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Swelling of the Polyester-resins by Sorption with Reference to Water, NaCl, Cu(II) and Urea Solution as Swelling Agents

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Series of polyester-resins prepared by partially esterifying poly(vinyl alcohol) (PVA) with different acid chlorides, such as terephthalic (TPA), isophthalic (IPTA), salicylic (SAA) and *p*-hydroxybenzoic (Hb) acid chlorides. Swelling of these products in water, dilute solutions of NaCl, copper sulphate, *i.e.*, Cu(II) and urea have been studied. The solubilities (g/mL) and swelling degree (g/g) with reference to above solvents as swelling agents were calculated. Also the degree of salting out of the polyester-resin from NaCl and Cu(II) solutions was calculated. Increase in hydrophilic groups increases swellable sites and hence swellability of the products. It was observed that salt was not sorbed by the resin during the sorption process and the presence of salt lowers the degree of swelling and solubility of the polyester-resins.

Key Words: Polyvinyl alcohol, Terephthalic acid, Isophthalic acid, Salicylic acid and *p*-hydroxy benzoic acid, Copper sulphate.

INTRODUCTION

Poly(vinyl alcohol) (PVA) prepared from poly(vinyl ester) is available in various grades depending on its degree of hydrolysis and degree of polymerization[1]. Various polymers have been prepared from poly(vinyl alcohol) and studied for their solubility and swelling[2–7]. The process of forming, water-absorbing cross-linked polyacrylates, which are water insoluble, absorbs large quantities of aqueous fluid and exhibits a relative good stability. A process for the preparation of potentially biodegradable polyacrylates using functionalized PVA as a cross linking agent has been studied. As PVA is known to biodegrade[8–14], such structures will be biodegradable in principle, leading to low molecular weight polyacrylates, depending on the ratio of acrylic acid to functionalized PVA used. Its hydrogels have been studied as swollen elastic network and as water sorbents[15]. Such study can help in evaluating the utility of products in soil, lenses, lubricants, etc. Swelling studies were performed at room temperature using water, dilute solutions of NaCl (saline), Cu(II) and urea as swelling agents. The present experimental results were carried out on independent anions. When PVA is partially esterified with different mono and dibasic acids, the ester content increases, OH group content decreases, cross-

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linking gets introduced and hence relative changes in hydrophilic-hydrophobic groups and chain length affect solubility and swelling.

EXPERIMENTAL

A series of polyester-resins using different acid chlorides and varying proportion of PVA as 1 : 1, 1 : 2, 1 : 3, 1 : 5 and 1 : 10 (g/g) were prepared. PVA esters have been prepared by partial esterification of PVA (having degree of polymerization 1640 and degree of hydrolysis 97%) of Koch-Light make (England) using TPA, IPTA, SAA and Hb acid chlorides. The acid-chlorides were prepared by treating the acid with thionyl chloride in dimethyl formamide (DMF) in presence of pyridine. The completion of reactions was depending on the formation of polyesters. The progress of reaction was studied at constant concentration and at 150°C temperature and *p*-hydroxy benzoic acid reaction was carried out at 120°C temperature. We suggest the formulae (Table-1) in agreement with C and H analysis, ester content and water content of alcohol-ester molecular units.

TABLE-1
FORMULAE C and H ANALYSIS, WATER CONTENT AND ESTER CONTENT OF POLYESTER RESINS

No.	Product	Formula	Analysis							
			C (%)		H (%)		Water content (%)		Ester content (meq/g)	
			found	(reqd)	found	(reqd)	Found	(reqd)	Found	(reqd)
01	K-P-TPA(1)	$C_{6.5}H_8O_{3.5}$	55.80	56.52	6.32	5.80	12.0	14.2	8.0	7.9
02	K-P-TPA(2)	$C_7H_{10}O_4$	54.44	53.16	6.75	6.33	15.0	17.1	6.3	6.3
03	K-P-TPA(3)	$C_8H_{12}O_{4.5}$	53.20	53.33	7.68	6.67	13.0	15.0	5.6	5.6
04	K-P-TPA(5)	$C_{10}H_{17}O_6$	52.83	51.50	7.40	7.30	14.0	15.5	4.5	4.3
05	K-P-TPA(10)	$C_{14}H_{26}O_{8.5}$	51.10	50.91	7.76	7.88	11.0	13.6	2.9	3.0
06	K-P-IPTA(1)	$C_{6.5}H_8O_{3.25}$	56.38	56.52	5.90	5.80	12.5	14.2	8.0	7.9
07	K-P-IPTA(2)	$C_7H_{10}O_4$	52.85	53.16	6.20	6.33	15.5	17.1	6.4	6.3
08	K-P-IPTA(3)	$C_8H_{12}O_{4.5}$	51.55	53.33	6.76	6.77	13.0	15.0	5.6	5.6
09	K-P-IPTA(5)	$C_{10}H_{17}O_6$	50.80	51.50	7.58	7.30	13.5	15.4	4.6	4.3
10	K-P-IPTA(10)	$C_{14}H_{27}O_9$	50.05	49.56	8.10	7.96	15.5	15.9	2.9	3.0
11	K-P-SAA(1)	$C_{15}H_{21}O_{6.5}$	61.18	59.02	7.41	6.89	3.0	3.0	3.0	3.3
12	K-P-SAA(2)	$C_{17}H_{25}O_{7.5}$	60.20	58.43	7.75	7.17	2.0	2.6	2.6	2.9
13	K-P-SAA(3)	$C_{21}H_{33}O_{9.5}$	59.49	57.66	8.03	7.55	2.0	2.1	2.3	2.3
14	K-P-SAA(5)	$C_{29}H_{50}O_{14}$	58.14	55.95	8.24	8.04	3.0	2.9	1.5	1.6
15	K-P-SAA(10)	$C_{43}H_{77}O_{20.5}$	57.85	56.03	7.92	8.33	1.0	0.9	1.1	1.1
16	K-P-Hb(1)	$C_{15}H_{23}O_{7.5}$	56.35	55.73	7.72	7.12	9.0	8.4	3.0	3.1
17	K-P-Hb(2)	$C_{17}H_{28}O_9$	53.32	54.25	7.95	7.45	9.0	9.6	2.6	2.7
18	K-P-Hb(3)	$C_{21}H_{36}O_{11}$	52.42	54.31	8.26	7.76	8.0	7.8	2.1	2.2
19	K-P-Hb(5)	$C_{29}H_{54}O_{16}$	51.49	52.89	8.95	8.20	8.0	8.2	1.4	1.5
20	K-P-Hb(10)	$C_{41}H_{80}O_{23}$	50.44	52.34	8.76	8.51	7.0	7.7	1.1	1.1

Theoretical values of above products, calculated by using our suggested formulae, and practical values of these products are compatible. This can be observed in Table-1; therefore, suggested formulae are correct. Amount of reactants used, yields, colour, softening temperature are presented in Table-2.

TABLE-2
AMOUNT OF REACTANTS USED, YIELD, COLOUR, SOFTENING TEMPERATURE OF THE PRODUCTS

No.	Product	Poly (vinyl alcohol) (mmol)	Acid chloride (mmol)	Yield (%)	Melting/ softening temp. (°C)	Colour
(a) Acid: Terephthalic, temp. of reaction: 150°C; Time of reaction 6 h						
1	KPTPA (1)	2.7	4.9	67	d*	black
2	KPTPA (2)	45.5	4.9	100	d	brown
3	KPTPA (3)	68.2	4.9	100	d	brown
4	KPTPA (5)	113.6	4.9	100	d	brown
5	KPTPA (10)	227.0	4.9	100	d	brown
(b) Acid: Isophtalic, temp. of reaction: 150°C; Time of reaction 6 h						
6	KPI PTA (1)	22.7	4.9	67	d	black
7	KPI PTA (2)	45.5	4.9	100	d	brown
8	KPI PTA (3)	68.2	4.9	100	d	brown
9	KPI PTA (5)	113.6	4.9	100	d	brown
10	KPI PTA (10)	227.0	4.9	100	d	brown
(c) Acid: Salicylic, temp. of reaction: 150°; Time of reaction 6 h						
11	KPSAA (1)	22.7	6.4	68	122	black
12	KPSAA (2)	45.5	6.4	100	141	brown
13	KPSAA (3)	68.2	6.4	100	167	brown
14	KPSAA (5)	113.6	6.4	85	181	pink
15	KPSAA (10)	227.0	6.4	85	188	brown
(d) Acid: p-hydroxy benzoic, temp. of reaction: 120°C; Time of reaction 2 h						
16	KPHb (1)	22.7	6.4	100	103	brown
17	KPHb (2)	45.5	6.4	100	110	brown
18	KPHb (3)	68.2	6.4	100	139	brown
19	KPHb (5)	113.6	6.4	100	151	brown
20	KPHb (10)	227.0	6.4	100	163	brown

*- Decomposition.

These products were studied for swelling and solubility in water and dilute solutions of sodium chloride, Cu(II) and urea solutions. The degradation of cross-linked polyester samples were investigated by determining their swelling behaviour in same solution at room temperature. These samples were cut into discs of 0.3 mm thickness using diamond blade and weighed to determine the dry weight. The disks were swollen in 20 mL of 10% saline, Cu(II) and urea solution at room temperature for 1 h. During the experiments the disks were weighed every 24 h until maximum degradation (*i.e.*, loss of weight). The solubility (g/mL) and the swelling degree (g/g) were studied in each solvent or swelling agent.

RESULTS AND DISCUSSION

The polymeric alcohol-esters in each series have varying proportions of alcohol and ester groups and hence can sorb water to varying extents[16, 17]. But as increasing esterification takes place, solubility in water decreases and polymer swells in water. The cross-linked K-P-TPA, K-P-IPTA, K-P-SAA and K-P-Hb samples containing PVA were prepared. PVA is known as potentially biodegradable in principle, leading to low molecular weight polyesters depending upon the ratio of acid chlorides to functionalized PVA used. From the knowledge of weight of alcohol-ester before sorption (W_{BS}), after sorption (W_{AS}) after drying it from the sorbed state (W_{DS}) and water content of the alcohol-ester (q), we can evaluate weight loss due to dissolution of the alcohol-ester (dry basis) in each swelling agent. Similarly, weight gain due to sorption of swelling agent by alcohol-ester (dry basis) can be evaluated. Hence the solubility (g/mL) of the alcohol-ester is evaluated as:

$$\text{Weight loss} = W_{BS} - W_{DS} - qW_{BS} \quad \text{(i)}$$

$$\text{Weight gain} = W_{AS} - W_{DS} - [qW_{DS}/(1 - q)] \quad \text{(ii)}$$

$$\text{Solubility (Sol)} = \frac{1000 \times \text{weight loss}}{V_{BS} - \text{weight gain}} \quad \text{(iii)}$$

where V_{BS} is the volume of the swelling agent used in the experiment and weight gain corresponds to the weight of the swelling agent taken up by the alcohol-ester in sorption. Similarly, swelling degree (g/g) of the alcohol-ester is evaluated as:

$$\text{Swelling degree (SD)} = \frac{\text{Weight gain}}{W_{DS}} \quad \text{(iv)}$$

The results obtained for solubility (g/mL) and swelling degree (g/g) of each swelling agent are presented in Tables 3 and 4. It has been observed that the values of DS and sol show gradation in each series in general. It is also observed that DS is in decreasing order for products as KPTPA > KPIPTA and KPTPA > KPSAA > KPHb and sol in decreasing order for the products as KPHb > KPTPA > KPIPTA. When 10% NaCl solution was used in place of water in the sorption process, an additional measurement was carried out by washing the dried sample and weighing it after drying the washed sample (W_{DW}). It was found that W_{DW} was same as W_{DS} indicating that salt was not sorbed by the sample during the sorption process. The exclusion of the salt by the product can be of technological importance. It is also observed that the presence of salt lowers DS and sol of the sample such decrease in DS has been observed earlier[18].

TABLE-3
SOLUBILITY (g/mL) OF THE RESIN IN DIFFERENT SWELLING AGENTS

No.	Product	Water	NaCl solution	Urea solution	Cu(II) solution
1	K-P-TPA (1)	0.0507	0.0242	—	0.0114
2	K-P-TPA (2)	0.0445	0.0171	—	0.0828
3	K-P-TPA (3)	0.0418	0.0207	0.0350	0.0773
4	K-P-TPA (5)	0.0478	0.0217	0.0272	0.0622
5	K-P-TPA (10)	0.0437	0.0146	0.0189	0.0608
6	K-P-IPTA (1)	0.0391	0.0205	—	0.0969
7	K-P-IPTA (2)	0.0314	0.0168	—	0.0721
8	K-P-IPTA (3)	0.0326	0.0128	0.0172	0.0358
9	K-P-IPTA (5)	0.0314	0.0104	0.0160	0.0280
10	K-P-IPTA (10)	0.0268	0.0140	0.0148	0.0178
11	K-P-SAA (1)	0.0443	0.0260	—	0.0902
12	K-P-SAA (2)	0.0593	0.0251	—	0.0833
13	K-P-SAA (3)	0.0557	0.0201	0.0176	0.0104
14	K-P-SAA (5)	0.0474	0.0146	0.0207	0.0800
15	K-P-SAA (10)	0.0397	0.0217	0.0221	0.0773
16	K-P-Hb (1)	0.0424	0.0261	—	0.0108
17	K-P-Hb (2)	0.0449	0.0246	—	0.0092
18	K-P-Hb (3)	0.0468	0.0239	0.0202	0.0080
19	K-P-Hb (5)	0.0496	0.0308	0.0025	0.0088
20	K-P-Hb (10)	0.0467	0.0209	0.0220	0.0000

It is observed that there is no weight gain due to salt uptake. It indicates the exclusion at the electrolyte by the resin in the sorption process. This type of exclusion is generally observed with various ion-exchange resins[19–23]. These resins concentrate dilute salt solutions. Degree of salting out at constant salt concentration $(DSO)_C$ can be suggested as

$$DSO_C = \frac{\text{Solubility in water} - \text{Solubility in salt}}{\text{Solubility in water}} \qquad \text{(v)}$$

It is observed in general that the values of DSO_C are close to 0.5 in most of the cases. It indicates that the effect is not related to number of hydroxyl groups.

Sorption studies of some of these resins from urea and Cu(II) solution have been made. It is assumed that there is weight gain due to urea uptake from urea column, as is observed in case of salt solution. We observed that the solubility in Cu(II) solution is much lower than that in salt solution. The solubility in different solutions in general was observed in decreased order.

Water > Urea solution > Salt solution > Cu(II) solution.

TABLE-4
SWELLING DEGREE (g/g) OF THE RESINS IN DIFFERENT SWELLING AGENTS

No.	Product	Water	NaCl solution	Urea solution	Cu(II) solution
1	K-P-TPA (1)	6.29	1.39	—	3.55
2	K-P-TPA (2)	6.15	2.46	—	3.75
3	K-P-TPA (3)	6.33	2.83	3.65	3.73
4	K-P-TPA (5)	6.13	2.39	3.10	3.11
5	K-P-TPA (10)	5.75	3.08	3.38	3.06
6	K-P-IPTA (1)	4.22	1.40	—	2.12
7	K-P-IPTA (2)	4.57	1.80	—	3.56
8	K-P-IPTA (3)	4.81	1.89	2.65	3.66
9	K-P-IPTA (5)	3.85	1.75	2.68	2.94
10	K-P-IPTA (10)	4.53	2.70	3.25	2.21
11	K-P-SAA (1)	2.20	1.57	—	3.34
12	K-P-SAA (2)	6.57	3.56	—	4.36
13	K-P-SAA (3)	5.80	3.34	2.74	4.40
14	K-P-SAA (5)	4.13	2.76	2.78	3.21
15	K-P-SAA (10)	3.38	3.67	3.80	2.38
16	K-P-Hb (1)	1.86	1.63	—	2.43
17	K-P-Hb (2)	2.51	1.73	—	2.16
18	K-P-Hb (3)	2.44	1.61	2.01	1.81
19	K-P-Hb (5)	2.34	1.66	2.26	1.79
20	K-P-Hb (10)	2.71	1.65	2.70	1.76

We can explain the lower solubility in salt solution as follows: In case of polymer, its hydroxyl groups would have a solublizing effect; water molecules diffuse through the polymer and as they approach hydroxyl groups, interaction between them would take place; increased interaction would increase mobility of the chains and weaken their inter- and intra-links and cause solubilization of polyester resin. In case of salt solution, salt ions are sorbed by water. Hence instead of simple water molecules, there are 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) solution, Cu(II) ions would interact with hydroxyl groups of polymer and insolubilize them. Hence the solubility would be further reduced in Cu(II) solution. Degree of salting out due to Cu(II) at constant concentration can be calculated as:

$$DSO(Cu)_C = \frac{\text{Solubility in salt solution} - \text{Solubility in copper solution}}{\text{Solubility in salt solution}} \quad \text{(vi)}$$

The values indicate that in general the salting out due to Cu(II) is comparable to that due to salt.

The values of degree of salting out of the resin in salt and Cu(II) are presented in

Table-5. We observed in general that the degree of salting out increases with increase in the number of hydroxyl groups (X) in the product.

For the purpose of comparing solubility with structural characteristics, molar solubility is calculated as

$$\text{Molar solubility (g-mol/mL)} = \frac{\text{Solubility (g/mL)}}{W_{F(a)}} \quad \text{(vii)}$$

where F(a) is formula weight of product.

TABLE-5
DEGREE OF SALTING OUT OF THE RESIN FROM NaCl AND Cu(II) SOLUTIONS

No.	Product	NaCl solution	Cu(II) solution
1	K-P-TPA (1)	0.523	0.527
2	K-P-TPA (2)	0.615	0.516
3	K-P-TPA (3)	0.504	0.649
4	K-P-TPA (5)	0.547	0.713
5	K-P-TPA (10)	0.666	0.584
6	K-P-IPTA (1)	0.476	0.527
7	K-P-IPTA (2)	0.466	0.469
8	K-P-IPTA (3)	0.609	0.719
9	K-P-IPTA (5)	0.668	0.731
10	K-P-IPTA (10)	0.479	0.872
11	K-P-SAA (1)	0.413	0.653
12	K-P-SAA (2)	0.577	0.668
13	K-P-SAA (3)	0.699	0.485
14	K-P-SAA (5)	0.693	0.450
15	K-P-SAA (10)	0.453	0.664
16	K-P-Hb (1)	0.383	0.589
17	K-P-Hb (2)	0.451	0.519
18	K-P-Hb (3)	0.490	0.667
19	K-P-Hb (5)	0.379	0.816
20	K-P-Hb (10)	0.552	0.604

The values are presented in Table-6 for each series of products. These values are plotted *vs.* the number of hydroxyl groups (X) in Fig. 1. It was observed that molar solubility decreases with increase in hydroxyl groups.

The values of swelling degree mole are calculated using the formula and are presented in Table-7.

$$\text{Swelling degree (mol) (g/g mol)} = \text{swelling degree (g/g)} \times W_{F(a)} \quad \text{(viii)}$$

The plots of swelling degree mole versus hydroxyl groups for each series of products are shown in Fig. 2. The values are plotted *vs.* number of hydroxyl groups (X). It was observed that these values are increasing with increase in X. This is in accordance with our conclusion that increase in hydrophilic groups would increase swellable sites and hence swellability of these products.

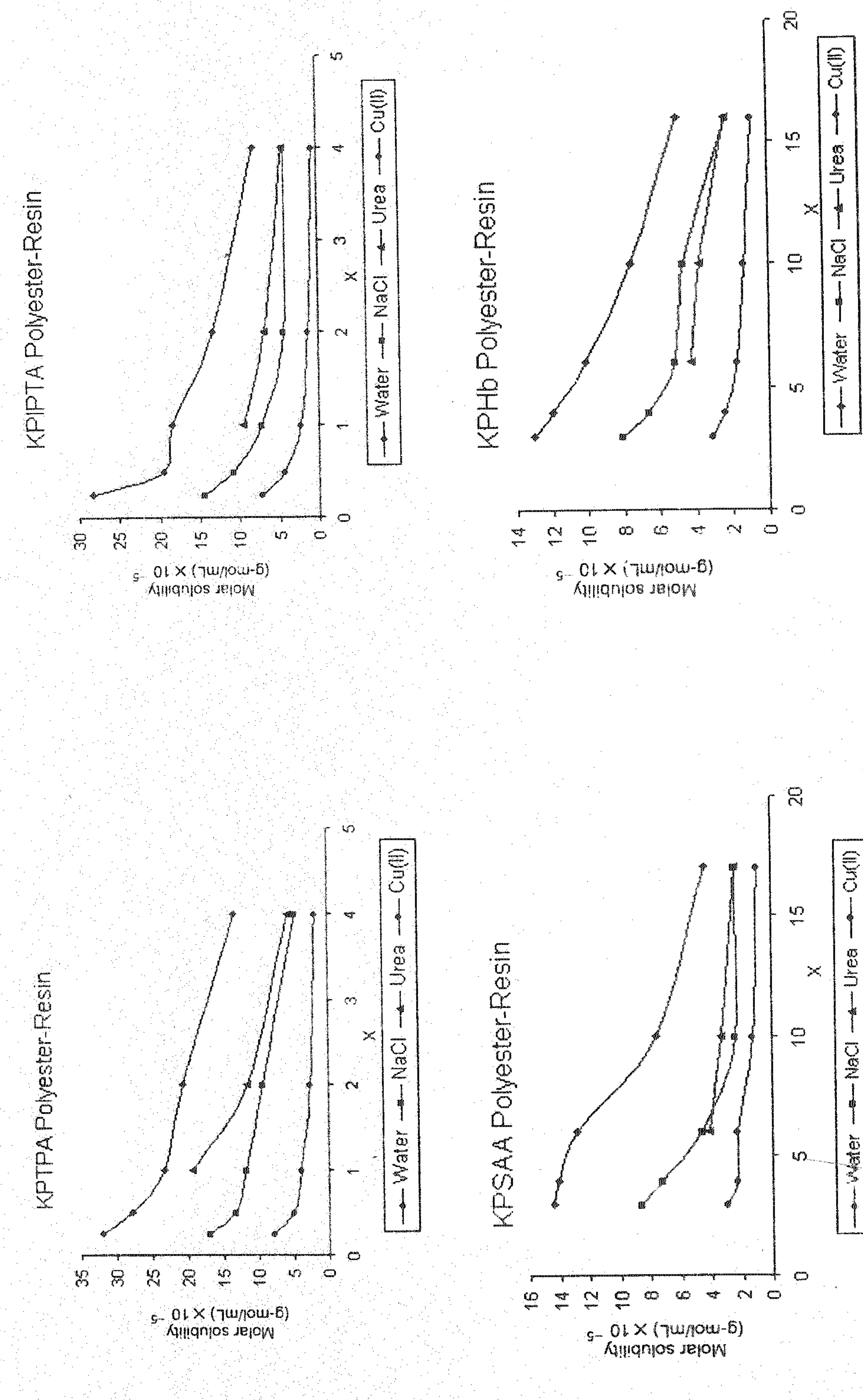
KPIPTA Polyester-Resin
KPTPA Polyester-Resin
KPHb Polyester-Resin
KPSAA Polyester-Resin
Molar solubility (g-mol/mL) × 10 -5
X
Water
NaCl
Urea
Cu(II)

Fig. 1

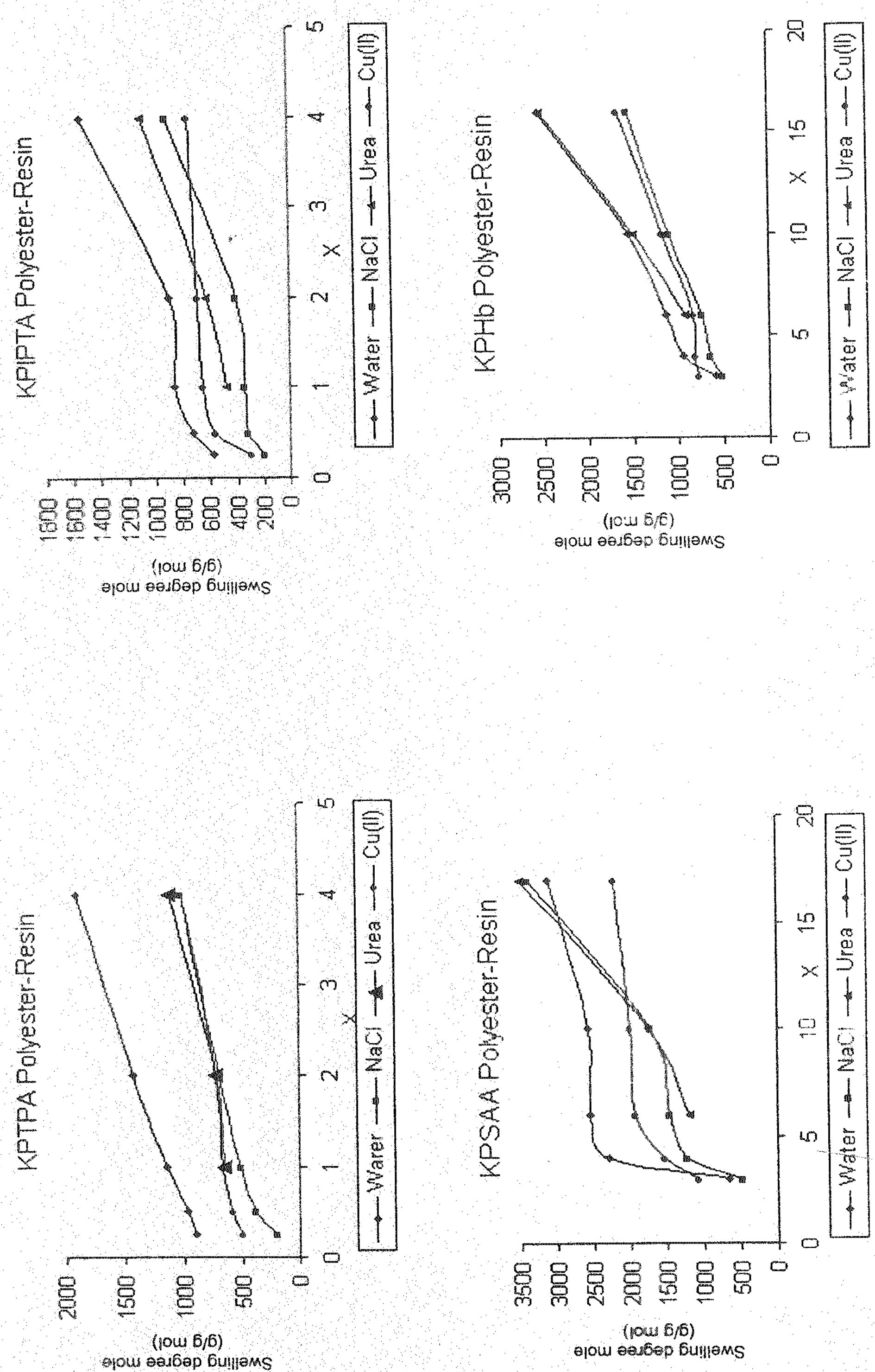
KPIPTA Polyester-Resin
KPTPA Polyester-Resin
KPHb Polyester-Resin
KPSAA Polyester-Resin
Swelling degree mole (g/g mol)
X
Water
Warer
NaCl
Urea
Cu(II)

Fig. 2

TABLE-6
MOLAR SOLUBILITY (g-mole/mL) OF THE RESINS IN DIFFERENT SWELLING AGENTS

No.	Product	Water 10^{-5}	NaCl 10^{-5}	Urea 10^{-5}	Cu(II) 10^{-5}	X
1	K-P-TPA (1)	31.91	16.90	—	7.74	0.25
2	K-P-TPA (2)	27.84	13.29	—	5.06	0.50
3	K-P-TPA (3)	23.33	11.66	19.44	3.88	1.00
4	K-P-TPA (5)	20.60	9.44	11.58	2.57	2.00
5	K-P-TPA (10)	13.33	4.54	5.75	1.81	4.00
6	K-P-IPTA (1)	28.26	14.49	—	7.24	0.25
7	K-P-IPTA (2)	19.62	10.75	—	4.43	0.50
8	K-P-IPTA (3)	18.33	7.22	9.44	2.22	1.00
9	K-P-IPTA (5)	13.30	4.29	6.86	1.28	2.00
10	K-P-IPTA (10)	7.96	4.12	4.42	0.58	4.00
11	K-P-SAA (1)	14.42	8.52	—	2.95	3.00
12	K-P-SAA (2)	14.04	7.16	—	2.29	4.00
13	K-P-SAA (3)	12.81	4.57	4.11	2.28	6.00
14	K-P-SAA (5)	7.55	2.41	3.37	1.28	10.00
15	K-P-SAA (10)	4.34	2.38	2.38	0.86	17.00
16	K-P-Hb (1)	13.00	8.04	—	3.09	3.00
17	K-P-Hb (2)	11.96	6.64	—	2.39	4.00
18	K-P-Hb (3)	10.12	5.17	4.31	1.72	6.00
19	K-P-Hb (5)	7.59	4.71	3.79	1.36	10.00
20	K-P-Hb (10)	5.00	2.23	2.34	0.85	16.00

TABLE-7
SWELLING DEGREE MOLE (g/g mol) OF THE RESINS IN DIFFERENT SWELLING AGENTS

No.	Product	Water	NaCl	Urea	Cu(II)	X
1	K-P-TPA (1)	893.18	197.38	—	504.10	0.25
2	K-P-TPA (2)	971.70	388.68	—	592.50	0.50
3	K-P-TPA (3)	1139.40	509.40	657.00	671.40	1.00
4	K-P-TPA (5)	1428.29	699.00	722.30	724.63	2.00
5	K-P-TPA (10)	1897.50	1016.40	1115.40	1009.80	4.00
6	K-P-IPTA (1)	582.36	193.20	—	292.56	0.25
7	K-P-IPTA (2)	722.06	316.00	—	562.48	0.50
8	K-P-IPTA (3)	865.80	340.20	477.00	658.80	1.00
9	K-P-IPTA (5)	897.05	407.75	624.44	685.02	2.00
10	K-P-IPTA (10)	1535.67	915.30	1101.75	749.19	4.00
11	K-P-SAA (1)	671.00	478.85	—	1078.70	3.00
12	K-P-SAA (2)	2292.93	1242.44	—	1521.64	4.00
13	K-P-SAA (3)	2534.46	1459.58	1197.38	1922.80	6.00
14	K-P-SAA (5)	2568.86	1716.72	1729.16	1996.62	10.00
15	K-P-SAA (10)	3112.98	3380.07	3499.80	2191.98	17.00
16	K-P-Hb (1)	600.78	526.49	—	784.89	3.00
17	K-P-Hb (2)	943.76	650.48	—	812.16	4.00
18	K-P-Hb (3)	1132.16	747.04	932.64	839.84	6.00
19	K-P-Hb (5)	1539.72	1092.28	1487.08	1177.82	10.00
20	K-P-Hb (10)	2547.74	1551.00	2538.80	1654.40	16.00

Conclusion

It was observed that simultaneous occurrence of swelling and solibility takes place in the sorption process.

We suggest that effective concentration of water molecules to hydroxyl groups should be much less, which decreases the solubility of the resin. In case of Cu(II); Cu(II) ions would interact with hydroxyl groups of polymer and insolubilize them. The resin did not sorb NaCl during the sorption process. Presence of salts lowers degree of swelling and solubility of the polyester resins.

REFERENCES

1. C.A. Finch, Poly Vinyl Alcohol: Properties and Applications, Wiley, New York (1973).
2. Y. Sone and I. Sakurada, *Kobunshi Kogeku,* **14,** 145, 235 (1957).
3. R. Hubney, G.M.H, Ger. Pat., 3, 328 (1985).
4. A.M. Talati and B.N. Narkhede, *Popular Plastics,* **32,** 19 (1987).
5. A.B. Argade and A.N. Peppas, *J. Appl. Polym. Sci.,* **70,** 817 (1998).
6. T. Suzuki, *J. Appl. Polym. Symp.,* **25,** 431 (1979).
7. E. Chiellini and T.St. Pierre, *J. Bioact. Comput. Polym.,* **2,** 238 (1987).
8. M. Matsuguchi, S. Umeda, Y. Sadoka and Y. Sakai, *Sens Actuators,* **49B** (1988).
9. R. Zelko, K. Suvegh, S. Mortan and I. Racz, *Pharm. Res.,* **17,** 1030 (2000).
10. T. Tanaka, H. Shigeno and S. Matsumura, *Polym. Prepr. Jpn* (*Eng. Ed.*), **40,** E904 (1991).
11. M. Tsugi and Y. Omoda, *Polym. Prepr. Jpn.* (*Eng. Ed.*) **40,** E905 (1991).
12. Y. Takabe, N. Nohara and M. Kitano, *Polym. Prepr. Jpn. (Eng. Ed.),* **40,** E907 (1991).
13. V.A. Grigserva, L. Rogovina and Salominskii, *Vysokomol Soedin Sec.,* **B16,** 144 (1974).
14. V.A. Waclaw, *Polimetry* (*Warsaw*), **28,** 153 (1983).
15. N.A. Pappas and B.N. Merill, *J. Appl. Polym. Sci.,* **21,** 1763 (1977).
16. Kuraray Co., Jap. Pat., 81, 149 (1981).
17. Kuraray Co., Jap. Pat., 2 908, 805 (1979)
18. C.A. Finch (Eds.), Chemistry and Technology of Water Soluble Polymers, Plenum Press, New York (1983).
19. J.A. Kitchner, Ion Exchange Resin, Methuen, London (1957).
20. V.J. Dhimar, Ionic Polymers, Ph.D. Thesis, M.S. University of Baroda, India (1987).
21. F. Helferich, Ion Exchange, McGraw-Hill, New York (1962).
22. R. Kunui, Ion Exchange Resins, Wiley, New York (1958).
23. A. Sugii and N. Ogawa, *Talanta,* **26,** 970 (1979).

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