA(5)	1.77	1.60
5	K-P-4ABA(10)	1.68	1.61

Table III.4(1)

No.	Product	$\frac{W_R}{(1 + x)/(1 + D)}$	$\frac{W_V}{W_{F(a)}}$
1	K-P-4HBA(1)	0.89	0.93
2	K-P-4HBA(2)	1.42	1.27
3	K-P-4HBA(3)	1.52	1.38
4	K-P-4HBA(5)	1.62	1.49
5	K-P-4HBA(10)	2.09	1.94

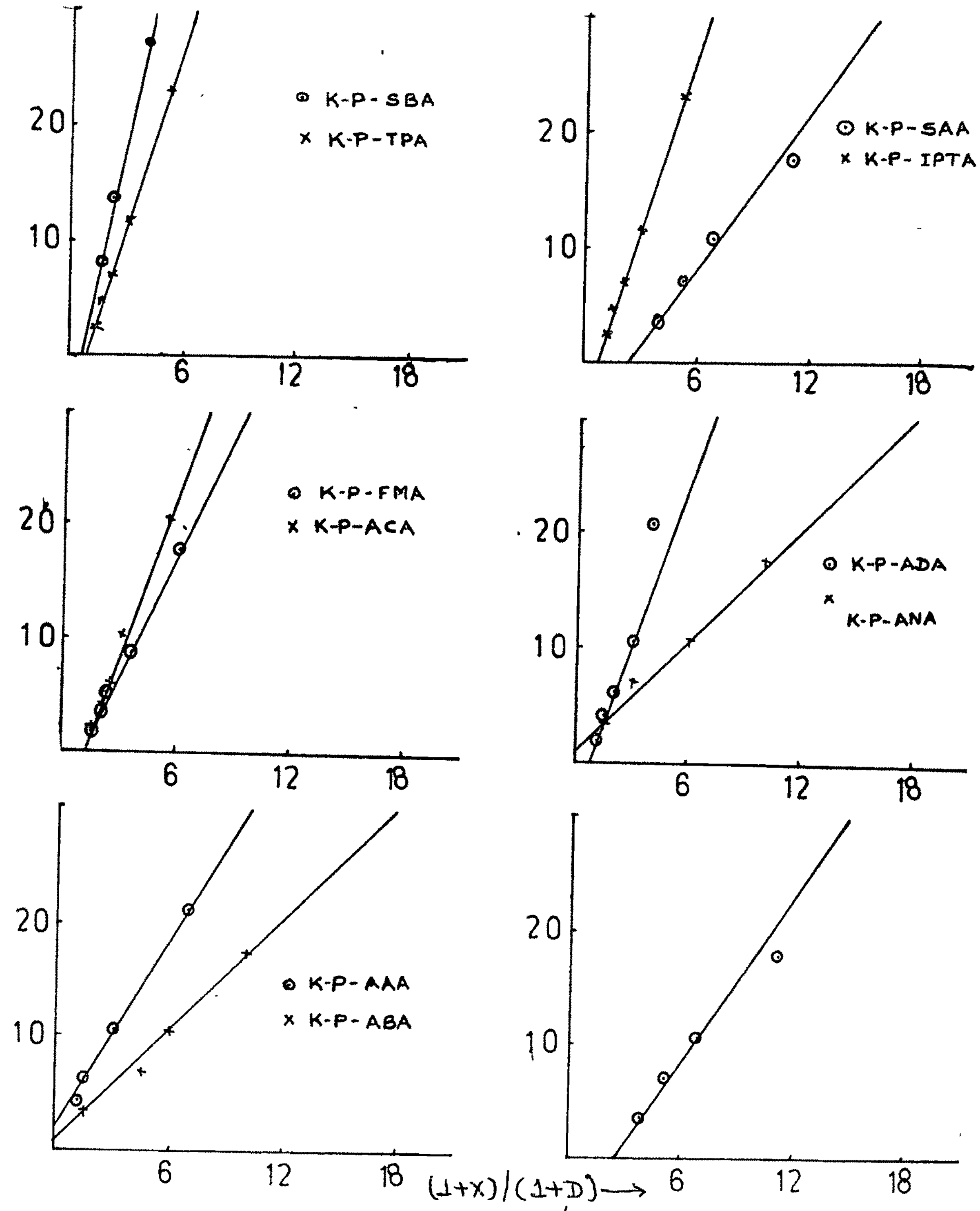

Fig III. 3 W_R vs (1+X)/(1+D)

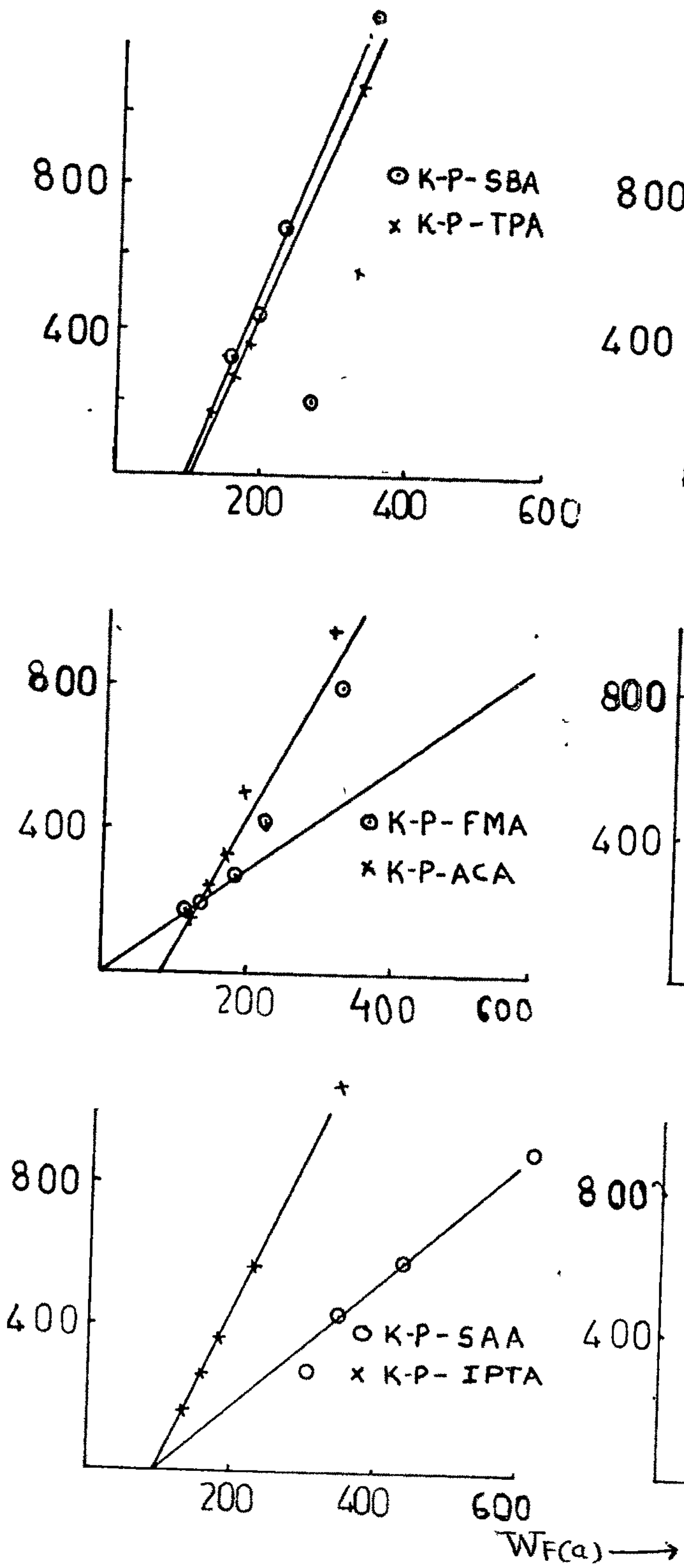

Fig III 4 Wv vs $W_{F(a)}$

We observe that (1) curves for products with acids of similar types have nearly the same values of slope and intercept, e.g. (a) K-P-SBA and K-P-ADA (b) K-P-TPA and K-P-IPTA, (c) K-P-ANA and K-P-ABA (d) K-P-SBA and K-P-HBA, etc. and (2) slopes of the curves for products of dibatic aliphatic (saturated) and aromatic acids are nearly the same. If the slope of the curve in Fig. III.4 was unity with zero intercept, it would imply that W_v would be the same as $W_{F(a)}$. However the curves show that W_v is greater than $W_{F(a)}$ for any point in curve with $W_v > 400$ and that the difference increases with increase in W_v. Similarly curves in Fig. III.3 indicate that $(1 + x)/(1 + D)$ is smaller than W_R for any point on the curve with $W_R > 5$ and that the difference increases with increase in W_R.

These observations imply that the ester content of the product is more than anticipated. This can be explained to a large extent in terms of the ester content of the poly (vinyl alcohol) used. Since the composition of the unhydrolysed ester group in poly(vinyl alcohol) is not known, it has introduced arbitrariness in our consideration of ester group in the product and the values suggested can be treated as average.

We now consider the esterification of poly(vinyl alcohol),. From the knowledge of the formulae of the products (alcohol-esters), we calculate the degree of esterification (DE) as

DE = 100 x no. of ester groups formed/no. of OH groups. The calulated values are presented in Table III.5. We observe that

(i) in case of aromatic acids, the degree of esterification increases in order,

hydroxy acid $<$ amino acid $<$ di acid.

(ii) in case of aliphatic acids, the degree of esterification increases in order,

unsaturated acid $<$ saturated acid.

Recent studies (117) have shown that the degree of esterification of poly(vinyl alcohol) by methacryloyl chloride increases with increasing concentration of the acid chloride.

III.4 SORBENTS_SORPTION AND SWELLING .

Poly(vinyl alcohol) was acetalized with palmitic aldehyde and the product, with the degree of acetalization of 82 %, would swell in benzene, chloroform, pyridine, etc. (124).

Monoesters of poly(vinyl alcohol) with many di and tribasic acids were prepared and found water-soluble(61).

Poly(vinyl alcohol), cross-linked with per iodic acid and spun, has the capacity of high water sorption and swelling (78). Poly(vinyl acetal)-based porous adsorbing

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Table III.5

No.	Product	Degree of esterification (%)				
	Z =	1	2	3	5	10
1	K-P-SBA(z)	÷	100	66.7	50	25
2	K-P-TPA(z)	80	66.7	50	33.3	20
3	K-P-FMA(z)	66.7	50	40	28.6	16.7
4	K-P-ACA(z)	66.7	50	40	33.3	18.2
5	K-P-SAA(z)	25	20	14.3	9.1	5.6
6	K-P-IPTA(z)	80	66.7	50	33.3	20
7	K-P-ADA(z)	80	66.7	50	33.3	25

Table III.5 contd.

No.	Product	Degree of esterification (%)				
		Z = 1	2	3	5	10
8	K-P-ANA(z)	66.7	33.3	16.7	10	4.8
9	K-P-AAA(z)	-	80	66.7	33.3	14.3
10	K-P-4ABA(z)	66.7	22.2	16.7	10	4.8
11	K-P-4HBA(z)	25	20	14.3	9.1	5.9
		Z = 1/3	1/2			
12	K-P-TCAA(z)	100	-			
13	K-P-TMAN(z)	-	80			

materials have been reported (81, 125-126).

Studies of water vapour sorption by water soluble acrylic polymers showed that high concentration of polar or ionic groups caused anomalous concentration-dependant diffusion (82). Studies of water sorption by acrylic polymers showed that sorption is nearly independent of mol wt at 0 - 60°C (83, 127).

Water-swellable cross-linked acrylic copolymers have been patented for use as modifiers for water-holding capacity of soils (128-129) and as artificial soil for hydroponics (130-131).

Polyester staple fibres can be treated with a suitable copolyester to improve its water retention properties(132).

Cross-linked poly(vinyl alcohol) gels exhibited increase in swelling with reticulation degree upto a certain limit after which higher reticulation degree decreases swelling capality(133).

Water uptake behaviour of acrylic polymers has been explained by dual sorption theory (134). Donnan theory of swelling has been capplied to weakly charged ionic gels(135), Sorption capacity of a resin has been calculated from thermodynamic data (136). Ionic groups attached at wide intervals along nonpolar polymer chains produce strong associating interactions in water (137).

Kuraray Co (118-123) patented various poly(vinyl maleates) with varying degree of esterification and differing in solubility and swelling. Poly(vinyl alcohol), cross-linked with epichlorhydrin, has been patented having much reduced sorption capacity in salt solution (138).

Previous history of poly(vinyl alcohol) has effect on its swelling (139). Poly(vinyl alcohol) hydrogels have been studied as swollen elastic networks and as water sorbents (140-141).

Vasuo and Ichiro (142) prepared a wide range of poly(vinyl alcohol) films, studied their solubility and swelling and correlated them with various structural factors.

Cross-linked acrylic copolymers were studied for their swelling and salt content (143). Cross-linked vinyl acetal polymers having cellular structure and high water retention capacity have been patented (144). Cross-linked poly(vinyl alcohol) hydrogels were prepared and studied for their unidirectional deswelling (145).

III.5 WATER SORPTION :

The polymeric alcohol-esters in each series have varying proportions of alcohol and ester groups and hence can sorb water to a varying extent. Poly(vinyl alcohol) is soluble in water, but as increasing esterification takes place solubility in water would decrease and the polymer would swell in water. Solubility and swelling degree of the polymeric products with reference to water as solvent and swelling agent are presented in Table III.6.

From the knowledge of the wt of the alcohol-ester before sorption (W_{BS}), wt of the alcohol-ester after sorption (W_{AS}), wt of the alcohol-ester after drying it from its sorbed state (W_{DS}) and water-content of the alcohol-ester (q), we have evaluated (1) wt loss due to the dissolution of the alcohol-ester (dry basis) in water as

$$\text{wt loss} = W_{BS} - W_{DS} - qW_{BS}$$

and (2) wt gain due to sorption of water by the alcohol-ester (dry basis) as

$$\text{wt gain} = W_{AS} - W_{DS} - \frac{qW_{DS}}{(1-q)}$$

Hence solubility)(g/l) of the alcohol-ester is evaluated as

$$\text{Solubility} = \frac{1000 \times \text{wt loss}}{V_{BS} - \text{wt gain}} = \text{sol}$$

where V_{BS} is the volume of water used in the experiment and wt gain corrosponds to wt of water taken up by the alcohol-ester in sorption.

Similarly, swelling degree (g/g) of the alcohol-ester is evaluated as

$$\text{Swelling degree} = \frac{\text{wt gain}}{W_{DS}} = \text{SD} .$$

Table III.6(a)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-SBA(1)	0.150	2.448	19.86	3.78	75
2	K-P-SBA(2)	0.124	4.777	23.74	7.19	171
3	K-P-SBA(3)	0.179	5.970	44.42	9.36	416
4	K-P-SBA(5)	0.074	2.225	9.52	3.17	30
5	K-P-SBA(10)	0.081	1.946	10.06	2.54	26

Table III.6(b)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-TPA(1)	0.335	3.438	50.74	6.29	319
2	K-P-TPA(2)	0.292	3.433	44.46	6.15	274
3	K-P-TPA(3)	0.255	3.893	41.75	6.33	264
4	K-P-TPA(5)	0.320	3.312	47.84	6.13	293
5	K-P-TPA(10)	0.285	3.480	43.71	5.75	251

Table III.6(c)

Water sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.x Swelling degree (g/l)
1	K-P-FMA(1)	0.285	2.322	37.12	3.60	134
2	K-P-FMA(2)	0.260	4.275	45.41	6.36	289
3	K-P-FMA(3)	0.175	4.104	29.68	6.17	183
4	K-P-FMA(5)	0.195	3.891	31.91	5.76	184
5	K-P-FMA(10)	0.273	2.972	38.84	4.59	178

Table III.6(d)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-ACA(1)	0.374	3.400	56.67	5.48	311
2	K-P-ACA(2)	0.335	4.085	56.63	6.43	364
3	K-P-ACA(3)	0.352	3.689	55.57	5.87	323
4	K-P-ACA(5)	0.288	4.660	53.93	6.93	374
5	K-P-ACA(10)	0.291	4.326	51.28	6.56	337

Table III.6(e)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-SAA(1)	0.385	1.290	44.26	2.20	97
2	K-P-SAA(2)	0.355	4.107	59.33	6.57	390
3	K-P-SAA(3)	0.360	3.537	55.70	5.80	323
4	K-P-SAA(5)	0.353	2.549	47.37	4.13	196
5.	K-P-SAA(10)	0.305	2.318	39.70	3.38	134

Table III.6(f)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-IPTA(1)	0.295	2.450	39.07	4.22	167
2	K-P-IPTA(2)	0.225	2.832	31.38	4.57	143
3	K-P-IPTA(3)	0.225	3.104	32.62	4.81	157
4	K-P-IPTA(5)	0.238	2.416	31.38	3.85	120
5	K-P-IPTA(10)	0.188	2.978	26.77	4.53	121

Table III.6(g)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-ADA(1)	0.375	1.490	44.07	3.07	135
2	K-P-ADA(2)	0.388	1.747	46.04	3.46	159
3	K-P-ADA(3)	0.389	2.729	53.36	5.18	276
4	K-P-ADA(5)	0.340	2.897	47.86	5.63	269
5	K-P-ADA(10)	0.300	1.450	35.08	2.44	86

Table III.6(h)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-ANA(1)	0.325	1.154	36.73	1.82	67
2	K-P-ANA(2)	0.315	2.310	40.96	3.53	144
3	K-P-ANA(3)	0.320	1.974	39.87	3.08	123
4	K-P-ANA(5)	0.292	2.322	38.03	3.42	130
5	K-P-ANA(10)	0.268	2.902	37.75	4.13	156

Table III.6(j)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-AAA(1)	0.407	3.483	62.45	6.49	405
2	K-P-AAA(2)	0.405	1.606	48.24	3.06	147
3	K-P-AAA(3)	0.423	1.635	50.56	3.16	160
4	K-P-AAA(5)	0.330	1.906	40.77	3.03	102
5	K-P-AAA(10)	0.338	2.157	43.09	3.36	145

Table III.6(k)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-4ABA(1)	0.335	1.103	37.65	1.79	68
2	K-P-4ABA(2)	0.348	1.871	42.80	2.96	127
3	K-P-4ABA(3)	0.302	1.890	37.23	2.87	107
4	K-P-4ABA(5)	0.345	1.351	39.88	2.16	86
5	K-P-4ABA(10)	0.292	1.374	33.85	2.03	69

Table III.6(1)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-4HBA(1)	0.382	0.987	42.38	1.86	79
2	K-P-4HBA(2)	0.390	1.908	44.86	2.51	112
3	K-P-4HBA(3)	0.410	1.248	46.84	2.44	114
4	K-P-4HBA(5)	0.440	1.125	49.57	2.34	116
5	K-P-4HBA(10)	0.400	1.428	46.71	2.71	126

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Table III.6(m)

Water Sorption

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-TCAA(1/3)	0.284	0.651	30.38	3.26	98
2	K-P-TMAN(1/2)	0.209	0.478	21.95	1.84	40

The product of solubility and swelling degree is also presented in Table III.6.

Usually the degree of swelling is calculated by the expression

$$\text{degree of swelling} = \frac{W_{AS} - W_{BS}}{W_{BS}} = DS$$

However, we have not used this simple expression in the studies of swelling, because we consider that water content and solubility of the resin are important factors to be taken into consideration in the studies of swelling. For the purpose of comparison, calculations have been made using the above expression and the values will be presented later.

It has been observed that (1) the product of solubility and swelling degree for all resins lies between 26 and 416 (2) the average value of the product for each series is calculated as : 144 (K-P-SBA), 280 (K-P-TPA), 194(K-P-FMA), 342(K-P-ACA), 228 (K-P-SAA), 141(K-P-IPTA), 185 (K-P-ADA) 124 (K-P-ANA), 192 (K-P-AAA), 91 (K-P-ABA), and 109 (K-P-HBA), and (3) though the values of the products for each series are nearly constant, in some cases there is apparent gradation in values.

When water comes in contant with porous, hydrophilic resin, the small, mobile water molecules from water phase readily diffuse through water-resin interface and to the pores and hydrophilic groups of the resin in the resin phase. Sorption of water by the resin takes place, resulting in the swelling of the resin and weakening of inter-molecular (or interchain) forces. When sorption of water leads to the weakening of the inter-molecular (or inter chain) forces, some resin molecules may become free enough to diffuse through the interface into water phase. On the other hand, sorption of water may lead to uncoiling of the chains and mechanical expansion of the polymeric chains making the resin swollen. Thus mechanical expansion of chains and mechanical weakening of linkages of chains are two related and complementary processes. Usually one would believe that increase in swelling of the resin would lead to increase in solubility of the resin. This would be so if the polymer chains are weakly inter-linked. In such cases the solvent or sorbate molecules would readily overcome the forces inter-linking the chains and the polymer chains would swell and dissolve. On the other hand, if the crosslinks are strong, the sorbate molecules would not readily overcome the strong forces and hence solubility would be low, and swelling may be high. The equilibrium resulting between water and resin phases, i.e, solution of resin in water and of water in resin at equilibrium is shown in Fig. III.5.

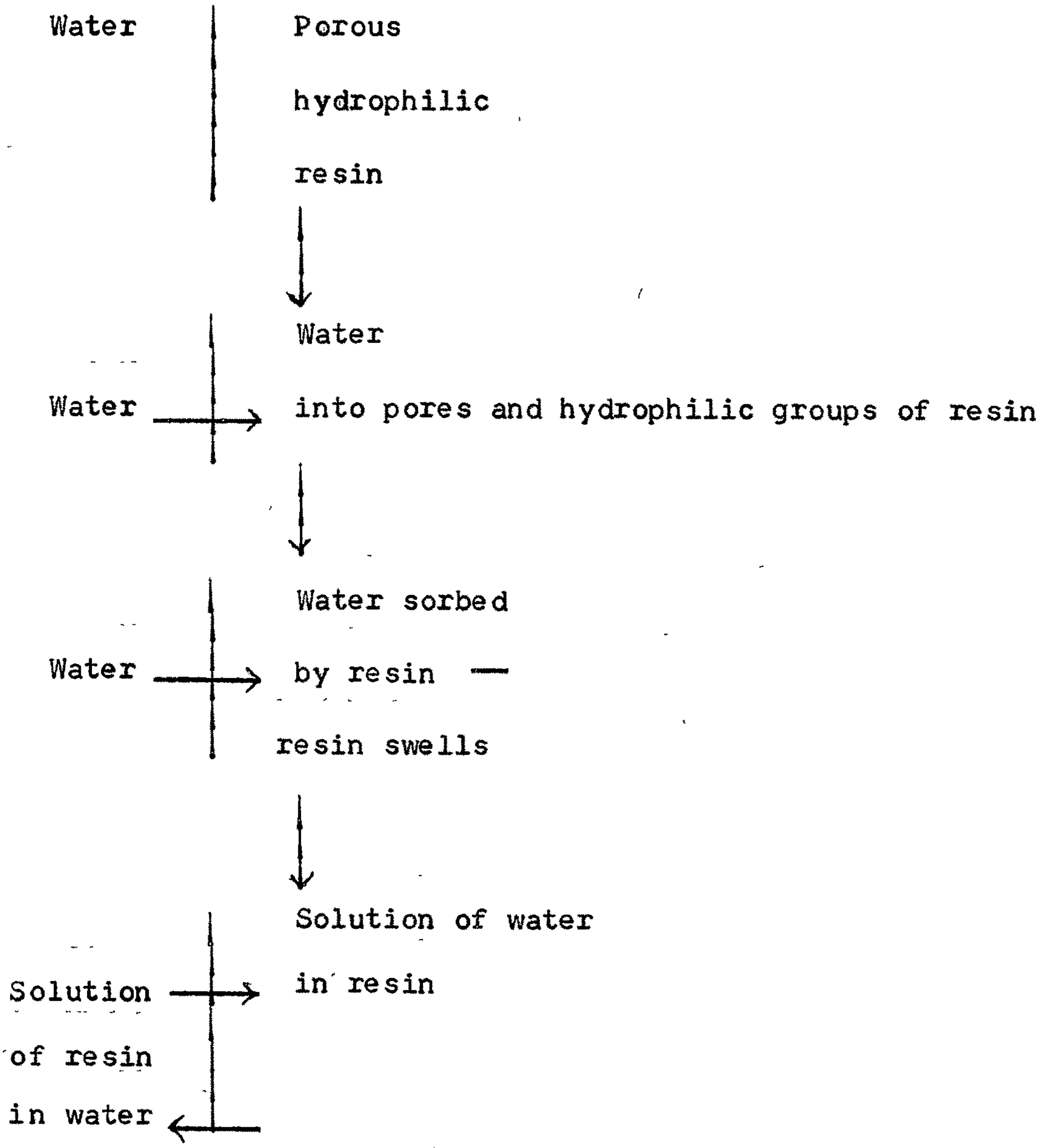

Water
Porous
hydrophilic
resin
Water
Water
into pores and hydrophilic groups of resin
Water sorbed
Water
by resin —
resin swells
Solution of water
in resin
Solution
of resin
in water

Fig. III.5

For the purpose of comparing solubility with structural characteristics, we calculate molar solubility as

$$\text{molar solubility (g-mole/l)} = \frac{\text{Sol (g/l)}}{W_{F(a)}}$$

These values are plotted versus x in Fig III.6. We observe that molar solubility decreases with increase in x. Since poly(vinyl alcohol) is soluble in water and poly(vinyl ester) is usually insoluble in water, increase in OH groups in alcohol-esters should increase their solubility. Hence observed trend in anomalous. We can say that hydrophilic groups would introduce swellable sites and that solubilization would depend on the mechanical loosening of the chains and imparting them mobility. It would imply that chains loosely packed and held together by weak forces can be more readily solubilized. We observe that in case of four series of alcohol-esters containing O- and p-amino benzoates and O- and p-hydroxy benzoates, the molar solubility is in the same range irrespective of the nature and position of the substituent. In case of alcohol esters of dibasic acids, solubility of products of different series is decreasing in order

K-P-ADA > K-P-TPA > K-P-FMA > K-P-IPTA > K-P-SBA

We now calculate swelling degree mole as

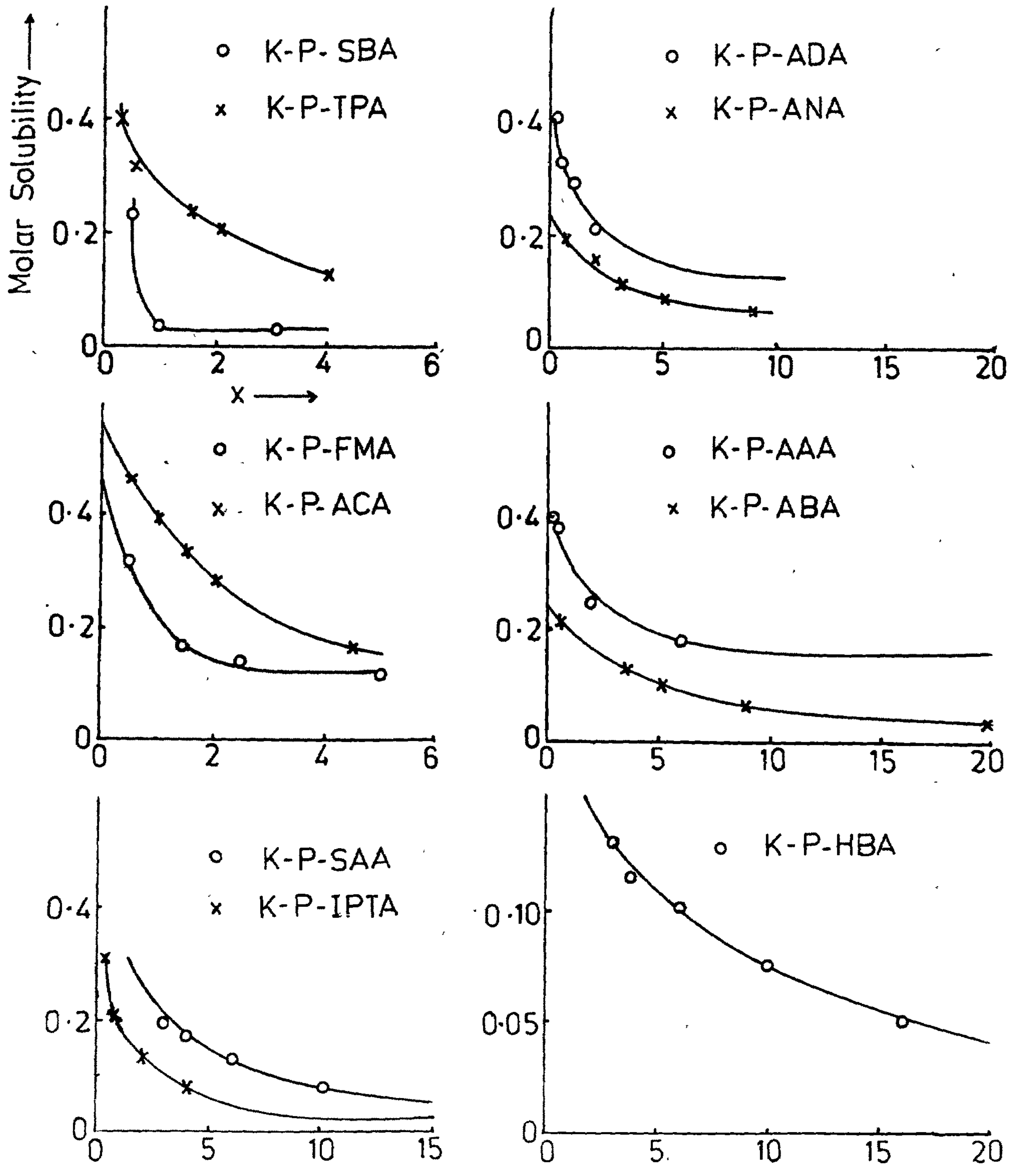


Fig III·6 Molar Solubility vs x

swelling degree mole (g/g mole) = swelling degree (g/g)x $W_{F(a)}$.

The values are plotted versus x in Fig.III.7 . We generally observe that the values are increasing with increase in x. This is in accordance with our consideration that increase in hydrophilic groups would increase swellable sites and hence swellability of the products. It may be noted that alcohol-sebacetes behave abnormally.

Swelling in its broader sense is considered as either limited or unlimited. When the substance sorbs water, it swells. Swelling by sorption takes place upto a certain limit. When further sorption takes place beyond this limit, the substance will solubilize. Another limit will be reached when the substance would get totally dissolved . These two limits can be evaluated as under.

The number of moles of water sorbed by the resin during maximum swelling can be calculated as follow . On the basis of the assumption that increase in wt is due to sorption of water by the resin:

$$\frac{\text{Water(moles)sorbed}}{\text{resin unit wt(g-mole)}} = \frac{\text{Swelling degree(g/g)x}W_{F(a)}}{18} = A$$

Similarly, number of moles of water required just to dissolve fully one g-mole of the resin is calculated as

$$\frac{\text{Water(moles)required to dissolve}}{\text{resin Unit wt(g-mole)}} = \frac{W_{F(a)} \text{ x } 1000}{\text{sol(g/l)x18}} = B$$

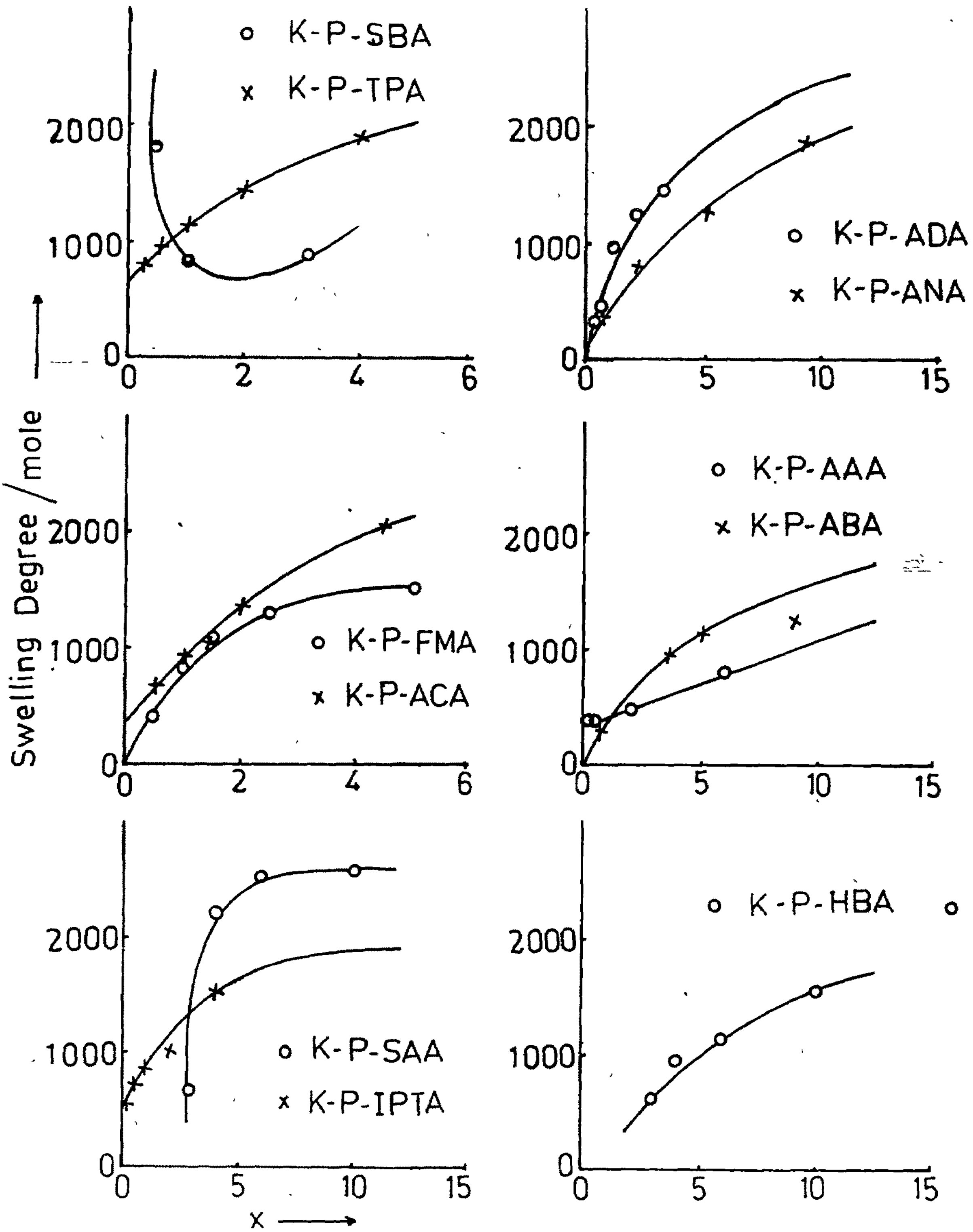


Fig III·7 Swelling Degree / mole vs x

We plot $\log_{10}A$ (or $\log_{10}B$) versus x in Fig. III.8. The two curves represent the two limits (limited and unlimited swelling) and the shaped region between the curves represent equilibrium of limited and unlimited swelling.

III.6 WATER RESORPTION :

To study how the solubility and swelling of the resin are affected by repeated sorption, we thrice carried out sorption and desorption of three products of each series, used for sorption once. The results have been utilized to calculate (i) solubility of the resin, (ii) swelling degree of the resin and (iii) the product (solubility x swelling degree).

Weight loss is calculated as

$$\text{wt loss(I)} = W_{DS} - W_{DR(I)}$$

$$\text{wt loss(II)} = W_{DR(I)} - W_{DR(II)}$$

and $$\text{wt loss(III)} = W_{DR(II)} - W_{DR(III)}$$

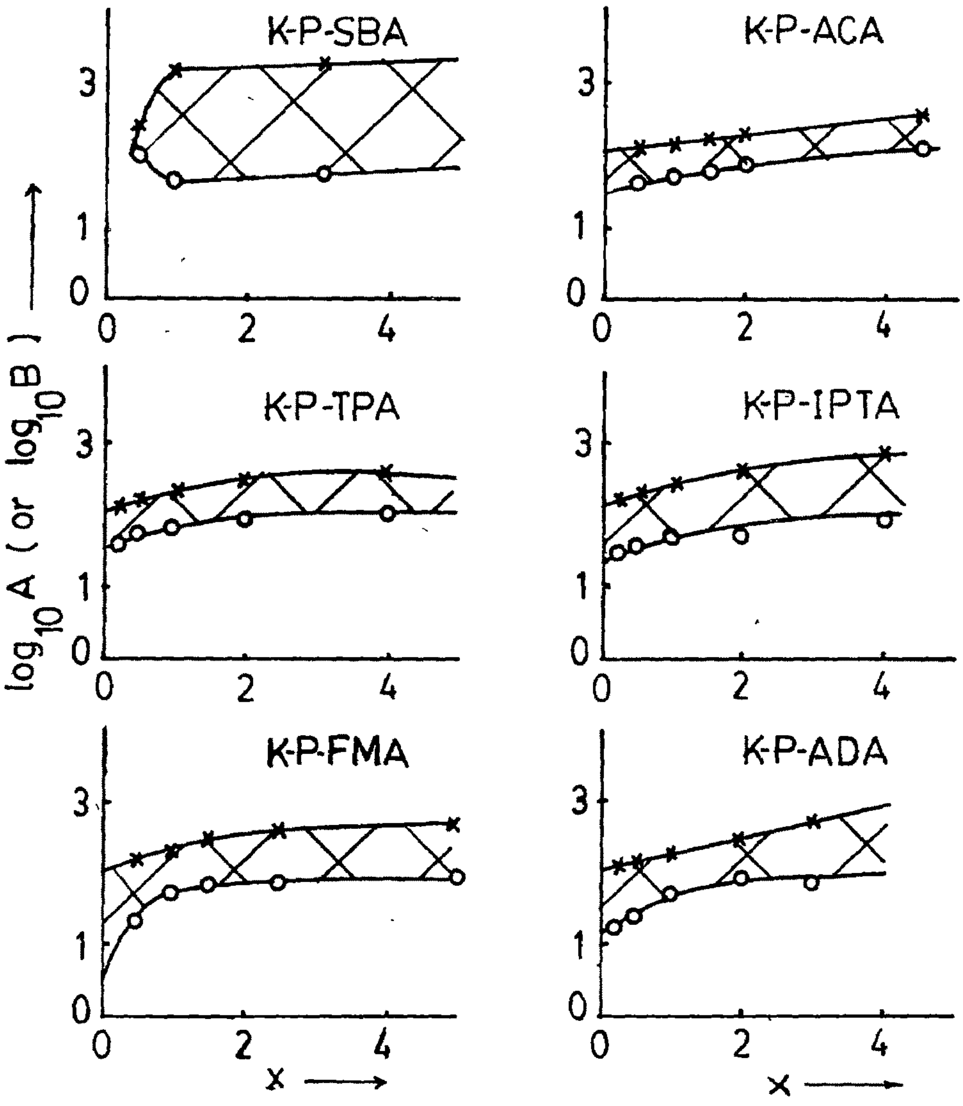
Similarly, weight gain is calculated as

$$\text{wt gain (I)} = W_{AR(I)} - W_{DR(I)}$$

$$\text{wt gain (II)} = W_{AR(II)} - W_{DR(II)}$$

and $$\text{wt gain(III)} = W_{AR(III)} - W_{DR(III)}$$

Hence solubility of the resin is calculated as



o $\log_{10}A$, x $\log_{10}B$

Fig III-8(a) $\log_{10}A$ (or $\log_{10}B$) vs x

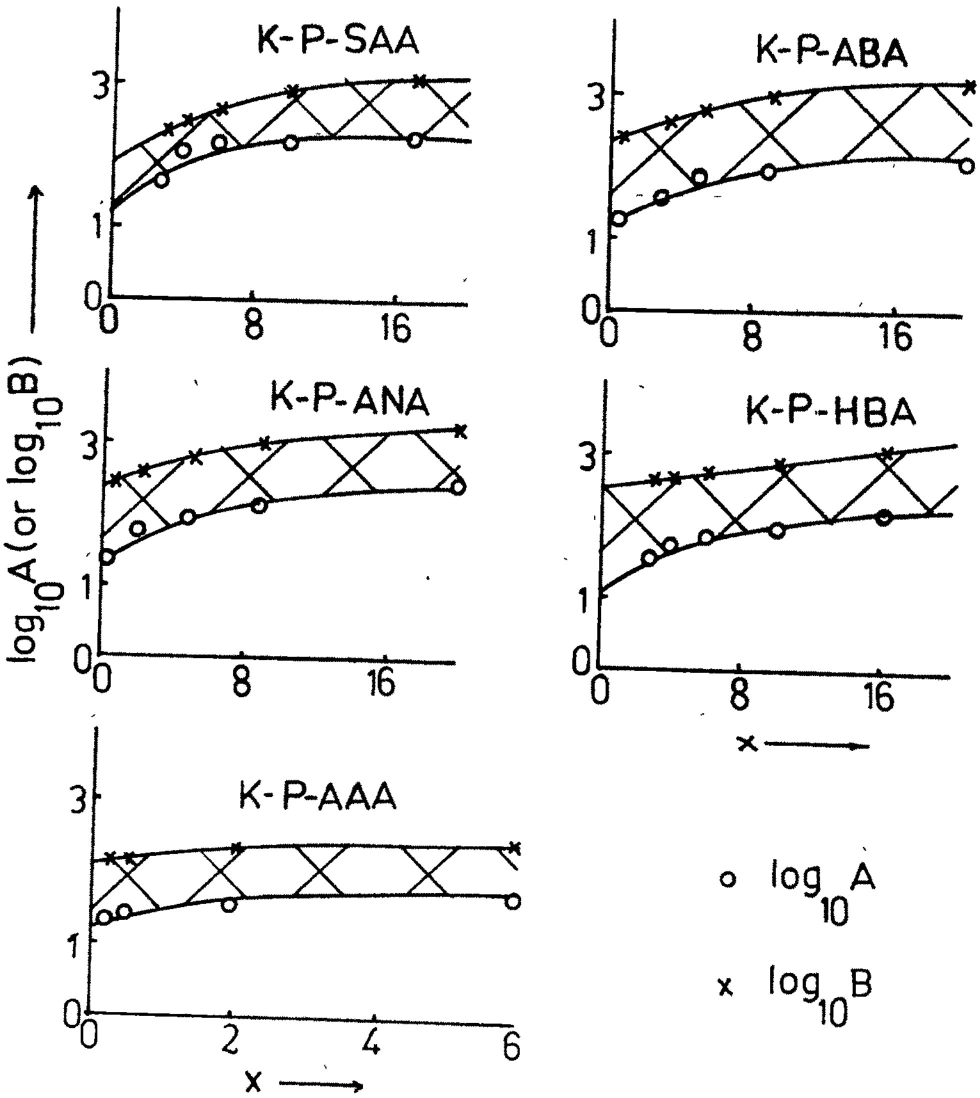


Fig III·8(b) $\log_{10}A$ (or $\log_{10}B$) vs x

$$\text{sol R(I)} \quad (g/l) = \frac{1000 \times \text{wt loss(I)}}{V_{BS} - \text{wt gain(I)}}$$

$$\text{sol R(II)} \quad (g/l) = \frac{1000 \times \text{wt loss(II)}}{V_{BS} - \text{wt gain (II)}}$$

$$\text{sol R(III)} \quad (g/l) = \frac{1000 \times \text{wt loss(III)}}{V_{BS} - \text{wt gain (III)}}$$

and swelling degree of the resin was evaluated as

$$\text{Swelling degree R(I)} \quad (g/g) = \frac{\text{wt gain(I)}}{W_{DR(I)}}$$

$$\text{Swelling degree R(II)} \quad (g/g) = \frac{\text{wt gain (II)}}{W_{DR(II)}}$$

and $$\text{Swelling degree R(III)} \quad (g/g) = \frac{\text{wt gain (III)}}{W_{DR(III)}}$$

The calculated values are presented in Table III.7.1, III.7.2 and III.7.3 . The values of the product (solubility x swelling degree) are found to lie over a narrow range in each series, confirming our earlier observation.

To compare the values of (i) solubility and (ii) swelling degree for repeated sorption, we present the plots of solubility vs x in Fig.III.9 and of swelling degree vs x in Fig.III.10.

When the resin is subjected to repeated sorption and desorption, a part of the resin dissolves (in water) every time. The solubility of the resin in water observed in the first sorption experiment (Sol. I) decreases considerably in subsequent sorption experiments (sol.II and Sol. III). The ratio (sol. I/Sol. III) varies

Table III.7-1(a)

Water sorption R(I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/l)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/l)
1	K-P-SBA(3)	0.198	1.726	23.93	5.72	136.87
2	K-P-SBA(5)	0.161	0.820	17.54	2.42	42.45
3	K-P-SBA(10)	0.148	0.658	15.84	1.87	29.62

Table III.7-1(b)

Water sorption R (I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/l)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/l)
1	K-P-TPA(3)	0.215	2.124	27.30	7.45	203.46
2	K-P-TPA(5)	0.225	1.410	26.19	5.13	134.29
3	K-P-TPA(10)	0.227	1.660	27.22	6.08	165.51

Table III.7-1(c)

Water sorption R (I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/l)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/l)
1	K-P-FMA(3)	0.215	0.887	23.59	3.11	73.36
2	K-P-FMA(5)	0.216	1.306	24.84	4.60	114.26
3	K-P-FMA(10)	0.205	1.364	23.74	4.62	109.68

Table III.7-1(d)

Water sorption R(I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/l)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/l)
1	K-P-ACA(3)	0.198	1.828	24.23	6.05	146.59
2	K-P-ACA(5)	0.208	1.894	25.66	6.49	166.53
3	K-P-ACA(10)	0.217	0.779	23.53	2.75	64.71

Table III.7-1(e)

Water sorption R(I)

No.	Product	First weight loss (g)	First weight gain (g)	solubility R(I) (g/l)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/l)
1	K-P-SAA(3)	0.222	1.557	26.29	5.60	147.22
2	K-P-SAA(5)	0.185	0.851	20.22	2.70	54.59
3	K-P-SAA(10)	0.225	1.467	26.31	5.33	140.23

Table III.7-1(f)

Water sorption R(I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/l)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/l)
1	K-P-IPTA(3)	0.185	1.283	21.22	4.07	86.37
2	K-P-IPTA(5)	0.195	0.872	21.36	2.86	61.09
3	K-P-IPTA(10)	0.185	0.977	20.50	3.10	63.55

Table III.7-1(g)

Water sorption R(I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/1)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/1)
1	K-P-ADA(3)	0.260	0.755	28.12	3.15	88.58
2	K-P-ADA(5)	0.245	0.685	26.30	2.69	70.75
3	K-P-ADA(10)	0.186	0.803	20.22	2.56	51.76

Table III.7-1(h)

Water sorption R(I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/1)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/1)
1	K-P-ANA(3)	0.183	0.698	19.67	2.20	43.27
2	K-P-ANA(5)	0.205	1.165	23.47	3.95	92.71
3	K-P-ANA(10)	0.188	0.800	20.43	2.56	52.31

Table III.7-1(j)

Water sorption R (I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/1)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/1)
1	K-P-AAA(3)	0.280	0.540	29.60	2.45	72.52
2	K-P-AAA(5)	0.225	0.649	24.06	2.36	56.78
3	K-P-AAA(10)	0.220	0.934	24.27	3.34	81.06

Table III.7-1(k)

Water sorption (R(I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/1)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/1)
1	K-P-4ABA(3)	0.204	0.706	21.95	2.39	52.46
2	K-P-4ABA(5)	0.300	0.588	31.87	2.94	93.70
3	K-P-4ABA(10)	0.214	0.626	22.83	2.19	49.99

Table III.7-1(1)

Water sorption R(I)

No.	Product	First weight loss (g)	First weight gain (g)	Solubility R(I) (g/l)	Swelling degree R(I) (g/g)	Sol.R(I)xSwelling degree R(I) (g/l)
1	K-P-4HBA(3)	0.270	0.328	27.92	1.43	39.93
2	K-P-4HBA(5)	0.338	0.342	35.00	2.11	73.85
3	K-P-4HBA(10)	0.262	0.432	27.38	1.82	49.83

Table III.7-2(a)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R)(II) (g/l)	Swelling degree R(II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/l)
1	K-P-SBA(3)	0.024	1.492	2.82	5.37	15.10
2	K-P-SBA(5)	0.002	0.685	0.21	2.03	0.43
3	K-P-SBA(10)	0.002	0.535	0.32	1.53	0.49

Table III.7-2(b)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/l)	Swelling degree R(II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/l)
1	K-P-TPA(3)	0.017	1.422	1.99	5.31	10.50
2	K-P-TPA(5)	0.027	1.012	3.00	4.08	12.20
3	K-P-TPA(10)	0.019	1.461	2.23	5.75	12.80

Table III.7-2(c)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/l)	Swelling degree R(II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/l)
1	K-P-FMA(3)	0.023	0.715	2.48	2.73	6.77
2	K-P-FMA(5)	0.039	0.890	4.28	3.59	15.40
3	K-P-FMA(10)	0.009	0.954	0.99	3.34	3.30

Table III.7-2(d)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/1)	Swelling degree R(II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/1)
1	K-P-ACA(3)	0.014	1.522	1.65	5.28	8.71
2	K-P-ACA(5)	0.022	1.100	2.47	4.07	10.10
3	K-P-ACA(10)	0.016	1.053	1.79	3.94	7.05

Table III.7-2(e)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/l)	Swelling degree R(II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/l)
1	K-P-SAA(3)	0.030	1.082	3.36	4.36	14.60
2	K-P-SAA(5)	0.039	0.704	4.20	2.55	10.70
3	K-P-SAA(10)	0.041	0.896	4.50	3.82	17.20

Table III.7-2(f)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/1)	Swelling degree R (II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/1)
1	K-P-IPTA(3)	0.025	1.050	2.79	3.62	10.10
2	K-P-IPTA(5)	0.005	0.975	0.55	3.25	1.79
3	K-P-IPTA(10)	0.003	0.698	0.32	2.24	0.72

Table III.7-2(g)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/l)	Swelling degree R (II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/l)
1	K-P-ADA(3)	0.028	0.568	2.97	2.68	8.00
2	K-P-ADA(5)	0.055	0.525	5.80	2.63	15.30
3	K-P-ADA(10)	0.012	0.548	1.27	1.81	2.30

Table III.7-2(h)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/l)	Swelling degree R (II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/l)
1	K-P-ANA(3)	0.067	0.770	7.26	3.08	22.40
2	K-P-ANA(5)	0.082	1.213	9.33	5.69	53.10
3	K-P-ANA(10)	0.010	0.668	1.07	2.21	2.40

Table III.7-2(j)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/1)	Swelling degree R (II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/1)
1	K-P-AAA(3)	0.070	0.217	7.16	1.45	10.40
2	K-P-AAA(5)	0.0022	0.481	2.31	1.90	4.40
3	K-P-AAA(10)	0.054	0.662	5.78	2.93	16.90

Table III.7-2(k)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/l)	Swelling degree R (II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/l)
1	K-P-4ABA(3)	0.012	0.774	1.30	2.73	3.60
2	K-P-4ABA(5)	0.093	0.411	9.70	3.84	37.20
3	K-P-4ABA(10)	0.042	0.603	4.47	2.47	11.00

Table III.7-2(1)

Water Sorption R(II)

No.	Product	Second weight loss (g)	Second weight gain (g)	Solubility (R) (II) (g/1)	Swelling degree R (II) (g/g)	Sol.R(II)xSwelling degree R(II) (g/1)
1	K-P-4HBA(3)	0.013	0.355	1.35	1.64	2.21
2	K-P-4HBA(5)	0.014	0.066	1.41	4.46	6.29
3.	K-P-4HBA(10)	0.021	0.431	2.19	1.99	4.36

Table III.7-3(a)

Water sorption R (III)

No	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-SBA(3)	0.006	1.378	0.70	5.47	3.83
2	K-P-SBA(5)	0.002	0.550	0.21	1.64	0.34
3	K-P-SBA(10)	0.002	0.530	0.21	1.52	0.32

Table III.7-3(b)

Water sorption R (III)

No	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-TPA(3)	0.007	1.307	0.31	5.00	4.05
2	K-P-TPA(5)	0.014	0.844	1.53	3.61	5.52
3	K-P-TPA(10)	0.014	1.012	1.56	4.22	6.6

Table III.7-3(c)

Water Sorption R (III)

No	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-FMA	0.001	0.708	0.11	2.71	0.30
2	K-P-FMA(5)	0.021	0.574	2.23	2.56	5.71
3	K-P-FMA(10)	0.001	0.941	0.11	3.30	3.63

Table III.7-3(d)

Water Sorption R(III)

No	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-ACA(3)	0.009	1.520	1.06	5.45	5.77
2	K-P-ACA(5)	0.007	0.979	0.78	3.72	2.90
3	K-P-ACA(10)	0.002	1.035	0.22	3.91	0.86

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Table III.7-3(e)

Water Sorption R(III)

No	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-SAA(3)	0.020	1.057	2.24	4.64	10.40
2	K-P-SAA(5)	0.006	0.684	0.64	2.53	1.62
3	K-P-SAA(10)	0.004	0.825	0.44	3.59	1.58

Table III.7-3(f)

Water Sorption R(III)

No	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-IPTA(3)	0.015	1.050	1.68	3.82	6.41
2	K-P-IPTA(5)	0.005	0.870	0.55	2.95	1.62
3	K-P-IPTA(10)	0.002	0.668	0.21	2.15	0.45

Table III.7-3(g)

Water Sorption R(III)

No.	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-ADA(3)	0.002	0.550	0.21	2.62	0.55
2	K-P-ADA(5)	0.008	0.398	0.83	2.07	1.72
3	K-P-ADA(10)	0.002	0.558	0.21	1.86	0.39

Table III.7-3(h)

Water sorption R (III)

No.	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/1)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/1)
1	K-P-ANA(3)	0.008	0.762	0.87	3.15	2.74
2	K-P-ANA(5)	0.028	1.130	3.16	6.10	19.30
3	K-P-ANA(10)	0.006	0.644	0.64	2.18	1.40

Table III.7-3(j)

Water Sorption R (III)

No.	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-AAA(3)	0.005	0.240	0.51	1.66	0.84
2	K-P-AAA(5)	0.013	0.442	1.36	1.84	2.50
3	K-P-AAA(10)	0.004	0.592	0.43	2.67	1.14

Table III.7-3(k)

Water sorption R (III)

No.	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-4ABA(3)	0.010	0.764	1.08	2.79	3.01
2	K-P-4ABA(5)	0.004	0.411	0.42	3.99	1.68
3	K-P-4ABA(10)	0.004	0.595	0.43	2.48	1.07

Table III.7-3(1)

Water sorption R (III)

No.	Product	Third weight loss (g)	Third weight gain (g)	Solubility R(III) (g/l)	Swelling degree R(III) (g/g)	Sol.R(III)xSwelling degree R(III) (g/l)
1	K-P-4HBA(3)	0.011	0.229	1.13	1.11	1.26
2	K-P-4HBA(5)	0.010	0.080	1.01	0.58	0.59
3	K-P-4HBA(10)	0.005	0.426	0.52	2.01	1.04

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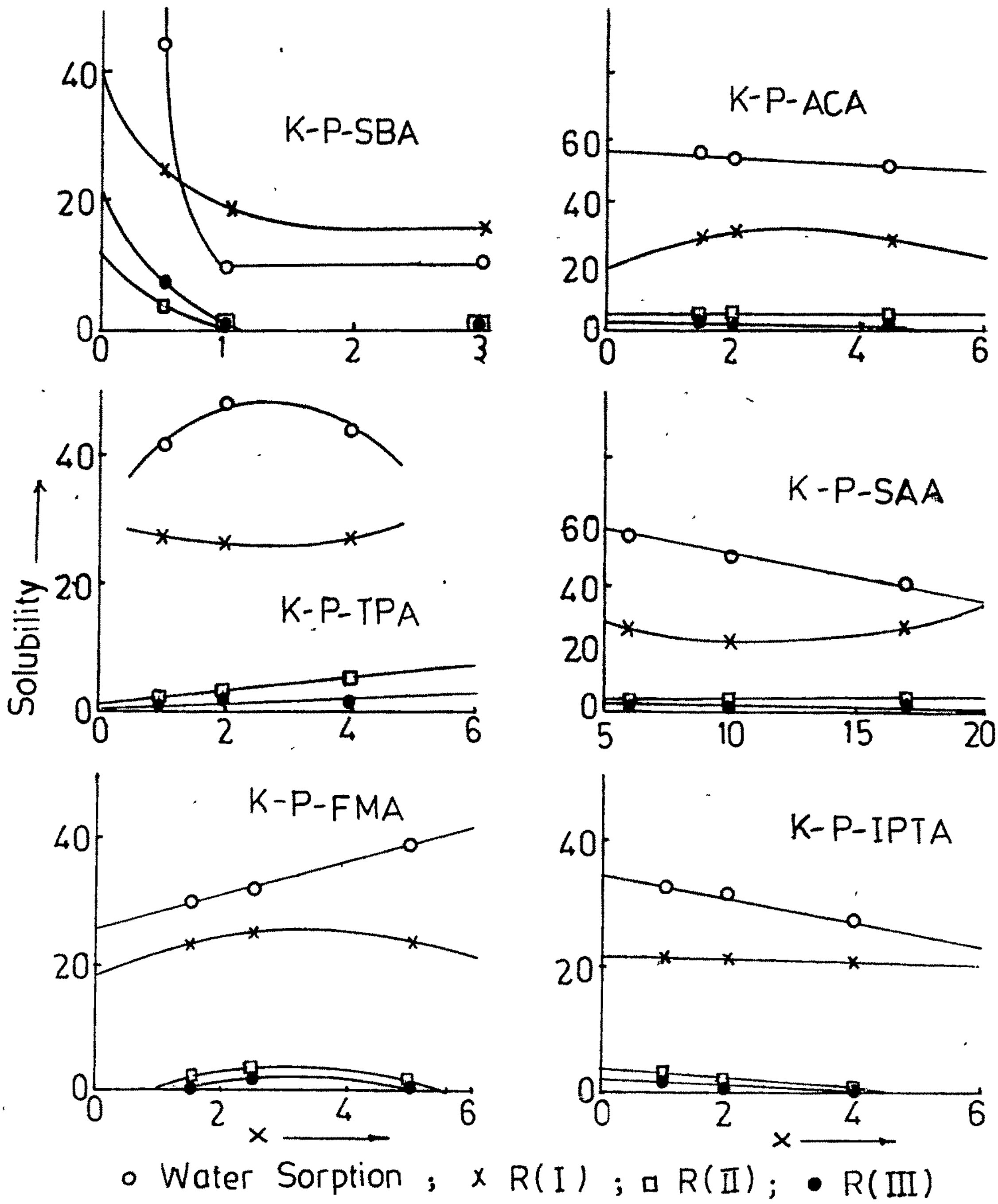

Fig. III 9(a) Solubility vs x

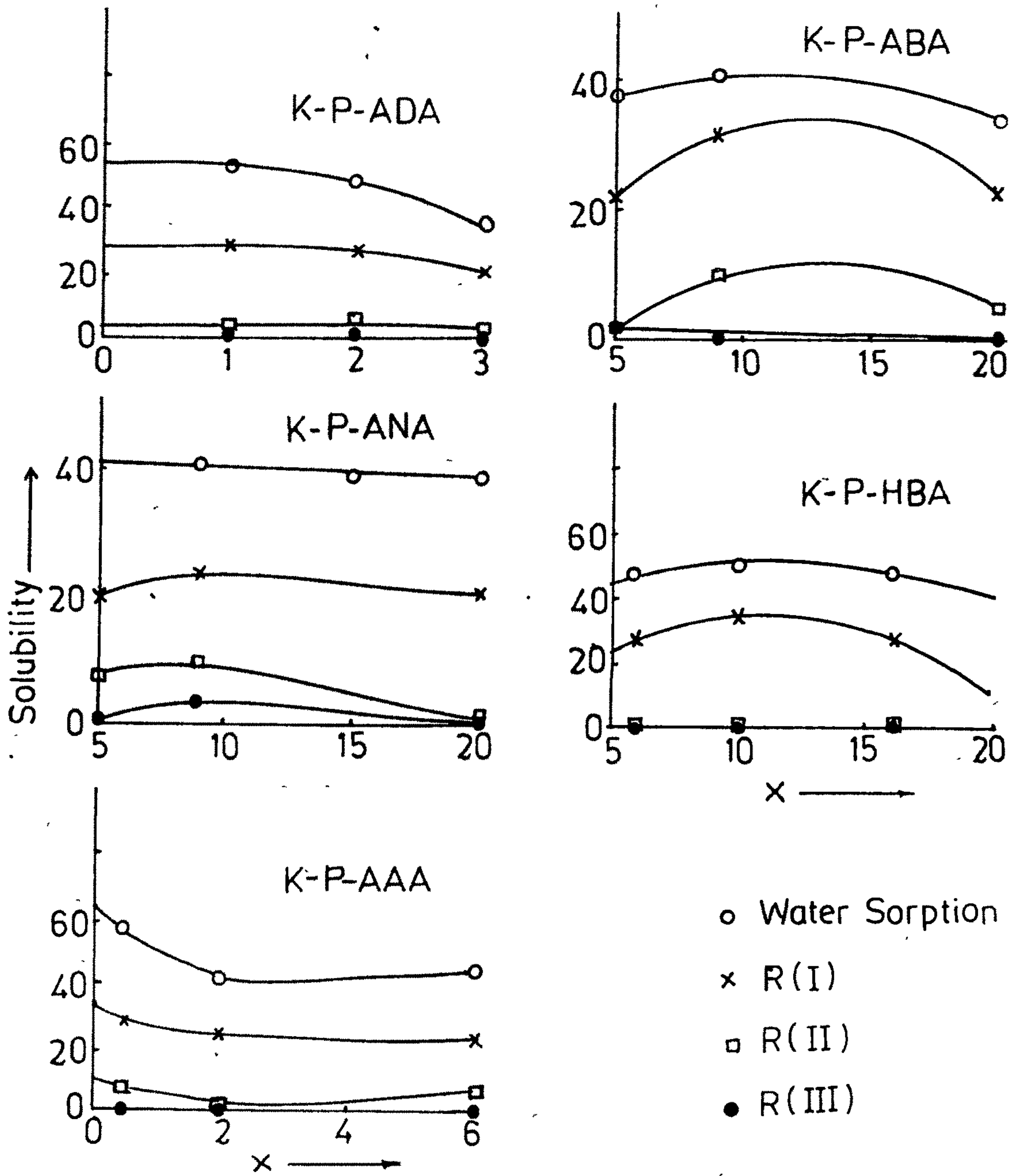

Fig III. 9 (b) Solubility vs x

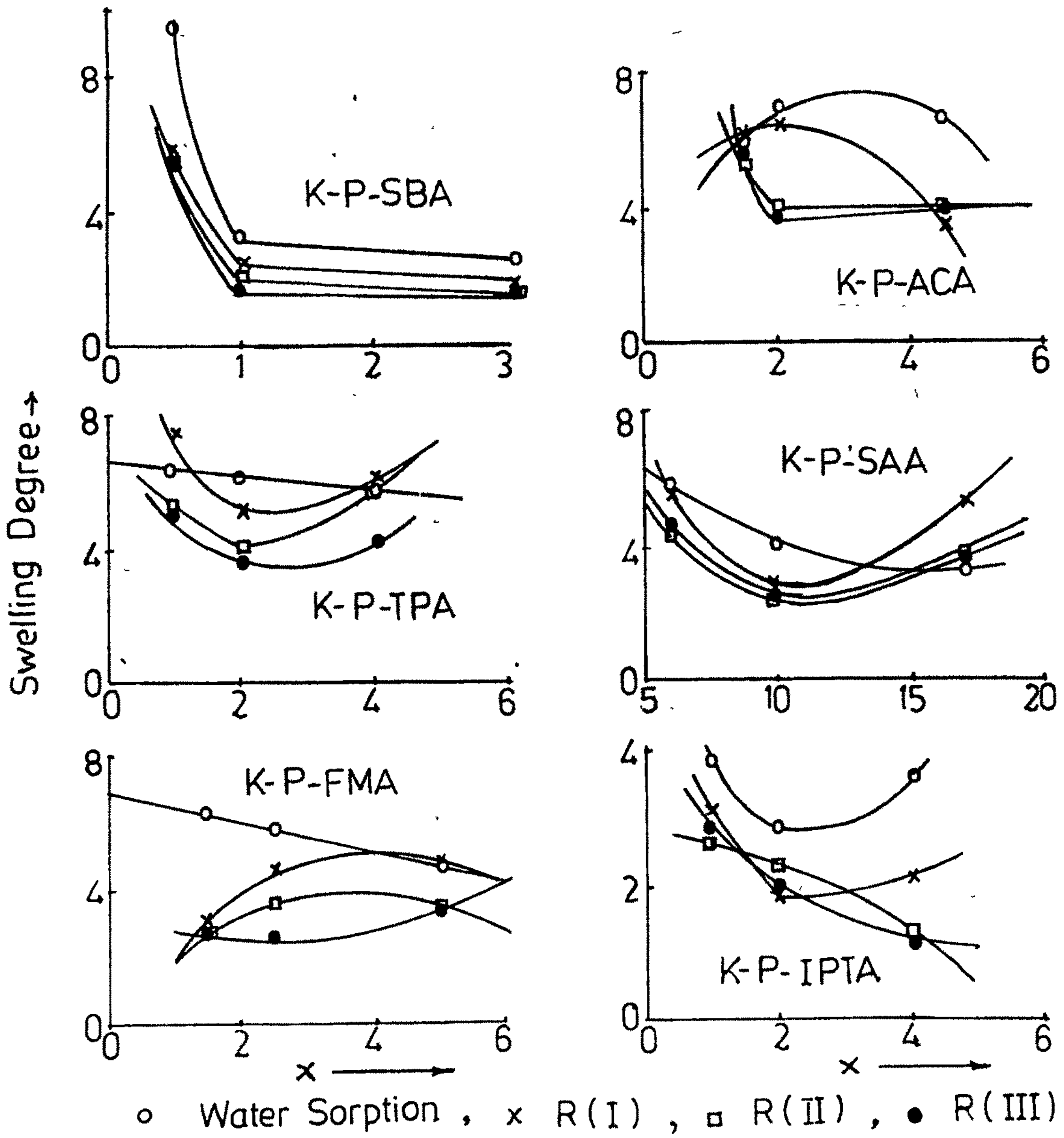

Fig III 10(a) Swelling Degree vs x

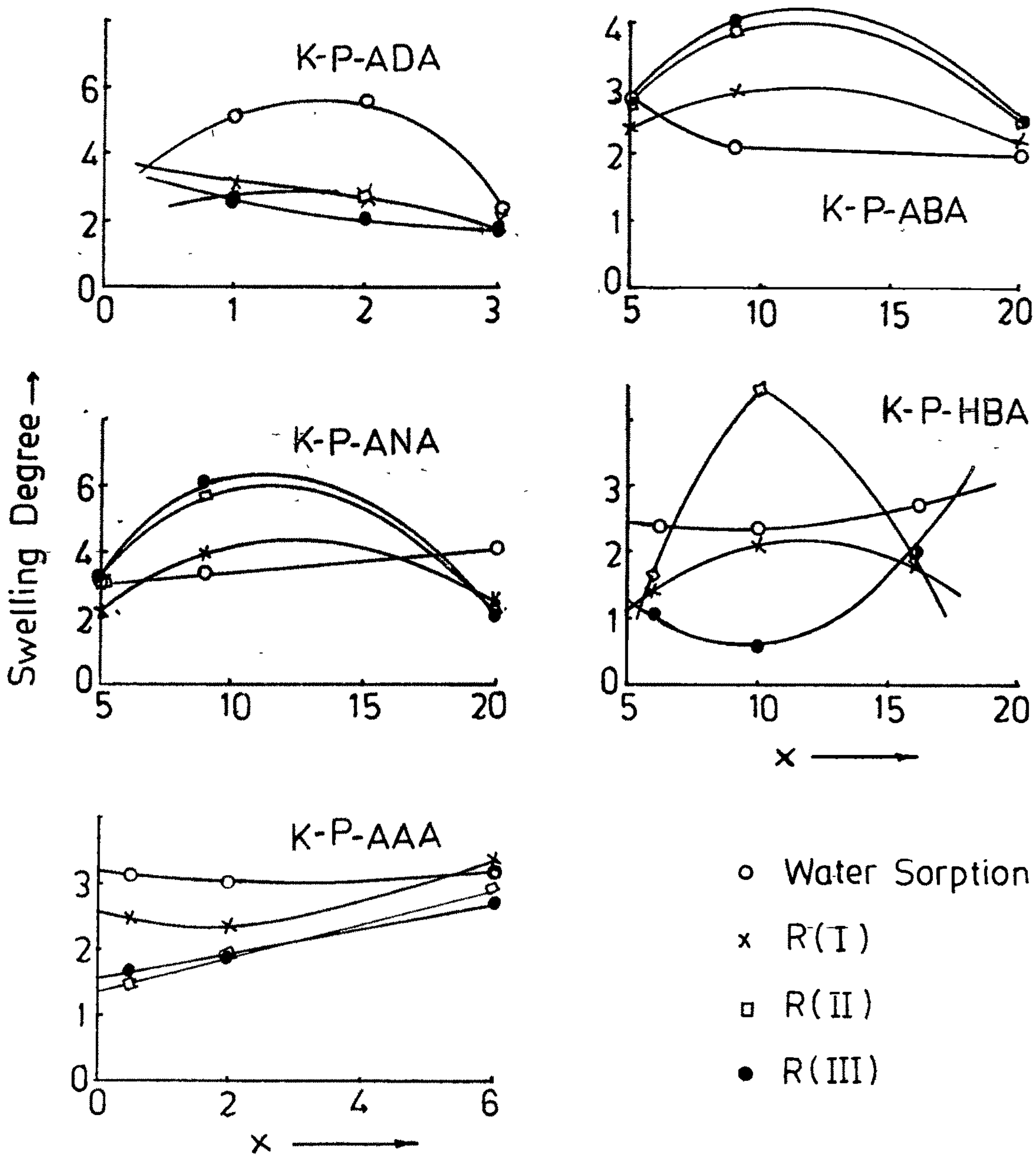

Fig III. 10 (b) Swelling Degree vs x

between 5 and 180 and shows (i) increasing tendency in the series K-P-ACA, K-P-SAA, K-P-HBA, (ii) decreasing tendency in the series K-P-SBA, and (iii) maximum or minimum in the series K-P-FMA, K-P-TPA, K-P-IPTA, K-P-ANA, K-P-ABA, K-P-AAA.

The upper and lower limits of solubility for all these resins are :

	Upper limit	Lower limit
Solubility(I)	35.00	17.54
Solubility(II)	9.70	0.21
Solubility(III)	3.16	0.11

When the resin is subjected to repeated sorption and desorption, the swelling degree of the undissolved resin varies over a very narrow range. The upper and lower limits of the swelling degree for all these resins are :

	Upper limit	Lower limit
Swelling degree(I)	7.45	1.43
Swelling degree(II)	5.75	0.45
Swelling degree(III)	6.10	0.58

These results imply that the swelling capacity of the resin is practically unaffected by the dissolution of the fraction of the resin, in other words, the fraction of the resin dissolved in water would not have higher swelling capacity than the fraction remaining undissolved.

III.7 SORPTION FROM SALT SOLUTIONS :

Sorption studies of these resins from sodium chloride solution have been made and calculations are as follows :

$$\text{Wt loss} = W_{BS} - W_{DS} - qW_{BS}$$

$$\text{Wt gain (due to salt uptake)} = W_{DS} - W_{WD}$$

$$\text{Wt gain (due to salt + water uptake)} = W_{AS} - W_{DS} - \frac{qW_{DS}}{(1-q)}$$

$$\text{Wt gain (due to water uptake)} = W_{AS} - 2W_{DS} + W_{WD} - \frac{qW_{DS}}{(1-q)}$$

$$\text{Solubility} = \frac{1000 \times \text{Wt loss}}{V_{BS} - \text{Wt gain due to water uptake}}$$

$$\text{Swelling degree} = \frac{\text{Wt gain due to water uptake}}{W_{DS}}$$

The calculated values are presented in table III.8 . It is observed that there is no wt gain due to salt uptake. It indicates the exclusion of the electrolyte by the resin in the sorption process. This type of exclusion is generally observed with various ion exchange resins (146). Dilute salt solutions can get concentrated by these resins.

Table III-9(a)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/1)	(g/g)	(g/1)
1.	K-P-SBA(1)	0.089	0.000	1.572	1.572	10.56	5.07	53.54
2.	K-P-SBA(2)	0.112	0.000	1.766	1.766	13.60	6.24	84.86
3.	K-P-SBA(3)	0.111	0.000	1.145	1.145	12.54	3.84	48.15
4.	K-P-SBA(5)	0.071	0.000	0.650	0.650	7.59	2.05	15.56
5.	K-P-SBA(10)	0.102	0.000	0.670	0.670	10.93	2.08	22.73

Table III-8(b)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/l)	(g/g)	(g/l)
1.	K-P-TPA(1)	0.235	0.000	0.285	0.285	24.19	1.39	33.62
2.	K-P-TPA(2)	0.160	0.000	0.651	0.651	17.11	2.46	42.09
3.	K-P-TPA(3)	0.193	0.000	0.684	0.684	20.72	2.83	58.64
4.	K-P-TPA(5)	0.162	0.000	2.516	2.516	21.65	9.39	20.33
5.	K-P-TPA(10)	0.132	0.000	0.965	0.965	14.61	3.08	45.00

Table III-8(c)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/1)	(g/g)	(g/1)
1.	K-P-FMA(1)	0.195	0.000	0.295	0.295	20.09	1.09	21.90
2.	K-P-FMA(2)	0.190	0.000	0.764	0.764	20.57	2.73	56.16
3.	K-P-FMA(3)	0.177	0.000	0.621	0.621	18.87	2.56	48.21
4.	K-P-FMA(5)	0.148	0.000	0.750	0.750	16.00	2.61	41.76
5.	K-P-FMA(10)	0.144	0.000	0.757	0.757	15.58	2.40	37.39

Table III-8(d)

Salt Solution

No.	Product	Weight loss (g)	Weight gain: Due to salt uptake (g)	Weight gain: Due to salt + water uptake (g)	Weight gain: Due to water uptake (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-ACA(1)	0.300	0.000	0.410	0.410	31.28	2.09	65.38
2	K-P-ACA(2)	0.255	0.000	0.703	0.703	27.43	3.06	83.94
3	K-P-ACA(3)	0.233	0.000	0.908	0.908	25.63	3.53	90.47
4	K-P-ACA(5)	0.214	0.000	1.094	1.094	24.03	4.11	98.83
5	K-P-ACA(10)	0.171	0.000	0.660	0.660	18.31	2.17	39.73

Table III-8(e)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/1)	(g/g)	(g/1)
1	K-P-SAA(1)	0.250	0.000	0.368	0.368	25.96	1.57	40.76
2	K-P-SAA(2)	0.220	0.000	1.231	1.231	25.09	4.56	114.41
3	K-P-SAA(3)	0.180	0.000	1.036	1.036	20.08	3.34	67.07
4	K-P-SAA(5)	0.135	0.000	0.719	0.719	14.55	2.05	29.83
5	K-P-SAA(10)	0.193	0.000	1.107	1.107	21.70	3.67	79.64

Table III-8(f)

Salt Solution

No.	Product	Weight loss (g)	Weight gain: Due to salt uptake (g)	Weight gain: Due to salt + water uptake (g)	Weight gain: Due to water uptake (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-IPTA(1)	0.198	0.000	0.337	0.337	20.49	1.40	28.77
2	K-P-IPTA(2)	0.155	0.000	0.751	0.751	16.76	2.80	46.93
3	K-P-IPTA(3)	0.120	0.000	0.596	0.596	12.76	1.89	24.72
4	K-P-IPTA(5)	0.098	0.000	0.585	0.585	10.41	1.75	18.22
5	K-P-IPTA(10)	0.127	0.000	0.800	0.800	13.96	2.70	37.69

Table III-g(g)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/l)	(g/g)	(g/l)
1	K-P-ADA(1)	0.287	0.000	0.334	0.334	29.69	2.10	62.35
2	K-P-ADA(2)	0.228	0.000	0.409	0.409	23.77	1.90	45.16
3	K-P-ADA(3)	0.196	0.000	0.528	0.528	20.69	2.02	41.70
4	K-P-ADA(5)	0.191	0.000	0.565	0.565	20.24	2.38	48.17
5	K-P-ADA(10)	0.163	0.000	0.667	0.667	17.46	2.34	40.86

Table III-8(h)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/l)	(g/g)	(g/l)
1	K-P-ANA(1)	0.268	0.000	0.365	0.365	27.82	1.72	47.85
2	K-P-ANA(2)	0.250	0.000	0.473	0.473	24.14	1.85	44.46
3	K-P-ANA(3)	0.223	0.000	0.394	0.394	23.21	1.53	35.50
4	K-P-ANA(5)	0.161	0.000	0.634	0.634	17.19	1.96	33.69
5	K-P-ANA(10)	0.168	0.000	0.683	0.683	18.03	2.15	38.85

Table III-8(j)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/1)	(g/g)	(g/1)
1	K-P-AAA(1)	0.217	0.000	0.785	0.785	23.55	3.08	72.53
2	K-P-AAA(2)	0.220	0.000	0.727	0.727	23.72	2.97	70.45
3	K-P-AAA(3)	0.245	0.000	0.531	0.531	25.87	2.36	61.05
4	K-P-AAA(5)	0.200	0.000	0.623	0.623	21.33	2.23	47.57
5	K-P-AAA(10)	0.192	0.000	0.792	0.792	20.85	2.66	55.46

Table III-8(k)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/l)	(g/g)	(g/l)
1	K-P-4ABA(1)	0.165	0.000	0.348	0.348	17.09	1.33	22.70
2	K-P-4ABA(2)	0.246	0.000	0.541	0.541	26.01	2.22	57.74
3	K-P-4ABA(3)	0.220	0.000	0.517	0.517	23.20	1.99	46.17
4	K-P-4ABA(5)	0.222	0.000	0.599	0.599	23.61	2.28	53.83
5	K-P-4ABA(10)	0.183	0.000	0.529	0.529	19.32	1.75	33.81

Table III-8(1)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/1)	(g/g)	(g/1)
1	K-P-4HBA(1)	0.253	0.000	0.330	0.330	26.16	1.63	42.64
2	K-P-4HBA(2)	0.237	0.000	0.378	0.378	24.63	1.73	42.61
3	K-P-4HBA(3)	0.230	0.000	0.370	0.370	23.88	1.61	38.45
4	K-P-4HBA(5)	0.298	0.000	0.319	0.319	30.78	1.66	51.14
5	K-P-4HBA(10)	0.200	0.000	0.437	0.437	20.91	1.65	34.50

Table III-8(m)

Salt Solution

No.	Product	Weight loss	Weight gain			Solubility	Swelling degree	Sol.xSwelling degree
			Due to salt uptake	Due to salt + water uptake	Due to water uptake			
		(g)	(g)	(g)	(g)	(g/1)	(g/g)	(g/1)
1	K-P-TCAA(1/3)	0.278	0.000	0.510	0.510	29.29	2.59	75.86
2	K-P-TMAN(1/2)	0.189	0.000	0.436	0.436	19.76	1.56	30.83

The product of the solubility and swelling degree is fairly constant in many of the series.

We calculate molar solubility (g-mole/l) and present it versus x in Fig. III.11. We again observe that molar solubility decreases with increase in x. Further we observe that molar solubility is higher in water than in salt solution. Hence we calculate the degree of salting out at fixed salt concentration (DSO_c) by the relation

$$DSO_c = \frac{Sol_w - Sol_s}{sol_w}$$

Where sol_w and sol_s represent the solubility in water and salt solution respectively. The calculated values are presented in table III.9. We observe in general that the values of DSO_c is close to 0.5 in most of the cases. It indicates that the effect is not related to the number of hydroxyl groups.

We present the plots of swelling degree/g-mole versus x in Fig. III.12. We observe in general that swelling degree/g-mole increase with increase in x. We also observe that swelling degree/g-mole is lower in salt solution than in water. Such lowering has been observed earlier.

Values of A and B are calculated as follows :

$$A : \frac{\text{Swelling degree(g/g)} \times W_{F(a)}}{18}$$

$$B : \frac{W_{F(a)} \times 1000}{\text{sol(g/l)} \times 18}$$

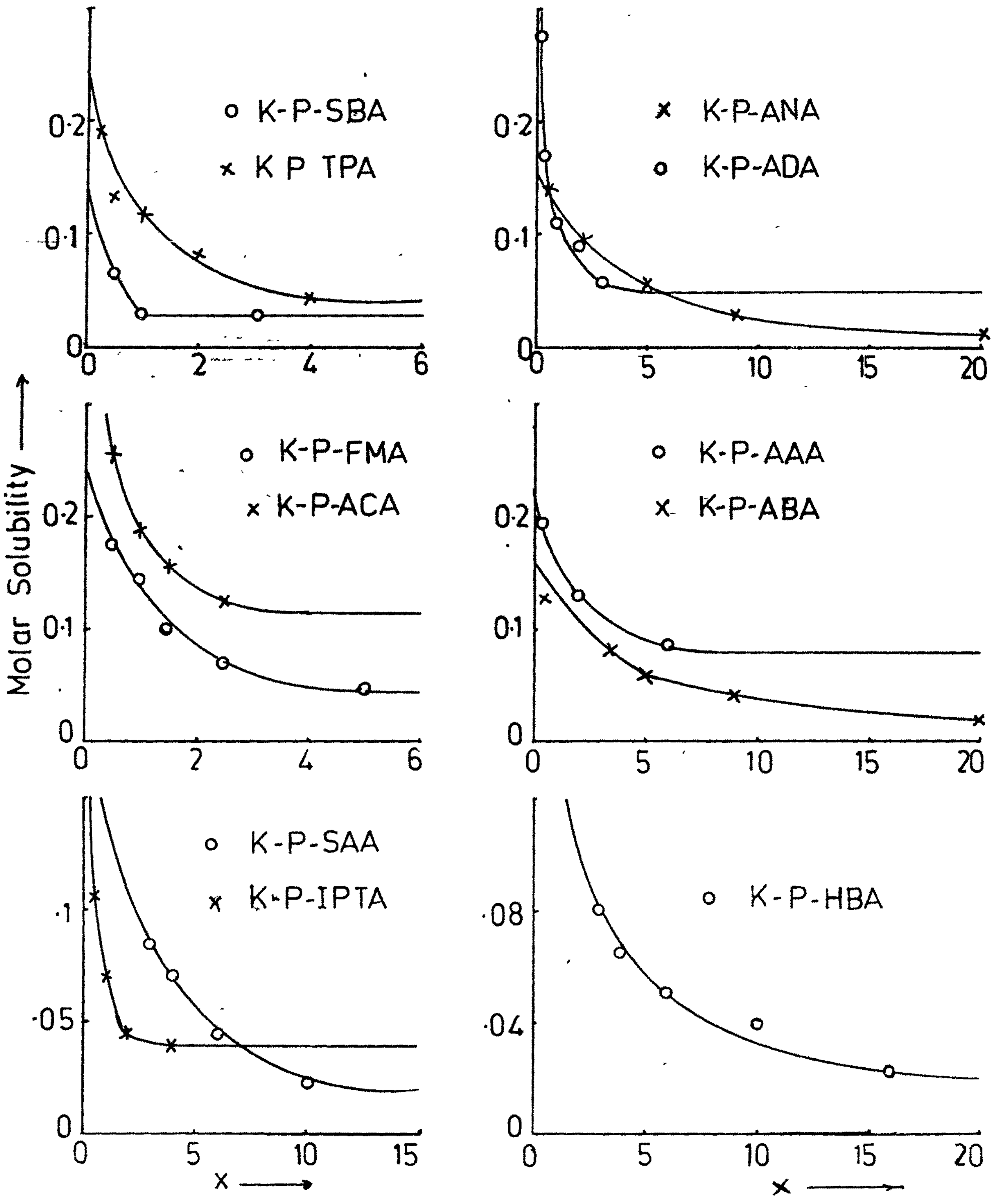

Fig III·11 Molar Solubility vs x

Table III.9

Salting out from salt solution

No.	Product	Z =	Degree of Salting out of resin				
			1	2	3	5	10
1	K-P-SBA(Z)		0.468	0.427	0.718	0.203	[illegible]
2	K-P-TPA(Z)		0.523	0.615	0.504	0.547	0.666
3	K-P-FMA(Z)		0.459	0.547	0.364	0.499	0.599
4	K-P-ACA(Z)		0.448	0.516	0.539	0.554	0.643
5	K-P-SAA(Z)		0.413	0.577	0.639	0.693	0.453
6	K-P-IPTA(Z)		0.476	0.466	0.609	0.668	0.479
7	K-P-ADA(Z)		0.326	0.484	0.612	0.577	0.502

Table III.9 (contd.)

Salting out from salt solution

No.	Product		Degree of Salting out of resin				
		Z =	1	2	3	5	10
8	K-P-ANA(Z)		0.243	0.411	0.418	0.548	0.522
9	K-P-AAA(Z)		0.623	0.508	0.488	0.477	0.516
10	K-P-4ABA(Z)		0.546	0.392	0.377	0.408	0.429
11	K-P-4HBA(Z)		0.383	0.451	0.490	0.379	0.552
		Z =		1/3	1/2		
12	K-P-TCAA(Z)			0.036			
13	K-P-TMAN(Z)				0.100		

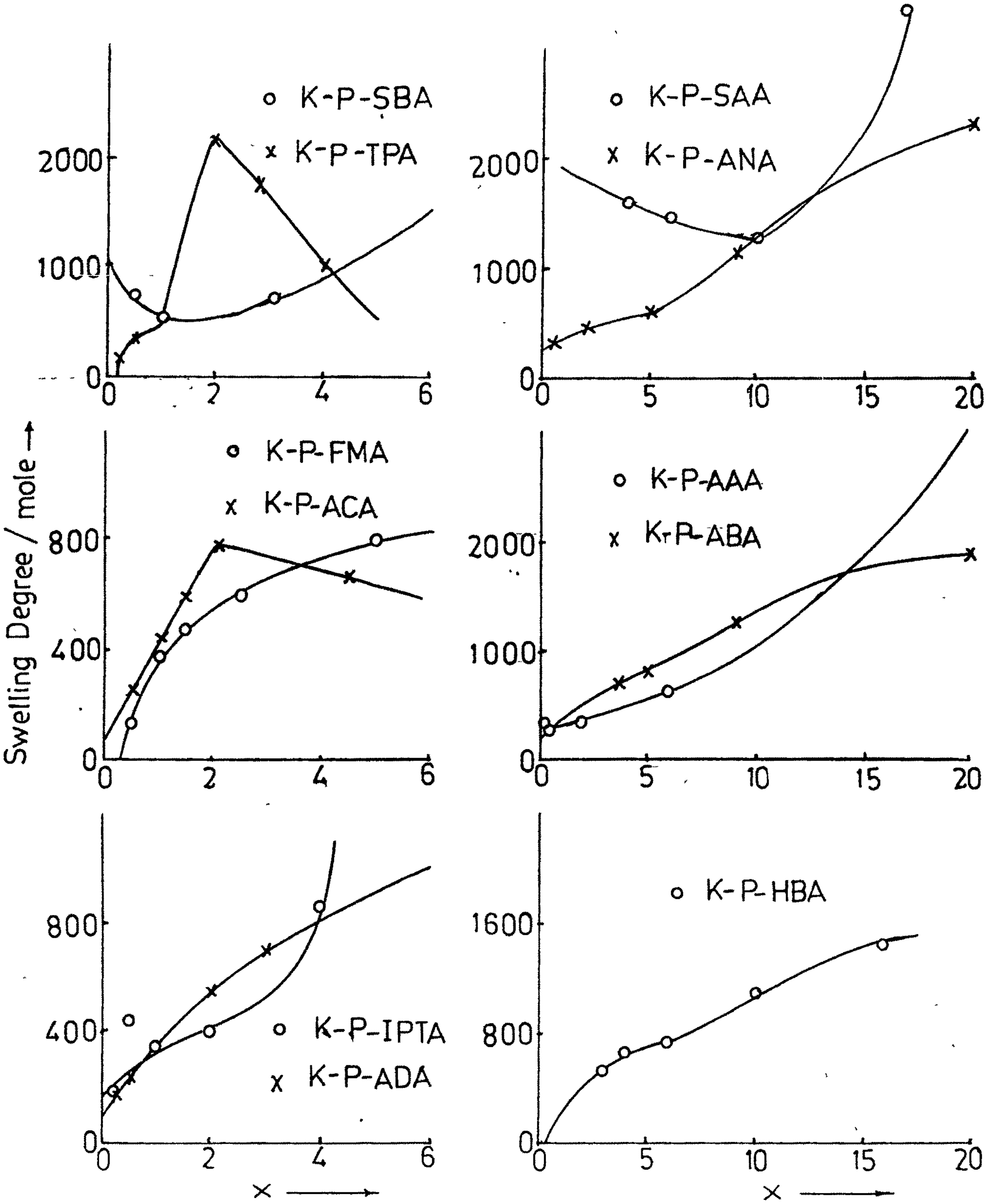

Fig III 12 Swelling Degree/mole vs x

We plot $\log_{10} A$ (or $\log_{10} B$) versus x in Fig.III.13. The two curves represent the two limits (limited and unlimited swelling) in salt solution and the shaded region between the curves represent equilibrium of limited and unlimited swelling.

III.8 SORPTION FROM UREA SOLUTION :

Sorption studies of some of these resins from Urea solution have been made . It is assumed that these is no wt gain due to urea uptake from urea column as is observed in case of salt from salt solution. Calculations have been made as follows.

$$\text{Wt loss} = W_{BS} - W_{DS} - qW_{BS}$$

$$\text{Wt gain} = W_{AS} - W_{DS} - \frac{qW_{DS}}{(1-q)}$$

$$\text{Solubility} = \frac{1000 \times \text{wt loss}}{V_{BS} - \text{wt gain}}$$

$$\text{Swelling degree} = \frac{\text{wt gain}}{W_{Ds}}$$

The calculated values are presented in Table III.10. It is observed in general that solubility of the resin in Urea solution is comparable to that in salt solution and much different from that in water .

Since the solubility is lower in urea solution than in water, we calculate the degree of salting as

$$DSO_c = sol_w - Sols / Sol_w$$

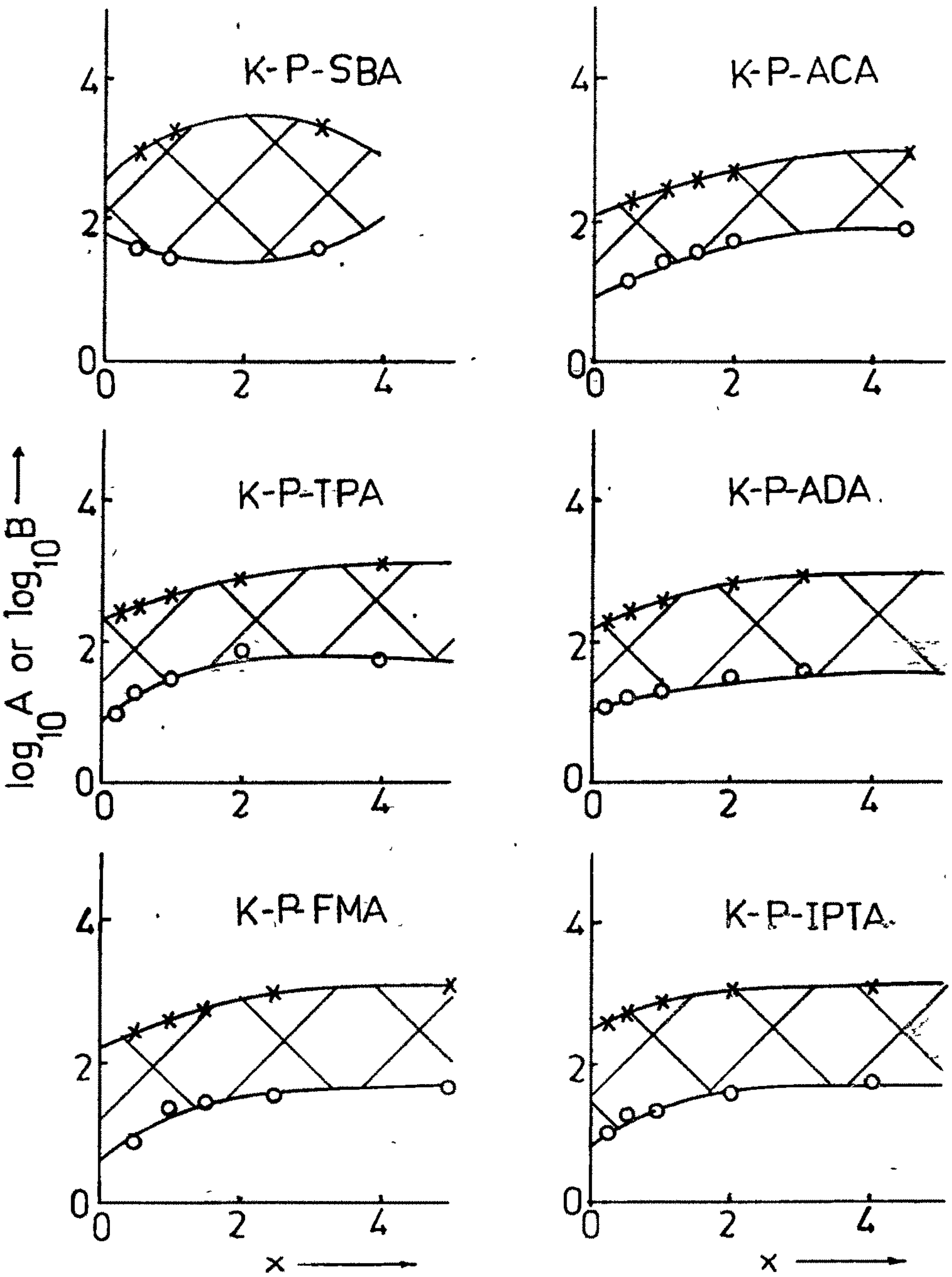

Fig III.13 (a) $\log_{10}A$ or $\log_{10}B$ vs x

o - $\log_{10}A$, x - $\log_{10}B$

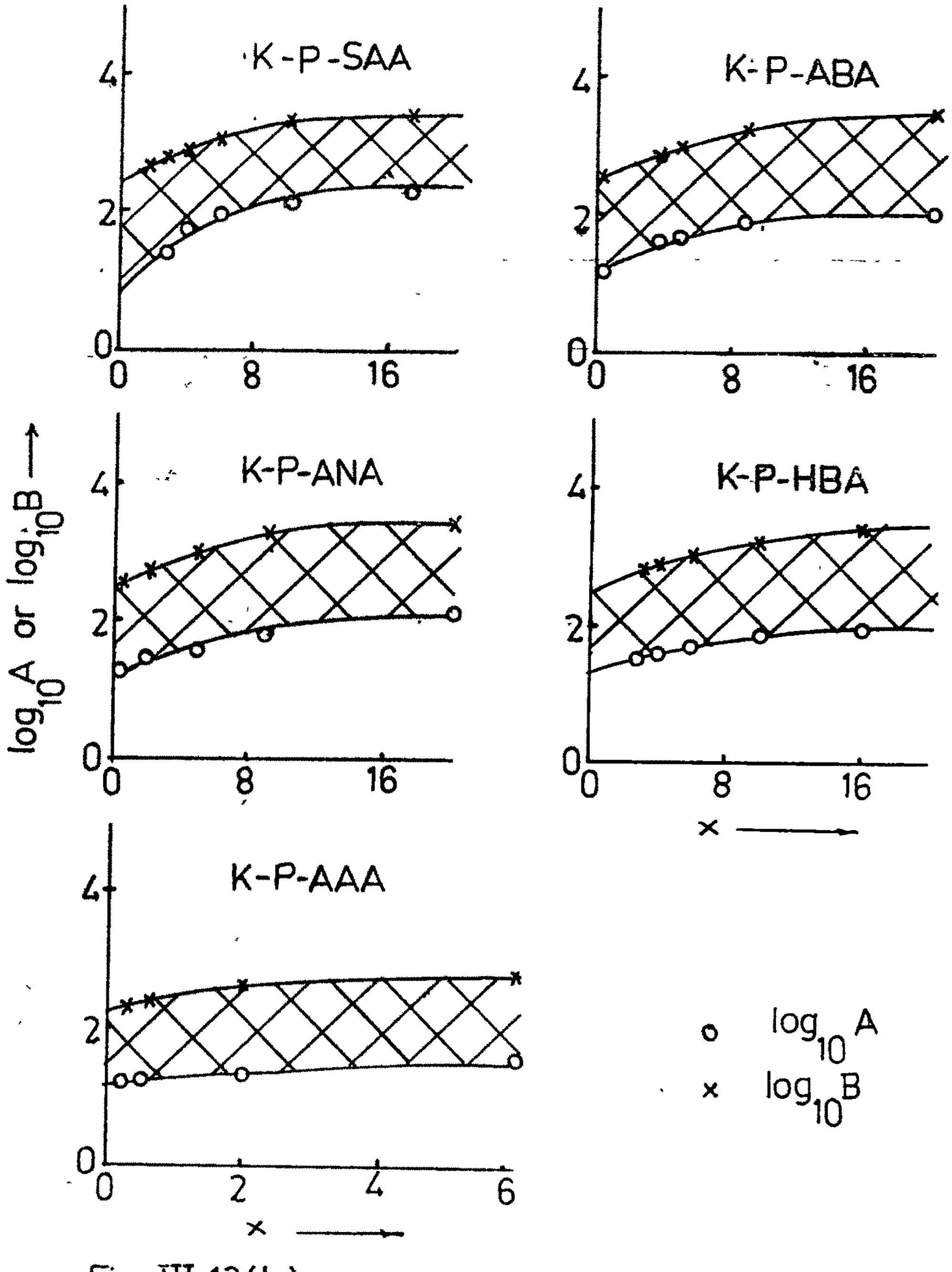

Fig III.13(b) $\log_{10}A$ or $\log_{10}B$ vs x

Table III.10(a)

Solution of Urea

No	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-SBA(3)	0.168	2.142	21.38	8.90	190.28
2	K-P-SBA(5)	0.056	0.736	6.05	2.22	13.43

Table III.10(b)

Solution of Urea

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-TPA(3)	0.270	2.389	35.47	0.15	5.14
2	K-P-TPA(5)	0.230	1.542	27.19	7.71	209.6

Table III.10(c)

Solution of Urea

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-FMA(3)	0.115	0.896	12.63	2.94	37.13
2	K-P-FMA(5)	0.159	1.580	18.88	5.72	108.00

Table III.10(d)

Solution of Urea

No	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-ACA(3)	0.205	1.722	24.76	6.04	149.55
2	K-P-ACA(5)	0.130	1.961	16.17	5.60	90.55

Table III.10(e)

Solution of Urea

No	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-SAA(3)	0.148	1.476	17.36	4.32	75.0
2	K-P-SAA(5)	0.190	0.820	20.70	2.78	57.5

Table III.10(f)

Solution of Urea

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-IPTA(3)	0.149	1.331	17.19	4.65	80.00
2	K-P-IPTA(5)	0.147	0.767	15.92	2.68	42.67

Table III.10(g)

Solution of Urea

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1.	K-P-ADA(3)	0.168	0.975	18.61	3.36	62.6
2.	K-P-ADA(5)	0.162	0.693	17.41	2.61	45.4

Table III.10(h)

Solution of Urea

No.	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1.	K-P-ANA(3)	0.237	0.717	25.53	2.95	75.3
2.	K-P-ANA(5)	0.171	0.812	18.61	2.59	48.10

Table III.10(ز)

Solution of Urea

No	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-AAA(3)	0.240	0.693	25.79	3.01	77.7
2	K-P-AAA(5)	0.212	0.702	22.80	2.62	59.7

Table III.10(K)

Solution of Urea

No	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-4ABA(3)	0.168	0.752	18.17	2.41	43.8
2	K-P-4ABA(5)	0.278	0.505	29.28	2.44	71.4

Table III.10(λ)

Solution of Urea

No	Product	Weight loss (g)	Weight gain (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.xSwelling degree (g/l)
1	K-P-4HBA(3)	0.152	0.618	16.20	2.01	32.6
2	K-P-4HBA(5)	0.312	0.334	32.28	2.26	72.8

Table III.10(ฆ)

Solution of Urea

No	Product	Weight loss (g)	Weight gain (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-TCAA(/3)	0.254	0.564	26.92	2.45	66.00
2	K-P-TMAN(1/2)	0.209	0.548	22.11	2.11	46.4

where sol_w and sol_s represent the solubility in water and urea solution respectively . These values are presented in Table III.11. The average of these values is 0.474.

III.9 SORPTION FROM Cu(II) SOLUTION :

Since Cu (II) reacts with poly(vinyl alcohol), swelling studies would be complicated by the precipitation (sorption) of Cu(II) by alcohol ester. To simplify taking into consideration the amount of without Cu sorbed by the resin, we calculate as follows :

$$\text{Wt loss (uncorrected for Cu)} = W_{BS}\,(1-q) - W_{DS}$$

$$\text{Wt gain (due to water)} = W_{AS} - W_{DS} - \frac{qW_{DS}}{(1-q)}$$

$$\text{Solubility} = \frac{1000 \times \text{Wt loss}}{V_{BS} + \text{Wt gain}}$$

$$\text{Swelling degree} = \frac{\text{Wt gain}}{W_{DS}}$$

The Calculated values are presented in Table III.12-1.

We observe that solubility in Cu(II) solution is much lower than that in water or salt solution, whereas swelling degree in Cu(II) solution is comparable to that in salt solution.

Table III.11

Salting out from Urea solution

No	Product	Degree of Salting out		No	Product	Degree of Salting out	
	Z =	3	5			3	5
1	K-P-SBA(Z)	0.519	0.364	7	K-P-ADA(Z)	0.651	0.636
2	K-P-TPA(Z)	0.150	0.432	8	K-P-ANA(Z)	0.360	0.511
3	K-P-FMA(Z)	0.574	0.408	9	K-P-AAA(Z)	0.490	0.441
4	K-P-ACA(Z)	0.554	0.700	10	K-P-4ABA(Z)	0.512	0.266
5	K-P-SAA(Z)	0.688	0.563	11	K-P-4HBA(Z)	0.654	0.349
6	K-P-IPTA(Z)	0.473	0.493		Z =		1/3
				12	K-P-TCAA(Z)		0.114

Table III.12-1(a)

Cu (II) Solution

No	Product	Wt loss (uncorrected for (u)) (g)	Wt. gain due to water (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.x Swelling degree (g/1)
1	K-P-SBA(1)	0.109	1.898	4.72	6.54	30.89
2	K-P-SBA(2)	0.135	1.945	5.85	7.48	43.76
3	K-P-SBA(3)	0.104	1.183	4.37	3.88	16.95
4	K-P-SBA(5)	0.073	0.576	2.99	1.83	5.47
5	K-P-SBA(10)	0.099	0.152	3.98	0.47	11.86

Table III.12-1(b)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/l)	Swelling degree (g/g)	Sol. x Swelling degree (g/l)
1	K-P-TPA(1)	0.279	0.586	11.43	3.55	40.59
2	K-P-TPA(2)	0.200	0.843	8.28	3.75	31.02
3	K-P-TPA(3)	0.175	0.969	7. 28	3.73	27.13
4	K-P-TPA(5)	0.150	0.872	6.22	3.11	19.37
5	K-P-TPA(10)	0.150	0.314	6.08	1.06	6.47

Table III.12-1(c)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.x Swelling degree (g/l)
1	K-P-FMA(1)	0.137	0.507	5.59	1.55	8.64
2	K-P-FMA(2)	0.180	0.909	7.47	3.13	23.41
3	K-P-FMA(3)	0.085	0.894	3.53	2.67	9.42
4	K-P-FMA(5)	0.105	0.629	4.31	1.91	8.22
5	K-P-FMA(10)	0.105	0.564	4.30	1.59	6.83

Table III.12-1(d)

Cu(II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.x Swelling degree (g/l)
1	K-P-ACA(1)	0.322	0.794	13.30	4.54	60.34
2	K-P-ACA(2)	0.230	0.870	9.53	3.41	32.50
3	K-P-ACA(3)	0.125	0.584	5.12	1.60	8.19
4	K-P-ACA(5)	0.120	1.370	5.08	3.81	19.35
5	K-P-ACA(10)	0.085	0.271	3.44	0.695	2.39

Table III.12-1(e)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/l)	Swelling degree (g/g)	Sol. x Swelling degree (g/l)
1	K-P-SAA(1)	0.215	1.174	9.02	4.34	39.22
2	K-P-SAA(2)	0.195	1.582	8.33	5.36	44.65
3	K-P-SAA(3)	0.245	1.323	10.35	5.40	55.89
4	K-P-SAA(5)	0.195	0.641	8.00	2.21	17.68
5	K-P-SAA(10)	0.190	0.422	7.73	1.38	10.70

Table III.12-1(f)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.x Swelling degree (g/l)
1	K-P-IPTA(1)	0.238	0.435	9.69	2.12	20.56
2	K-P-IPTA(2)	0.168	1.686	7.21	6.61	47.67
3	K-P-IPTA(3)	0.085	1.280	3.58	3.66	13.09
4	K-P-IPTA(5)	0.068	0.708	2.80	1.94	5.43
5	K-P-IPTA(10)	0.043	0.840	1.78	2.21	3.93

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Table III.12-1(g)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.xSwelling degree (g/1)
1	K-P-ADA(1)	0.220	0.640	9.03	2.84	25.69
2	K-P-ADA(2)	0.238	0.514	9.72	2.51	24.40
3	K-P-ADA(3)	0.173	0.919	7.18	3.22	23.15
4	K-P-ADA(5)	0.153	0.746	6.31	2.71	17.12
5	K-P-ADA(10)	0.158	0.691	6.50	2.38	15.49

Table III.12-1(h)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.x Swelling degree (g/l)
1	K-P-ANA(1)	0.285	0.552	11.66	2.33	53.01
2	K-P-ANA(2)	0.245	0.473	9.99	1.97	19.69
3	K-P-ANA(3)	0.228	0.995	9.50	3.95	27.51
4	K-P-ANA(5)	0.230	0.702	9.47	2.75	26.07
5	K-P-ANA(10)	0.215	0.738	8.36	2.73	22.85

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Table III.12-1(j)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.x Swelling degree (g/l)
1	K-P-AAA(1)	0.207	0.769	8.54	2.90	24.78
2	K-P-AAA(2)	0.170	0.608	6.97	2.06	14.37
3	K-P-AAA(3)	0.260	0.459	10.59	2.19	23.15
4	K-P-AAA(5)	0.165	0.547	6.75	1.74	11.72
5	K-P-AAA(10)	0.155	0.663	6.37	1.98	12.61

Table III.12-1(k)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/1)	Swelling degree (g/g)	Sol. x Swelling degree (g/1)
1	K-P-4ABA(1)	0.230	0.470	9.38	1.81	16.96
2	K-P-4ABA(2)	0.240	0.810	9.92	3.24	32.14
3	K-P-4ABA(3)	0.265	1.554	11.30	7.23	81.68
4	K-P-4ABA(5)	0.230	0.885	9.54	3.47	33.11
5	K-P-4ABA(10)	0.215	0.550	8.79	2.04	17.91

Table III.12-1(1)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to (g)	Solubility (g/1)	Swelling degree (g/g)	Sol.x Swelling degree (g/1)
1	K-P-4HBA(1)	0.265	0.461	10.80	2.43	26.20
2	K-P-4HBA(2)	0.288	0.334	11.84	2.00	23.68
3	K-P-4HBA(3)	0.195	0.480	7.95	1.81	14.40
4	K-P-4HBA(5)	0.215	0.439	8.75	1.79	15.68
5	K-P-4HBA(10)	0.203	0.462	8.27	1.76	14.58

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Table III.12-1(m)

Cu (II) Solution

No	Product	Wt loss (uncorrected for Cu) (g)	Wt gain due to water (g)	Solubility (g/l)	Swelling degree (g/g)	Sol.x Swelling degree (g/l)
1	K-P-TCAA(1/3)	0.374	0.516	15.28	4.69	71.68
2	K-P-TMAN(112)	0.324	1.072	13.54	7.39	100.10

III.10 SOLUBILITY :

We present the solubility of these resins in water, salt solution Urea solution and Cu(II) solution in Table III.13. We generally observe that solubility in different solutions decrease in order

water solution > urea solution > salt solution > Cu(II) solution

We can explain the lower solubility in salt solution as follows : In case of polymer, its hydroxyl groups would have the solubilizing effect. Water molecules diffuse through the polymer and as they approach hydroxyl groups, interactions between them would takes place, increased interactions would increase mobility of the chains and weaken their inter and intra links and cause solubilization of the resin. In the case of salt solution, salt ions are sorbed by water. Hence insted of simple water molecules we now have water molecules associated with ions. As these diffuse through the polymer and approach the hydroxyl groups, we would suggest that effective concentration of water molecules close to the hydroxyl groups would be much less. Hence the solubility would decrease. Similarly, in case of Cu(II) solutions, Cu(II) ions would interact with hydroxyl groups of the polymer and insolubilize them. Hence the solubility would be further reduced in Cu(II) solution. Degree of salting out due to Cu(II) can be calculated as follows :

Table III.13(a)

No.	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II) Solution
1	K-P-SBA(1)	19.86	10.56	-	4.72
2	K-P-SBA(2)	23.74	13.60	-	5.85
3	K-P-SBA(3)	44.42	12.54	21.38	4.37
4	K-P-SBA(5)	9.52	7.59	6.05	2.99
5	K-P-SBA(10)	10.06	10.93	-	3.98

Table III.13(b)

No.	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-TPA(1)	50.74	24.19	-	11.43
2	K-P-TPA(2)	44.46	17.11	-	8.28
3	K-P-TPA(3)	41.75	20.72	35.47	7.28
4	K-P-TPA(5)	47.84	21.65	27.19	6.22
5	K-P-TPA(10)	43.71	14.61	-	6.08

Table III.13(c)

No.	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1.	K-P-FMA(1)	37.12	20.09	-	5.59
2	K-P-FMA(2)	45.41	20.57	-	7.47
3	K-P-FMA(3)	29.68	18.87	12.63	3.53
4	K-P-FMA(5)	31.91	16.00	18.88	4.31
5	K-P-FMA(10)	38.84	15.58	-	4.30

Table III.13(d)

No	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II) Solution
1	K-P-ACA(1)	56.67	31.68	–	13.30
2	K-P-ACA(2)	56.63	27.43	–	9.53
3	K-P-ACA(3)	55.57	25.63	24.76	5.12
4	K-P-ACA(5)	53.93	24.03	16.17	5.08
5	K-P-ACA(10)	51.28	18.31	–	3.44

Table III.13(e)

No	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-SAA(1)	44.26	25.96	-	9.02
2	K-P-SAA(2)	59.33	25.09	-	8.33
3	K-P-SAA(3)	55.70	20.08	17.36	10.35
4	K-P-SAA(5)	47.37	14.55	20.70	8.00
5	K-P-SAA(10)	39.70	21.70	-	7.73

Table III.13(f)

No	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II) Solution
1	K-P-IPTA(1)	39.07	20.49	-	9.69
2	K-P-IPTA(2)	31.38	16.76	-	7.21
3	K-P-IPTA(3)	32.62	12.76	17.19	3.58
4	K-P-IPTA(5)	31.38	10.41	15.92	2.80
5	K-P-IPTA(10)	26.77	13.96	–	1.78

Table III.13(9)

No	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-ADA(1)	44.07	29.69	-	9.03
2	K-P-ADA(2)	46.04	23.77	-	9.72
3	K-P-ADA(3)	53.36	20.69	18.61	7.18
4	K-P-ADA(5)	47.86	20.24	17.41	6.31
5	K-P-ADA(10)	35.08	17.46	-	6.50

Table III.13(b)

No	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-ANA(1)	36.73	27.81	–	11.66
2	K-P-ANA(2)	40.96	24.14	–	9.99
3	K-P-ANA(3)	39.87	23.21	25.53	9.50
4	K-P-ANA(5)	38.03	17.19	18.61	9.47
5	K-P-ANA(10)	37.75	18.03	–	8.36

Table III.13(j)

No	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II) Solution
1	K-P-AAA(1)	62.45	23.55	-	8.54
2	K-P-AAA(2)	48.24	23.72	-	6.97
3	K-P-AAA(3)	50.56	25.87	25.79	10.59
4	K-P-AAA(5)	40.77	21.33	22.80	6.75
5	K-P-AAA(10)	43.09	20.85	-	6.37

Table III.13(K)

No	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-4ABA(1)	37.65	17.09	–	9.38
2	K-P-4ABA(2)	42.80	26.10	–	9.92
3	K-P-4ABA(3)	37.23	23.20	18.17	11.30
4	K-P-4ABA(5)	39.88	23.61	29.28	9.54
5	K-P-4ABA(10)	33.85	19.32	–	8.79

Table III.13(1)

No	Product	Solubility of resin (g/1) in			
		Water	Salt Solution	Urea Solution	Cu(II) Solution
1	K-P-4HBA(1)	42.38	26.16	–	10.80
2	K-P-4HBA(2)	44.86	24.63	–	11.84
3	K-P-4HBA(3)	46.84	23.88	16.20	7.95
4	K-P-4HBA(5)	49.57	30.78	32.28	8.75
5	K-P-4HBA(10)	46.71	20.91	–	8.27

Table III.13(m)

No	Product	Solubility of resin (g/l) in			
		Water	Salt Solution	Urea Solution	Cu(II) Solution
1	K-P-TCAA(1/3)	30.38	29.29	26.92	15.28
2	K.P.TMAN(1/2)	21.95	19.76	22.11	13.54

$$DSO\ (Cu)_c = \frac{sol_s - sol_{Cu}}{sol_s}$$

The results are presented in Table III.13.1 . The values indicate that in general degree of salting out due to Cu(II) is comparable to that due to salt and hence degree of salting out from Cu(II) would be nearly twice the degree of salting out from salt solution.

III.11 VOLUME SWELLING :

From the determination of the density of the product before sorption and after sorption (D_{BS} and D_{AS} respectively) we calculate volume swelling per unit mass and volume swelling per unit volume as follows :

$$\text{Sp vol of the resin before sorption (ml/g)} = \frac{1}{D_{BS}}$$

$$\text{Sp vol of the resin after sorption (ml/g)} = \frac{1}{D_{AS}}$$

$$\text{Vol swelling (ml/g) (uncorrected for sol)} = \frac{1}{D_{AS}} - \frac{1}{D_{BS}}$$

$$\text{Vol swelling(ml/ml)} = \frac{\frac{1}{D_{AS}} - \frac{1}{D_{BS}}}{\frac{1}{D_{BS}}}$$

The calculated values are presented in Table III.14.

Table III.13-1

Salting out due to Cu(II) Solution

No.	Product	Degree of Salting out of resin				
	Z =	1	2	3	5	10
1	K-P-SBA(Z)	0.553	0.569	0.652	0.606	0.636
2	K-P-TPA(Z)	0.527	0.516	0.649	0.713	0.584
3	K-P-FMA(Z)	0.722	0.637	0.812	0.731	0.724
4	K-P-ACA(Z)	0.580	0.652	0.800	0.789	0.812
5	K-P-SAA(Z)	0.653	0.668	0.485	0.450	0.644
6	K-P-IPTA(Z)	0.527	0.569	0.719	0.731	0.872

Table III.13-1(contd.)

No.	Product	Degree of Salting out of resin				
		Z = 1	2	3	5	10
7	K-P-ADA(Z)	0.696	0.591	0.653	0.688	0.628
8	K-P-ANA(Z)	0.581	0.586	0.591	0.449	0.536
9	K-P-AAA(Z)	0.637	0.706	0.590	0.684	0.694
10	K-P-4ABA(Z)	0.451	0.620	0.513	0.596	0.545
11	K-P-4ABA(Z)	0.587	0.519	0.667	0.716	0.604
		Z = 1/3	1/2			
12	K-P-TCAA(Z)	0.478				
13	K-P-TMAN(Z)		0.315			

Table III.14(a)

No.	Product	Sp.Volume of resin (ml/g)	Sp.Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol.Swelling (per ml) (ml/ml)
1	K-P-SBA(1)	0.90	8.55	7.65	8.50
2	K-P-SBA(2)	0.95	6.33	5.38	5.66
3	K-P-SBA(3)	0.85	5.50	4.65	5.47
4	K-P-SBA(5)	1.05	7.30	6.25	5.95
5	K-P-SBA(10)	0.85	7.42	6.57	7.73

Table III.14(b)

No.	Product	Sp. Volume of resin (ml/g)	Sp. Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol. Swelling (per ml) (ml/ml)
1	K-P-TPA(1)	0.87	12.02	11.15	12.82
2	K-P-TPA(2)	1.05	12.15	11.10	10.57
3	K-P-TPA(3)	0.85	10.90	10.05	11.82
4	K-P-TPA(5)	0.90	10.07	9.80	10.19
5	K-P-TPA(10)	1.05	13.60	12.55	11.95

Table III.14(c)

No.	Product	Sp. Volume of resin (ml/g)	Sp. Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol. Swelling (per ml) (ml/ml)
1	K-P-FMA(1)	1.07	9.50	8.43	7.88
2	K-P-FMA(2)	0.85	5.53	4.68	5.51
3	K-P-FMA(3)	0.85	6.35	5.50	6.47
4	K-P-FMA(5)	0.93	9.30	8.30	9.00
5	K-P-FMA(10)	1.10	8.40	7.30	6.64

Table III.14(d)

No.	Product	Sp. Volume of resin (ml/g)	Sp. Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol.Swelling (per ml) (ml/ml)
1	K-P-ACA(1)	0.90	8.40	7.50	8.33
2	K-P-ACA(2)	1.20	5.85	4.65	3.88
3	K-P-ACA(3)	1.08	7.15	6.07	5.62
4	K-P-ACA(5)	0.90	7.00	6.10	6.78
5	K-P-ACA(10)	0.85	9.10	8.25	9.71

Table III.14(e)

No.	Product	Sp. Volume of resin (ml/g)	Sp. Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol. Swelling (per ml) (ml/ml)
1	K-P-SAA(1)	0.87	10.50	9.63	11.07
2	K-P-SAA(2)	1.13	7.88	6.75	5.97
3	K-P-SAA(3)	0.85	6.80	5.95	7.00
4	K-P-SAA(5)	0.83	6.90	6.07	7.31
5	K-P-SAA(10)	1.05	7.10	6.05	5.76

Table III.14(f)

No.	Product	Sp.Volume of resin (ml/g)	Sp.Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol.Swelling (per ml) (ml/ml)
1	K-P-IPTA(1)	1.10	9.85	8.75	7.95
2	K-P-IPTA(2)	0.95	7.20	6.25	6.58
3	K-P-IPTA(3)	1.05	11.05	10.00	9.52
4	K-P-IPTA(5)	0.85	11.50	10.65	12.53
5	K-P-IPTA(10)	1.13	12.20	11.07	9.80

Table III.14(9)

No.	Product	Sp.Volume of resin (ml/g)	Sp. Volume of resin after 24 hrs. (ml/g)	Volume Sweeling (per g) (ml/g)	Vol.Swelling (per ml) (ml/ml)
1	K-P-ADA(1)	1.20	10.03	8.83	7.36
2	K-P-ADA(2)	0.85	8.55	7.70	9.06
3	K-P-ADA(3)	1.08	9.20	8.12	7.52
4	K-P-ADA(5)	0.83	11.65	10.82	13.04
5	K-P-ADA(10)	1.20	9.95	8.75	7.29

Table III.14(h)

No.	Product	Sp. Volume of resin (ml/g)	Sp. Volume of resin after 24hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol.Swelling (per ml) (ml/ml)
1	K-P-ANA(1)	1.15	10.38	9.23	8.03
2	K-P-ANA(2)	0.85	7.30	6.45	7.59
3	K-P-ANA(3)	0.85	9.95	9.10	10.71
4	K-P-ANA(5)	0.65	10.95	10.30	15.85
5	K-P-ANA(10)	1.05	10.83	9.78	9.31

Table III.14(j)

No.	Product	Sp. Volume of resin (ml/g)	Sp. Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Volume Swelling (per ml) (ml/ml)
1	K-P-AAA(1)	0.97	9.72	8.75	9.02
2	K.P.AAA(2)	0.85	9.50	8.65	10.18
3	K-P-AAA(3)	1.15	11.18	10.03	8.72
4	K-P-AAA(5)	1.15	12.75	11.60	10.09
5	K-P-AAA(10)	0.85	10.10	9.25	10.88

Table III.14(k)

No.	Product	Sp.Volume of resin (ml/g)	Sp.Volume of resin after 24hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol.Swelling (per ml) (ml/ml)
1	K-P-4ABA(1)	0.82	13.25	12.43	15.16
2	K-P-4ABA(2)	1.10	9.20	8.10	7.36
3	K-P-4ABA(3)	0.88	9.38	8.50	9.66
4	K-P-4ABA(5)	0.80	14.00	13.20	16.50
5	K-P-4ABA(10)	0.80	15.40	14.60	18.25

Table III.14(1)

No.	Product	Sp.Volume of resin (ml/g)	Sp. Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol.Swelling (per ml) (ml/ml)
1	K-P-4HBA(1)	0.87	11.07	10.20	11.72
2	K-P-4HBA(2)	0.95	13.00	12.05	12.68
3	K-P-4HBA(3)	1.15	12.13	10.98	9.55
4	K-P-4HBA(5)	0.80	12.30	11.50	14.38
5	K-P-4HBA(10)	1.15	12.25	11.10	9.65

Table III.14(m)

No.	Product	Sp.Volume of resin (ml/g)	Sp. Volume of resin after 24 hrs. (ml/g)	Volume Swelling (per g) (ml/g)	Vol.Swelling (per ml) (ml/ml)
1	K-P-TCAA(1/3)	0.89	3.60	2.71	3.04
2	K-P-TMAN(1/2)	1.10	5.85	4.75	4.32

The values of volume swelling (ml/ml) lie between 3.04 and18.25. Thus in some cases the volume increase may be as high as 18 times its original value. Such large increase in volume on sorption can be used for various technical applications.

III.12 AREA SWELLING AND LONGITUDINAL SWELLING :

From the determination of the area of a square piece of the resin before sorption and after sorption we have calculated area swelling per unit area. The values are presented in Table III.15.

We have also calculated increase in length per unit length and increase in breadth per unit breadth. From the knowledge of the volume swelling and area swelling we also calculate increase in height per unit height (uncorrected for solubility). All these values are also presented in table III.15.

We find that values of area swelling lie between 0.24 and 2.33.

Longitudinal swelling (LS) has been recorded in relation to length (LS_l), breadth (LS_b) and height (LS_h). We observe that the values of LS_l are comparable to those of LS_b and much lower than those of LS_h. This can be related to the same rate of swelling in all directions and to the fact that length of the piece was comparable to its

Table III.15(a)

No.	Product	Area of resin piece in presence of water: Immediately l x b (mm^2)	Area of resin piece in presence of water: After 24hrs l x b (mm^2)	Area swelling per unit area (mm^2/mm^2)	Increase in: Length per unit length (mm/mm)	Increase in: Breadth per unit breadth (mm/mm)	Height per unit height (mm/mm)
1	K-P-SBA(1)	7.50	15.55	1.07	0.36	0.53	3.59
2	K-P-SBA(2)	5.50	14.33	1.61	0.59	0.64	1.55
3	K-P-SBA(3)	8.10	24.10	1.97	0.67	0.78	1.18
4	K-P-SBA(5)	5.67	16.96	1.99	0.80	0.66	1.32
5	K-P-SBA(10)	6.25	16.24	1.60	0.64	0.58	2.36

Table III.15(b)

No.	Product	Area of resin piece in presence of water: Immediately l x b (mm^2)	Area of resin piece in presence of water: After 24hrs l x b (mm^2)	Area Swelling per unit area (mm^2/mm^2)	Increase in Length per unit length (mm/mm)	Increase in Breadth per unit breadth (mm/mm)	Height per unit height (mm/mm)
1	K-P-TPA(1)	4.80	8.38	0.75	0.31	0.33	6.89
2	K-P-TPA(2)	5.25	12.00	1.29	0.38	0.66	4.05
3	K-P-TPA(3)	4.95	11.20	1.29	0.74	0.30	4.67
4	K-P-TPA(5)	5.09	16.95	2.33	0.53	1.18	2.36
5	K-P-TPA(10)	4.05	9.63	1.38	0.52	0.56	4.44

Table III.15(c)

No.	Product	Area of resin piece in presence of water		Area Swelling per unit area	Increase in		Height per unit height
		Immediately 1 x b (mm^2)	After 24hrs 1 x b (mm^2)	(mm^2/mm^2)	Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	(mm/mm)
1	K-P-FMA(1)	9.30	11.76	0.26	0.13	0.12	6.05
2	K-P-FMA(2)	7.01	19.40	1.76	0.61	0.72	1.36
3	K-P-FMA(3)	4.73	14.14	1.99	0.73	0.73	1.49
4	K-P-FMA(5)	6.09	13.17	1.16	0.36	0.59	3.63
5	K-P-FMA(10)	10.26	20.88	1.04	0.47	0.38	2.75

Table III.15(d)

No.	Product	Area of resin piece in presence of water: Immediately l x b (mm^2)	Area of resin piece in presence of water: After 24hrs l x b (mm^2)	Area Swelling per unit area (mm^2/mm^2)	Increase in Length per unit length (mm/mm)	Increase in Breadth per unit breadth (mm/mm)	Height per unit height 2 (mm/mm)
1	K-P-ACA(1)	5.61	7.72	0.38	0.18	0.17	5.76
2	K-P-ACA(2)	5.59	9.29	0.66	0.24	0.35	1.94
3	K-P-ACA(3)	6.49	21.05	2.24	0.95	0.67	1.04
4	K-P-ACA(5)	6.08	14.35	1.36	0.56	0.51	2.30
5	K-P-ACA(10)	6.96	16.85	1.42	0.51	0.61	3.43

Table III.15(e)

No.	Product	Area of resin piece in presence of water		Area Swelling per unit area	Increase in		Height per unit height
		Immediately 1 x b (mm^2)	After 24hrs 1 x b (mm^2)	(mm^2/mm^2)	Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	(mm/mm)
1	K-P-SAA(1)	6.85	9.18	0.34	0.12	0.20	8.01
2	K-P-SAA(2)	8.69	27.40	2.15	1.01	0.56	1.21
3	K-P-SAA(3)	6.91	19.95	1.89	0.87	0.54	1.77
4	K-P-SAA(5)	6.63	17.11	1.58	0.79	0.44	2.22
5	K-P-SAA(10)	6.98	17.79	1.55	0.52	0.57	1.65

Table III.15(f)

No.	Product	Area of resin piece in presence of water: Immediately l x b (mm^2)	After 24hrs l x b (mm^2)	Area Swelling per unit area (mm^2/mm^2)	Increase in: Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	Height per unit height (mm/mm)
1	K-P-IPTA(1)	5.88	12.10	1.06	0.48	0.39	3.34
2	K-P-IPTA(2)	7.92	15.05	0.90	0.41	0.35	2.99
3	K-P-IPTA(3)	5.40	10.54	0.95	0.41	0.38	4.39
4	K-P-IPTA(5)	8.61	17.26	1.00	0.36	0.47	5.77
5	K-P-IPTA(10)	6.08	13.69	1.25	0.50	0.50	3.80

Table III.15(9)

No.	Product	Area of resin piece in presence of water		Area Swelling per unit area	Increase in		Height per unit height
		Immediately l x b (mm^2)	After 24hrs l x b (mm^2)	(mm^2/mm^2)	Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	(mm/mm)
1	K-P-ADA(1)	4.62	7.90	0.71	0.35	0.26	3.89
2	K-P-ADA(2)	5.75	12.47	1.17	0.48	0.47	3.64
3	K-P-ADA(3)	6.45	12.88	1.00	0.52	0.31	3.26
4	K-P-ADA(5)	7.02	14.35	1.04	0.43	0.43	5.88
5	K-P-ADA(10)	7.73	15.79	1.04	0.46	0.39	3.06

Table III.15(h)

No.	Product	Area of resin piece in presence of water: Immediately l x b (mm^2)	After 24hrs l x b (mm^2)	Area Swelling per unit area (mm^2/mm^2)	Increase in: Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	Height per unit height (mm/mm)
1	K-P-ANA(1)	5.15	13.57	1.63	0.59	0.66	2.43
2	K-P-ANA(2)	5.68	17.30	2.05	0.49	1.04	1.82
3	K-P-ANA(3)	9.67	20.70	1.14	0.47	0.45	4.47
4	K-P-ANA(5)	6.97	14.44	1.07	0.43	0.45	7.14
5	K-P-ANA(10)	6.13	12.95	1.11	0.48	0.43	3.89

Table III.15 (j)

No.	Product	Area of resin piece in presence of water		Area Swelling per unit area	Increase in		Height per unit height
		Immediately l x b (mm^2)	After 24 hrs l x b (mm^2)	(mm^2/mm^2)	Length per unit length (mm/mm)	Bredth per unit breadth (mm/mm)	(mm/mm)
1	K-P-AAA(1)	7.73	17.64	1.28	0.52	0.50	3.39
2	K-P-AAA(2)	9.67	22.59	1.34	0.61	0.45	3.78
3	K-P-AAA(3)	6.89	16.20	1.35	0.52	0.55	3.14
4	K-P-AAA(5)	13.84	31.32	1.26	0.54	0.47	3.91
5	K-P-AAA(10)	6.08	14.69	1.42	0.58	0.53	3.91

Table III.15(k)

No.	Product	Area of resin piece in presence of water		Area Swelling per unit area	Increase in		Height per unit height
		Immediately l x b (mm^2)	After 24hrs l x b (mm^2)	(mm^2/mm^2)	Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	(mm/mm)
1	K-P-4ABA(1)	4.73	10.70	1.26	0.53	0.48	6.15
2	K-P-4ABA(2)	6.15	15.16	1.47	0.62	0.52	2.38
3	K-P-4ABA(3)	8.42	17.70	1.10	0.55	0.35	4.08
4	K-P-4ABA(5)	6.25	15.33	1.45	0.64	0.50	6.14
5	K-P-4ABA(10)	8.97	11.15	0.24	0.15	0.88	14.52

Table III.15(1)

No.	Product	Area of resin piece in presence of water		Area Swelling per unit area	Increase in		Height per unit height
		Immediately l x b (mm^2)	After 24hrs l x b (mm^2)	(mm^2/mm^2)	Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	(mm/mm)
1	K-P-4HBA(1)	4.84	7.37	0.52	o.24	0.23	7.37
2	K-P-4HBA(2)	6.13	7.87	0.28	0.14	0.12	9.69
3	K-P-4HBA(3)	4.62	6.68	0.45	0.20	0.20	6.28
4	K-P-4HBA(5)	5.88	8.32	0.41	0.17	0.21	9.91
5	K-P-4HBA(10)	8.43	10.62	0.26	0.11	0.13	7.45

Table III.15(m)

No.	Product	Area of resin piece in presence of water		Area Swelling per unit area	Increase in		Height per unit height
		Immediately l x b (mm^2)	After 24hrs l x b (mm^2)	(mm^2/mm^2)	Length per unit length (mm/mm)	Breadth per unit breadth (mm/mm)	(mm/mm)
1	K-P-TCAA(1/3)	5.52	7.63	0.38	0.20	0.15	1.93
2	K-P-TMAN(1/2)	4.62	6.63	0.44	0.20	0.19	2.69

Table III.16(a)

No.	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-SBA(1)	2.26	2.92	-	3.52
2	K-P-SBA(2)	4.62	3.25	-	3.55
3	K-P-SBA(3)	5.75	2.02	3.91	2.11
4	K-P-SBA(5)	2.13	1.12	1.37	0.96
5	K-P-SBA(10)	1.85	1.10	-	0.07

Table III.16(b)

No.	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-TPA(1)	3.06	0.03	-	0.54
2	K-P-TPA(2)	3.09	0.93	-	1.22
3	K-P-TPA(3)	3.60	0.92	3.85	1.58
4	K-P-TPA(5)	2.94	4.66	2.58	1.40
5	K-P-TPA(10)	3.16	1.63	-	0.29

Table III.16(c)

No.	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-FMA(1)	2.02	0.17	-	0.72
2	K-P-FMA(2)	3.99	1.12	[illegible]	1.44
3	K-P-FMA(3)	3.90	0.82	1.57	1.59
4	K-P-FMA(5)	3.67	1.16	2.84	1.02
5	K-P-FMA(10)	2.68	1.20	-	0.90

Table III.16(d)

No.	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-ACA(1)	3.02	0.21	-	0.94
2	K-P-ACA(2)	3.74	0.88	-	1.27
3	K-P-ACA(3)	3.33	1.34	3.04	0.91
4	K-P-ACA(5)	4.36	1.74	3.68	2.49
5	K-P-ACA(10)	4.02	0.96	-	0.36

Table III.16(e)

No.	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-SAA(1)	0.91	0.22	-	1.90
2	K-P-SAA(2)	3.75	2.01	-	2.77
3	K-P-SAA(3)	2.97	1.70	2.66	2.15
4	K-P-SAA(5)	2.19	1.16	1.26	0.88
5	K-P-SAA(10)	2.01	1.82	-	0.46

Table III.16(f)

No.	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-IPTA(1)	2.11	0.02	-	0.33
2	K-P-IPTA(2)	2.57	1.14	-	2.98
3	K-P-IPTA(3)	2.85	0.92	2.36	2.36
4	K-P-IPTA(5)	2.14	0.94	1.24	1.26
5	K-P-IPTA(10)	2.76	1.30	-	1.58

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Table III.16(g)

No.	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-ADA(1)	1.04	0.02	-	0.79
2	K-P-ADA(2)	1.34	0.30	-	0.49
3	K-P-ADA(3)	2.31	0.63	1.61	1.46
4	K-P-ADA(5)	2.50	0.68	1.10	1.14
5	K-P-ADA(10)	1.12	0.97	-	1.03

Table III.16(h)

No	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-ANA(1)	0.82	0.17		0.51
2	K-P-ANA(2)	1.99	0.47		0.44
3	K-P-ANA(3)	1.64	0.32	0.96	1.52
4	K-P-ANA(5)	2.02	0.94	1.29	0.93
5	K-P.ANA(10)	2.63	1.26		1.03

Table III.16(j)

No	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-AAA(1)	3.05	1.11		1.10
2	K-P-AAA(2)	1.17	0.98		0.85
3	K-P-AAA(3)	1.19	0.54	0.90	0.36
4	K-P-AAA(5)	1.56	0.83	0.98	0.75
5	K-P-AAA(10)	1.81	1.19		1.01

Table III.16(k)

No	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-4 ABA(1)	0.75	0.30		0.47
2	K-P-4 ABA(2)	1.52	0.58		1.13
3	K-P-4 ABA(3)	1.58	0.58	1.18	2.56
4	K-P-4 ABA(5)	1.00	0.74	0.45	1.30
5	K-P-4 ABA(10)	1.07	0.68		0.66

Table III.16(1)

No	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-4HBA(1)	0.57	0.10		0.34
2	K-P-4HBA(2)	0.88	0.24		0.04
3	K-P-4HBA(3)	0.80	0.24	0.96	0.54
4	K-P-4HBA(5)	0.65	0.06	0.02	0.41
5	K-P-4HBA(10)	1.00	0.44		0.49

Table III.16(m)

No	Product	Degree of Swelling $(W_{AS}-W_{BS})/W_{BS}$ of resin in			
		Water	Salt Solution	Urea Solution	Cu(II)Solution
1	K-P-TCAA(1/3)	0.73	0.44	0.62	0.26
2	K-P-TMAN(1/2)	0.55	0.47	0.68	1.45

Table III.17(a)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	CU(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-SBA(1)	3.78	5.07		6.54	1.07	8.50
2	K-P-SBA(2)	7.19	6.24		7.48	1.61	5.66
3	K-P-SBA(3)	9.36	3.84	8.90	3.88	1.97	5.47
4	K-P-SBA(5)	3.17	2.05	2.22	1.83	1.99	5.95
5	K-P-SBA(10)	2.54	2.08		0.47	1.60	7.73

Table III.17(b)

No	Product	Swelling degree (g/g) of resin in				Area Swelling (mm^2/mm^2)	Volume Swelling (ml/ml)
		Water	NaCl Solution	Urea Solution	Cu(II) Solution		
1	K-P-TPA(1)	6.29	1.39		3.55	0.75	12.82
2	K-P-TPA(2)	6.15	2.46		3.75	1.29	10.57
3	K-P-TPA(3)	6.33	2.83	0.15	3.73	1.29	11.82
4	K-P-TPA(5)	6.13	9.39	7.71	3.11	2.33	10.19
5	K-P-TPA(10)	5.75	3.08		1.06	1.38	11.95

Table III.17(c)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-FMA(1)	3.60	1.09		1.55	0.26	7.88
2	K-P-FMA(2)	6.36	2.73		3.13	1.76	5.51
3	K-P-FMA(3)	6.17	2.56	2.94	2.67	1.99	6.47
4	K-P-FMA(5)	5.76	2.61	5.72	1.91	1.61	9.00
5	K-P-FMA(10)	4.59	2.40		1.59	1.04	6.64

Table III.17(d)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-ACA(1)	5.48	2.09		4.54	0.38	8.33
2	K-P-ACA(2)	6.43	3.06		3.41	0.66	3.88
3	K-P-ACA(3)	5.87	3.53	6.04	1.60	2.24	5.62
4	K-P-ACA(5)	6.93	4.11	5.60	3.81	1.36	6.78
5	K-P-ACA(10)	6.56	2.17		0.69	1.42	9.71

Table III.17(e)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-SAA(1)	2.20	1.57		4.34	0.34	11.07
2	K-P-SAA(2)	6.57	4.56		5.36	2.15	5.97
3	K-P-SAA(3)	5.80	3.34	4.32	5.40	1.89	7.00
4	K-P-SAA(5)	4.13	2.05	2.78	2.21	1.58	7.31
5	K-P-SAA(10)	3.38	3.67		1.38	1.55	5.76

Table III.17(f)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-IPTA(1)	4.22	1.40		2.12	1.06	7.95
2	K-P-IPTA(2)	4.57	2.80		6.61	0.90	6.58
3	K-P-IPTA(3)	4.81	1.89	4.65	3.66	0.95	9.52
4	K-P-IPTA(5)	3.85	1.75	2.68	1.94	1.00	12.53
5	K-P-IPTA(10)	4.53	2.70		2.21	1.25	9.80

Table III.17(g)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-ADA(1)	3.07	2.10		2.84	0.71	7.36
2	K-P-ADA(2)	3.46	1.90		2.51	1.17	9.06
3	K-P-ADA(3)	5.18	2.02	3.36	3.22	1.00	7.52
4	K-P-ADA(5)	5.63	2.38	2.61	2.71	1.04	13.04
5	K-P-ADA(10)	2.44	2.34		2.38	1.04	7.29

Table III.17(h)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-SBA(1)	1.82	1.72		2.33	1.63	8.03
2	K-P-SBA(2)	3.53	1.85		1.97	2.05	7.59
3	K-P-SBA(3)	3.08	1.53	2.95	3.95	1.14	10.71
4	K-P-SBA(5)	3.42	1.96	2.59	2.75	1.07	15.85
5	K-P-SBA(10)	4.13	2.15		2.73	1.11	9.31

Table III.17(j)

No.	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-AAA(1)	6.49	3.08		2.90	1.28	9.02
2	K-P-AAA(2)	3.06	2.97		2.06	1.34	10.18
3	K-P-AAA(3)	3.16	2.36	3.01	2.19	1.35	8.72
4	K-P-AAA(5)	3.03	2.23	2.62	1.74	1.26	10.09
5	K-P-AAA(10)	3.36	2.66		1.98	1.42	10.88

Table III.17(k)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-4ABA(1)	1.79	1.33		1.81	1.26	15.16
2	K-P-4ABA(2)	2.96	2.22		3.24	1.47	7.36
3	K-P-4ABA(3)	2.87	1.99	2.41	7.23	1.10	9.66
4	K-P-4ABA(5)	2.16	2.28	2.44	3.47	1.45	16.50
5	K-P-4ABA(10)	2.03	1.75		2.04	0.24	18.25

Table III.17(1)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-4HBA(1)	1.86	1.63		2.43	0.52	11.72
2	K-P-4HBA(2)	2.51	1.73		2.00	0.28	12.68
3	K-P-4HBA(3)	2.44	1.61	2.01	1.81	0.45	9.55
4	K-P-4HBA(5)	2.34	1.66	2.26	1.79	0.41	14.38
5	K-P-4HBA(10)	2.71	1.65		1.76	0.26	9.65

Table III.17(m)

No	Product	Swelling degree (g/g) of resin in				Area Swelling	Volume Swelling
		Water	NaCl Solution	Urea Solution	Cu(II) Solution	(mm^2/mm^2)	(ml/ml)
1	K-P-TCAA(1/3)	3.26	2.59	2.45	4.69	0.38	3.04
2	K-P-TCAA(1/2)	1.84	1.56	2.11	7.39	0.44	4.32

dissolved portion is taken into consideration in determining wt swelling but not in determining volume swelling.

III.14 WATER SORPTION :

Water sorption studies were carried out to study the solubility and swelling of these partially soluble alcohol - esters. Usually water sorption is related to the hydroxyl groups (hydrophilic groups), ester groups (hydrophobic groups) and amorphous regions. Number of moles of water sorbed per hydrophilic group in a resin has been evaluated and presented in Table III.18. One would expect that the number of moles of water sorbed per hydrophilic group (hydroxyl group corrected for amino group) would be nearly one and be reduced by the hydrophobic group but much more increased by the amorphous regions. The results had us to believe that these results have amorphous regions to a greater extent .

Table III.18

Water gain per hydroxyl group

No.	Product	Water gain (mol. water per hydroxyl group)									
		from water					From salt solution				
	Z =	1	2	3	5	10	1	2	3	5	10
1	K-P-SBA(Z)	-	-	201.8	45.8	16.0	-	-	82.8	29.6	13.1
2	K-P-TPA(Z)	177.5	107.9	63.9	39.7	26.4	39.2	43.2	28.3	60.8	14.1
3	K-P-FMA(Z)	46.0	48.4	42.5	29.2	16.9	13.9	20.8	17.6	13.2	8.8
4	K-P-ACA(Z)	74.6	52.3	36.6	37.5	25.4	28.4	24.9	22.0	22.3	8.4
5	K-P-SAA(Z)	9.32	25.5	20.1	12.9	9.6	6.6	17.7	11.6	6.4	10.4

Contd...

Table III.18(contd.)

No	Product	Water gain (mol. water per hydroxyl group)									
		from water					from salt solution				
	Z=	1	2	3	5	10	1	2	3	5	10
6	K-P-IPTA(Z)	119.1	80.2	48.1	24.9	21.3	39.5	49.2	18.9	11.3	12.7
7	K-P-ADA(Z)	73.0	53.4	52.7	34.9	13.5	49.9	29.3	20.5	4.8	12.9
8	K-P-ANA(Z)	13.08	17.0	11.4	11.0	11.8	12.4	8.9	5.7	6.3	6.1
9	K-P-AAA(Z)		16.5	15.5	9.0	6.5		16.0	11.5	6.7	5.1
10	K-P-4ABA(Z)	12.0	11.9	10.6	6.9	0.2	8.9	8.9	7.4	7.3	5.0
11	K-P-4HBA(Z)	8.4	10.5	8.9	7.8	8.3	7.3	7.2	5.9	5.5	5.1