V.

SUMMARY

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Poly (vinyl alcohol) prepared from poly (vinyl ester) is commercially available in various grades depending on its degree of hydrolysis and degree of polymerization(1). Its solubility in water depends on its degree of hydrolysis, degree of polymerization, tacticity, cross-linking, etc. Its many hydroxyl groups cause it to have high affinity for water with strong H-bonding between intra and inter molecular hydroxyl groups ; on the other hand, the residual ester groups in partly hydrolysed poly (vinyl alcohol) are essentially hydrophobic and weaken the inter and intra molecular H-bonds. This would be further affected by the amorphous regions of the resin which are capable of sorbing water.

Poly (vinyl alcohol) can be etherified, esterified and acetalized. It has been converted into inorganic esters (2, 3), organic esters of aliphatic and aromatic acids (4, 5), esters of long chain fatty acids (6, 7), carbamate esters (8) etc. These products have been studied for use in surface coating, in printed circuits, in printing screens, etc. (9).

When Poly (vinyl alcohol) is partially esterified with different mono and polybasic acids, ester content (hydrophobicity) would increase, hydroxyl content (hydrophilicity) would decrease, cross-links may get introduced, amorphous regions would change and all these changes would affect water sorption by the resin, solubility of the resin in water and the resultant (limited) swelling of the resin (10 - 15). Swelling of a polymer by a fluid is associated with the sorption of a low molecular weight fluid by a polymer. Swelling is not merely the penetration of small sorbate molecules into the polymer phase but it usually involves a change in polymer structure. Swelling may be limited or unlimited. Unlimited swelling is one that passes spontaneously into dissolution. Limited swelling is the interaction of the polymer with low molecular weight fluid, when it is short of spontaneous dissolution and is limited to sorption. Swelling is measured as degree of swelling by gravimetric and volumetric methods. Esters and acetals of poly (vinyl alcohol) have been investigated for swelling (16, 17).

Review of literature indicated that although various polymers had been widely studied for their solubility or swelling, relative and comparative studies of swelling and solubility of poly(vinyl alcohol) esters have been few (18 - 22). Such studies can help in evaluating the utility of such products in soils, lenses, lubricants, etc. The work on swelling was initiated in our laboratories(23) and interesting results were obtained. Hence the work has been continued and extended. It was planned.

(1) to prepare poly (vinyl alcohol) esters from poly (vinyl alcohol) and various mono and poly acids,

(2) to determine their melting point, water content, ester content, etc,

(3) to get the products analysed for C,N and H,

(4) to study the sorption of water by these products in absence and in presence of different salts acids

(5) to evaluate swelling and solubility of these products and to correlate them.

The plan was executed and the results are correlated and discussed as follows :

Poly(vinyl alcohol) of Koch-Light make and SD. chem. make was partially esterified using (1) adipic acid (2) sebacic acid, (3) fumaric acid (4) acrylic acid (5) glycine (6) isophthalic acid (7) terephthalic acid (8) salicylic acid (9) anthranilic acid, (10) p-amino benzoic acid (11) p-hydroxy benzoic acid (12) tri chloro acetic acid and (13) trimelletic anhydride, using different proportions and specific methods.

General observations on solubility in water and stability to solutions of acids and alkalis led us to discontinue our studies with partial esters made from SD chem make poly(vinyl alcohol). Detailed studies of partial esters prepared from Koch-Light make poly(vinyl alcohol) have been made.

Water content and ester content of the products were determined and used togather with C-H-N analysis to suggest their probable formulae. The general formula is

$$[\ (\text{ester})\ (\text{alcohol})_x\ (\text{water})_y\ ]_n$$

Water sorption by these alcohol-esters was investigated. It was observed that these products exhibit both solubility and swelling. Solubility and degree of swelling were evaluated. Hence molar solubility and swelling degree per g-mole were calculated. These values were used to evaluate number of moles of water sorbed by the products during maximum swelling and the number of moles of water required just to dissolve fully one g-mole of the product. These two values gave an indication of the limits of limited and unlimited swelling.

To study how the solubility and swelling of these products were affected by repeated sorption and desorption, these processes were recycled. The results are correlated and discussed.

When sorption studies were made from salt solutions, it was observed that these products do not sorb salt. Hence water sorption was evaluated as above. The general observation is that water sorption from salt solution is lower than that from water. Hence degree of salting out of these products in salt solution was evaluated.

Some of the products were used to study sorption from urea solution. Solubility and swelling of the products are considered.

Sorption studies were also made from Cu(II) solutions and solubility and degree of swelling of these products were evaluated.

Volume swelling and area swelling were determined and longitudinal swelling was evaluated. The results are correlated.

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SWELLING AND SOLUBILITY OF POLYESTER - POLYOLS

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Poly (vinyl alcohol) is commercially available in various grades depending on its degree of hydrolysis and degree of Polymerization[1]. Its solubility in water depends on its degree of hydrolysis, degree of polymerization, tacticity, cross-linking, etc. Its many hydroxyl groups cause it to have high affinity for water with strong H-bonding between intra and inter-molecular (chain) hydroxyl groups ; on the other hand, the residual ester groups in partly hydrolysed poly (vinyl alcohol) are essentially hydrophobic, and weaken the intra and inter-molecular (chain) H-bonding of hydroxyl groups. Various chemicals, like boric acid, etc. cause thickening and gelation of poly (vinyl alcohol) solution by chemical bonding with poly (vinyl alcohol).

When poly (vinyl alcohol) is partially esterified with different mono and di-basic acids, ester content would increase, OH group content would decrease, cross-links may get introduced and hence relative changes in hydropholic - hydrophobic groups and chain lengths would affect solubility and swelling.

The products of partial esterification of poly (vinyl alcohol) are polyester - polyols. These products are represented as PE_zH_x where z and x are the numbers of ester (E) and hydroxyl (H) groups in a polymeric vinyl chain (P).

Although various polymers have been widely studied for their solubility or swelling, relative and comparative studies of swelling and solubility of polyester-polyols have been few[2-6]. Such studies can help in evaluating the utility of such products in soils, lenses, lubricants, etc. Hence we undertook to prepare a series of polyester-polyols, using different acids, and varying the proportions of the reactants. In the present paper, we present and discuss (1) the preparation of polyester-polyols using poly (vinyl alcohol) and phthalic, isophthalic, salicylic and p-hydroxy benzoic acids and (2) the studies of their swelling and solubility in water and salt solution.

Poly (vinyl alcohol) (D.P. 1640 and degree of hydrolysis 97%) was esterified partially by reaction with acid chloride (prepared by treating the acid with thionyl chloride in DMF in presence of pyridine). Different amounts of reactants used, yield, colour, softening temp. of the products, etc., are presented in table I. (yield is calculated on the basis of the acid chloride used and the formula of the product proposed). The analysis of the products, together with their water content and ester content are presented in table II. The general formula of the product is represented as $V_{x+1} AQ_{y}$ where A represents one equivalent of acid involved in the esterification of one equivalent of vinyl hydroxyl, x represents the number of vinyl hydroxyls remaining unreacted per ester group and y represents the number of water molecules (Q) per ester group. The formulae are suggested in agreement with C–H analysis, ester content and water content of the products. As anticipated, there is a gradation in the degree of esterification in each series.

When the swelling of products in water was studied, it was found that the products dissolve to some extent, exhibiting the possibility and need of studying swelling and solubility simultaneously. Hence we determined (1) wt of the sample before sorption (W_{Bs}), (2) wt of the sample after sorption in water (W_{As}), (3) wt of the sample after drying the sorbed sample (W_{Ds}), (4) Vol of water used initially for sorption (V_{Bs}) and (5) Vol of water after sorption (V_{As}). Usually degree of swelling is determined as,

$$\text{degree of swelling} = \frac{W_{As} - W_{Bs}}{W_{Bs}}$$

Because a part of the sample gets solubilized during sorption, the degree of swelling (DS) (g/g) (dry basis) is better evaluated as

$$DS = \frac{W_{AS} - W_{DS} - \frac{qW_{DS}}{1 - q}}{W_{DS}}$$

where q represents the water content (g/g) of the sample.

Solubility (sol) (g/ml) (dry basis) of the sample is evaluated as

$$Sol = \frac{W_{BS}(1 - q) - W_{DS}}{(V_{BS} - V_{AS})}$$

where V_{AS} can be approximated for water as

$$V_{AS} = W_{AS} - W_{DS} - \frac{qW_{DS}}{1 - q}$$

It has been observed that the values of DS, sol and the product of DS and sol show a gradation in each series in general (Table III). It is also observed that DS is in decreasing order for the products as KVI, and KVT > KVSa > KVHb, and sol is in decreasing order for the products as KVHb > KVT > KVI.

When 10 % NaCl solution was used in place of water in the sorption process, 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. We also observe that the presence of salt lowers DS and sol of the sample. Such decrease in DS has been observed earlier[7]. Degree of salting-out at constant slat concentration (DSO_C) can be suggested as

$$DSO_C = \frac{Sol_W - Sol_S}{Sol_W}$$

Where Sol_W and Sol_S represent solubility of the sample in water and salt solution respectively. The results are presented in Table IV. We observe, in general, that degree of salting-out increases with increase in the number of hydroxyl groups (x) in the product.

From the studies of the swelling and solubility of the sample in water we can evaluate (1) A: number of moles of water required to cause maximum swelling of one g=mole of the sample, and (2) B = minimum number moles of water required to solubilize one g-mole of the same sample.

$$A : \frac{DS \times W_{F(a)}}{18} \quad \text{(sorption capacity)}$$

$$B : \frac{W_{F(a)}}{Sol \times 18}$$

Where $W_{F(a)}$ represents the formula wt of the sample in anhydrous form. We plot $\log_{10}A$ and $\log_{10}B$ verus x for each series of products in Fig I. The shaded region in the fig. I represents the simultaneous occurence of swelling and solubility of the sample. If swelling is considered as limited and unlimited, two curves in each plot represent the boundary conditions for limited and unlimited swelling.

Table - I

No	Product	Poly(Vinyal alcohol) (m-moles)	Acid Chloride (m-moles)	Yield (%)	Melting/ Softening temp	Colour
1	2	3	4	5	6	7
			(a) acid:terephthalic:temp of reaction:150^{o}C:time of reaction:6hr.			
1	KVI(1)	22.7	4.9	67	d*	black
2	KVI(2)	45.5	4.9	100	d	brown
3	KVI(3)	68.2	4.9	100	d	brown
4	KVI(5)	113.6	4.9	100	d	brown
5	KVI(10)	227.0	4.9	100	d	Brown

Table – I(contd.)

1	2	3	4	5	6	7
			(b) acid:isophthalic:temp of reaction:150^{0}C:time of reaction:6hr.			
6	KVI(1)	22.7	4.9	67	d	black
7	KVI(2)	45.5	4.9	100	d	brown
8	KVI(3)	68.2	4.9	99	d	brown
9	KVI(5)	113.6	4.9	100	d	brown
10	KVI(10)	227.0	4.9	100	d	brown

(d* : decomposition)

Table - I(contd.)

1	2	3	4	5	6	7
			(c) acid:salicylic:temp of reaction:150°C:time of reaction:6hr.			
11	KVSa(1)	22.7	6.4	68	122	black
12	KVSa(2)	45.5	6.4	100	141	brown
13	KVSa(3)	68.2	6.4	100	167	brown
14	KVSa(5)	113.6	6.4	85	181	pink
15	KVSa(10)	227.1	6.4	85	188	brown

Table - I(contd.)

1	2	3	4	5	6	7
			(d) acid:p-hydroxy benzoic:temp of reaction 120°C:time of reaction 2 hr.			
16	KVHb(1)	22.7	6.4	100	103	brown
17	KVHb(2)	45.4	6.4	100	110	brown
18	KVHb(3)	68.2	6.4	100	139	brown
19	KVHb(5)	113.6	6.4	100	151	brown
20	KVHb(10)	227.3	6.4	100	163	brown

Table - II

No	Product	Formula	analysis				content (%)		ester content (meg/g)	
			%C		%H					
			found	(reqd)	found	(reqd)	found	(reqd)	found	(reqd)
1	2	3	4	5	6	7	8	9	10	11
1	KVT(1)	$V_{1.25}TQ$	55.80	(56.51)	6.32	(5.80)	12.0	(14.2)	8.0	(7.9)
2	KVT(2)	$C_{1.5}TQ_{1.5}$	54.44	(53.16)	6.75	(6.33)	15.0	(17.1)	6.3	(6.3)
3	KVT(3)	$V_2TQ_{1.5}$	53.20	(53.33)	7.68	(6.67)	13.0	(15.0)	5.6	(5.6)
4	KVT(5)	V_3TQ_2	52.83	(51.50)	7.40	(7.30)	14.0	(15.5)	4.5	(4.3)
5	KVT(10)	$V_5TQ_{2.5}$	51.10	(50.91)	7.76	(7.88)	11.0	(13.6)	2.9	(3.0)

Table - II(contd.)

1	2	3	4	5	6	7	8	9	10	11
6	KVI(1)	$V_{1.25}IQ$	56.38	(56.52)	5.90	(5.80)	12.5	(14.2)	8.0	(7.9)
7	KVI(2)	$V_{1.5}IQ_{1.5}$	52.85	(53.16)	6.20	(6.33)	15.5	(17.1)	6.4	(6.3)
8	KVI(3)	V_2IQ	51.55	(53.33)	6.76	(6.77)	13.0	(15.0)	5.6	(5.6)
9	KVI(5)	V_3IQ_2	50.80	(51.50)	7.58	(7.30)	13.5	(15.4)	4.6	(4.3)
10	KVI(10)	V_5IQ_3	50.05	(49.56)	8.10	(7.96)	15.5	(15.9)	2.9	(3.0)

Table-II (Contd.)

1	2	3	4	5	6	7	8	9	10	11
11	KVSa(1)	$V_4SaQ_{.5}$	61.18	(59.02)	7.41	(6.89)	3.0	(3.0)	3.0	(3.3)
12	KVSa(2)	$V_5SaQ_{.5}$	60.20	(58.43)	7.75	(7.17)	2.0	(2.6)	2.6	(2.9)
13	KVSa(3)	$V_7SaQ_{.5}$	59.49	(57.66)	8.03	(7.55)	2.0	(2.1)	2.3	(2.3)
14	KVSa(5)	$V_{11}SaQ$	58.14	(55.95)	8.24	(8.04)	3.0	(2.9)	1.5	(1.6)
15	KVSa(10)	$V_{18}SaQ_{.5}$	57.85	(56.03)	7.92	(8.33)	1.0	(0.9)	1.1	(1.1)

Table-II (Contd.)

1	2	3	4	5	6	7	8	9	10	11
16	KVHb(1)	$V_4HbQ_{1.5}$	56.35	(55.73)	7.72	(7.12)	9.0	(8.4)	3.0	(3.1)
17	KVHb(2)	V_5HbQ_2	53.32	(54.25)	7.95	(7.45)	9.0	(9.6)	2.6	(2.7)
18	KVHb(3)	V_7HbQ_2	52.42	(54.31)	8.26	(7.76)	8.0	(7.8)	2.1	(2.2)
19	KVHb(5)	$V_{11}HbQ_3$	51.49	(52.89)	8.95	(8.20)	8.0	(8.2)	1.4	(1.5)
20	KVHb(10)	$V_{17}HbQ_4$	50.44	(52.34)	8.76	(8.51)	7.0	(7.7)	1.1	(1.1)

Table - III

No	Product	DS (g/g)	Sol (g/ml)	DS x Sol	NO	Product	DS (g/g)	Sol (g/ml)	DS x Sol
1	KVT(1)	6.29	0.051	0.32	6	KVI(1)	4.22	0.039	0.17
2	KVT(2)	6.15	0.044	0.27	7	KVI(2)	4.57	0.031	0.14
3	KVT(3)	6.33	0.042	0.26	8	KVI(3)	4.81	0.033	0.16
4	KVT(5)	6.13	0.048	0.29	9	KVI(5)	3.85	0.031	0.12
5	KVT(10)	5.73	0.044	0.25	10	KVI(10)	4.53	0.027	0.12

Table - III(Contd.)

No	Product	DS (g/g)	Sol (g/ml)	DS x Sol	No	Product	DS (g/g)	Sol (g/ml)	DS x Sol
11	KVSa(1)	2.23	0.044	0.10	16	KVHb(1)	1.86	0.042	0.08
12	KVSa(2)	6.57	0.059	0.39	17	KVHb(2)	2.51	0.045	0.11
13	KVSa(3)	5.80	0.056	0.32	18	KVHb(3)	2.44	0.047	0.11
14	KVSa(5)	4.13	0.047	0.20	19	KVHb(5)	2.34	0.050	0.12
15	KVSa(10)	3.38	0.040	0.13	20	KVHb(10)	2.71	0.047	0.13

Table - IV

No.	Product	Degree of salting out	No	Product	Degree of salting out
1	KVT(1)	0.52	11	KVSa(1)	0.41
2	KVT(2)	0.62	12	KVSa(2)	0.58
3	KVT(3)	0.50	13	KVSa(3)	0.62
4	KVT(5)	0.55	14	KVSa(5)	0.69
5	KVT(10)	-	15	KVSa(10)	0.85
6	KVT(1)	0.48	16	KVHb(1)	0.38
7	KVT(2)	0.50	17	KVHb(2)	0.45
8	KVT(3)	0.61	18	KVHb(3)	0.49
9	KVT(5)	0.67	19	KVHb(5)	0.37
10	KVT(10)	0.48	20	KVHb(10)	0.55

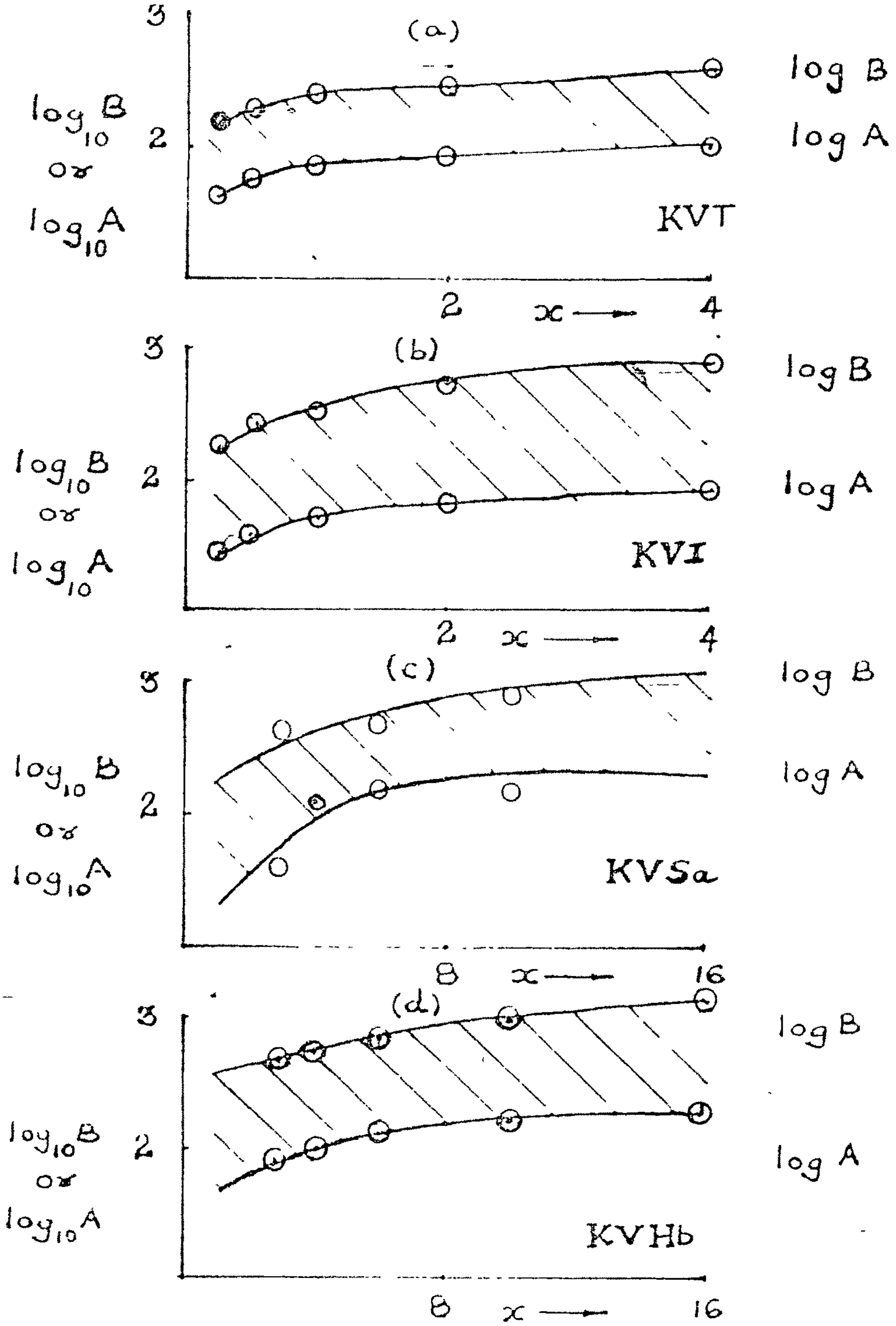

Fig. 1 Plot of $\log_{10} A$ or $\log_{10} B$ Vs x

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