Asian Journal of Chemistry Vol. 18, No. 1 (2006), 447–454

Effect of Sorption, Repeated Sorption and Desorption on Solubility and Swelling of the Polyester Resins

B.N. NARKHEDE*, S.D. RATHOD, A.S. MUNDE and F.R. CHAVAN†
Department of Chemistry, Milind College of Science
Nagsen Vana Cantt., Aurangabad-431 002, India
E-mail: bnnarkhede@yahoo.com

Different series of Polyester resins were prepared by partially esterifying poly (vinyl alcohol) with different amounts of terephthalic, isophthalic salicylic and *p*-hydroxy benzoic acid chlorides. Solubility and swelling degree of these products in water have been evaluated. To study how the solubility and swelling of the products were affected by repeated sorption, sorption and desorption of the product of each series used for sorption once were carried out. The solubility (g/mL) and swelling degree (g/g) were calculated. When the resin is subjected to reported sorption and desorption, a part of resin dissolves in water every time and swelling degree of the undissolved resin varies over a very narrow range.

Key Words: Poly (vinyl alcohol), Terephthalic acid, Isophthalic acid, Salicylic acid, *p*-Hydroxy benzoic acid.

Introduction

Poly (vinyl alcohol) (PVA) 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 its high affinity for water with strong H-bonding between intra- and intermolecular (chain) hydroxyl groups. On the other hand, the residual ester groups in partly hydrolysed PVA are essentially hydrophobic and weaken inter- and intramolecular H-bonds. Previous history of PVA has effect on its swelling[2]. Its hydroxyls have been studied as swollen elastic networks and as water sorbents[3–4]. Various polymers have been prepared from PVA and studied for their solubility and swelling to correlated them with various structural factors[5–9]. Its hydroxyls have been studied as having swollen elastic nature of water sorption[10].

When PVA is partially esterified with different mono- and dibasic acids, ester content increases, OH group content decreases, cross-links get introduced and hence relative changes in hydrophilic, hydrophobic groups and chain lengths affect solubility and swelling. The functional PVA was co-polymerized and/or

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†V.N. College, CIDCO, Aurangabad-431 004, India.

cross linked with acrylic acid or its partially neutralized form to give cross linked polyacrylates that could swell in water[12]. Sorption properties of the chelating ion exchange resin towards various divalent metal ions are studied by static batch equilibration technique as a function of pH and time of equilibration[12]. Various polymers have been prepared from PVA and studied for solubility and swelling[13–15].

EXPERIMENTAL

A series of polyester resins were prepared using different acid chlorides such as terephthalic acid (TPA), isophthalic acid (IPTA), salicylic acid (SAA), *p*-hydroxy benzoic acid (Hb) and varying proportions of PVA as 1 : 1, 1 : 2, 1 : 3, 1 : 5, 1 : 10 (having degree of polymerization 1640 and degree of hydrolysis 97% of Koch-Light, England) with thionyl chloride in dimethyl formamide (DMF) in presence of pyridine. These products were studied for sorption, resorption and desorption. The processes were recycled. The results are presented in Table-1.

TABLE-1
WATER RESORPTION

S. No.	Product	Water Resorption (I)		Water Resorption (II)		Water Resorption (III)	
		Solubility (g/mL)	Degree of swelling (g/g)	Solubility (g/mL)	Degree of swelling (g/g)	Solubility (g/mL)	Degree of swelling (g/g)
01	K-P-TPA(3)	0.027	7.45	0.002	5.31	0.00031	5.00
02	K-P-TPA(5)	0.026	5.13	0.003	4.08	0.0015	3.61
03	K-P-TPA(10)	0.027	6.08	0.0032	5.75	0.0015	4.22
04	K-P-IPTA(3)	0.021	4.07	0.0030	3.62	0.0016	3.82
05	K-P-IPTA(5)	0.021	2.86	0.00055	3.25	0.00055	2.95
06	K-P-IPTA(10)	0.026	3.10	0.00032	2.24	0.00021	2.15
07	K-P-SAA(3)	0.026	5.60	0.0033	4.36	0.0022	4.64
08	K-P-SAA(5)	0.020	2.70	0.0042	2.55	0.00064	2.53
09	K-P-SAA(10)	0.026	5.33	0.0045	3.82	0.00044	3.59
10	K-P-Hb(3)	0.028	1.43	0.0013	1.64	0.0011	1.11
11	K-P-Hb(5)	0.035	2.11	0.0014	4.46	0.0010	0.58
12	K-P-Hb(10)	0.027	1.82	0.0021	1.99	0.00052	2.01

The solubility and swelling degree (DS) of these products were calculated. The solubility and swelling degree for repeated sorption are compared with increase in number of hydroxyl groups (X). From the study of solubility and swelling degree of the sample in water, the number of moles of water required to cause maximum swelling of 1 g mol of resin and also the minimum number of moles of water required to solubilize 1 g mol of the resin sample were evaluated.

RESULTS AND DISCUSSION

When water comes in contact with porous hydrophilic resin, the small mobile water molecules from water phase readily diffuse through water-resin interface and to the porous hydrophilic groups of the resin in the resin phase. Sorption of water by resin takes place up to a certain limit. When further sorption takes place beyond the limit, the substance was solubilized. It was found that the products dissolve to some extent, exhibiting the possibility and need for studying swelling and solubility simultaneously. Hence were determined (1) weight of the sample before sorption (W_{BS}), (2) weight of the sample after sorption in water (W_{AS}), (3) weight after drying the sorbed sample (W_{DS}), (4) volume of the water used initially for sorption (V_{BS}), and (5) volume of water after sorption (V_{AS}). Usually the degree of swelling is determined as:

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

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

$$DS = \frac{W_{AS} - W_{DS} - \dfrac{q\,W_{DS}}{W_{BS}(1-q)}}{W_{DS}}$$

where q represents the water content (g/g) of the sample. Solubility (g/mL) dry basis of the sample is evaluated as:

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

where V_{AS} can be approximated for water as:

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

It has been observed that the values of DS sol show a graduation in series in general.

To study how the solubility and swelling of the resin are affected by repeated sorption (recycling), the sorption and desorption of the resins of each series used for sorption once were carried out. The results have been utilized to calculate solubility of the resin and swelling degree of the resin. The solubility (g/mL) of the resin is calculated as:

$$\text{Solubility (I) (g/mL)} = \frac{W_{DS} - W_{DR}(\text{I})}{W_{BS} - V_{AS}}$$

The results for 1 : 1 and 1 : 2 proportions of PVA and acid chlorides were unsatisfactory and hence are not mentioned in Table-1.

$$\text{Solubility R(II) (g/mL)} = \frac{W_{DR}(\text{I}) - W_{DR}(\text{II})}{W_{BS} - V_{AS}}$$

$$\text{Solubility R(III) (g/mL)} = \frac{W_{DR}(II) - W_{DR}(III)}{W_{BS} - V_{AS}}$$

where $W_{DR}(I)$, $W_{DR}(II)$ and $W_{DR}(III)$ are weights of the dried samples after first, second and third resorptions, respectively and V_{BS} is volume of the water used initially for sorption every time. V_{AS} is volume of water after sorption and resorption every time. It has been shown above how it can be approximated for water.

$$\text{Swelling degree R(I) (g/g)} = \frac{W_{AR}(I) - W_{DR}(I)}{W_{DR}(I)}$$

$$\text{Swelling degree R(II) (g/g)} = \frac{W_{AR}(II) - W_{DR}(II)}{W_{DR}(II)}$$

$$\text{Swelling degree R(III) (g/g)} = \frac{W_{AR}(III) - W_{DR}(III)}{W_{DR}(III)}$$

where $W_{AR}(I)$, $W_{AR}(II)$ and $W_{AR}(III)$ are weights of the samples after first, second and third resorptions, respectively.

To compare the values of solubility and swelling degree for repeated sorption, the plots of solubility *vs.* increase in number of hydroxyl groups (X) and swelling degree *vs.* increase in number of hydroxyl groups (X) are shown in Figs. 1 and 2, respectively. When the resin was subjected to repeated sorption and desorption, a part of resin dissolved in water every time. The solubility of the resin in first sorption experiment decreased considerably in subsequent sorption experiments. Similarly, the swelling degree of undissolved resins varied over a very narrow range.

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

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

$$B = \frac{W_{F(a)}}{\text{Solublity} \times 18}$$

where $W_{F(a)}$ represents the formula weight of the sample in anhydrous form. The plots $\log_{10}$ A and $\log_{10}$ *vs.* X (number of vinyl hydroxyls remaining unreacted per ester group) are shown in Fig. 3. The formulae are suggested in agreement with C-H analysis ester content and water content of the resins. The values of X and the formulae are presented in Table-2.

The above results imply that the swelling capacity of the resin is practically unaffected by the dissolution of the fraction of the resin and the fraction of resin dissolved in water would not have higher swelling capacity than the fraction remaining undissolved.

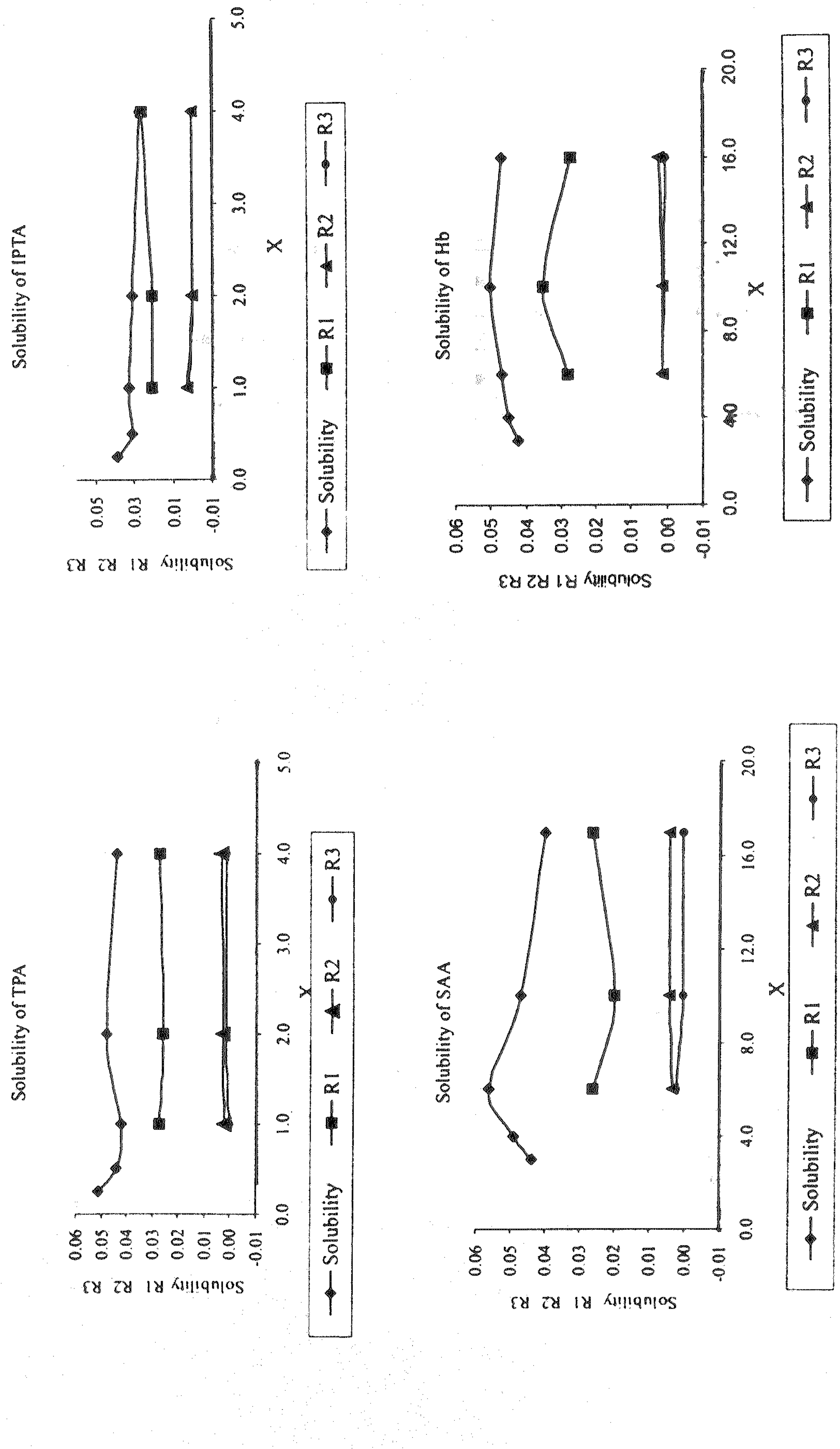
Solubility of IPTA
Solubility R1 R2 R3
0.05
0.03
0.01
-0.01
0.0
1.0
2.0
3.0
4.0
5.0
X
Solubility
R1
R2
R3
Solubility of Hb
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
0.0
4.0
8.0
12.0
16.0
20.0
Solubility of TPA
Solubility of SAA

Fig. 1

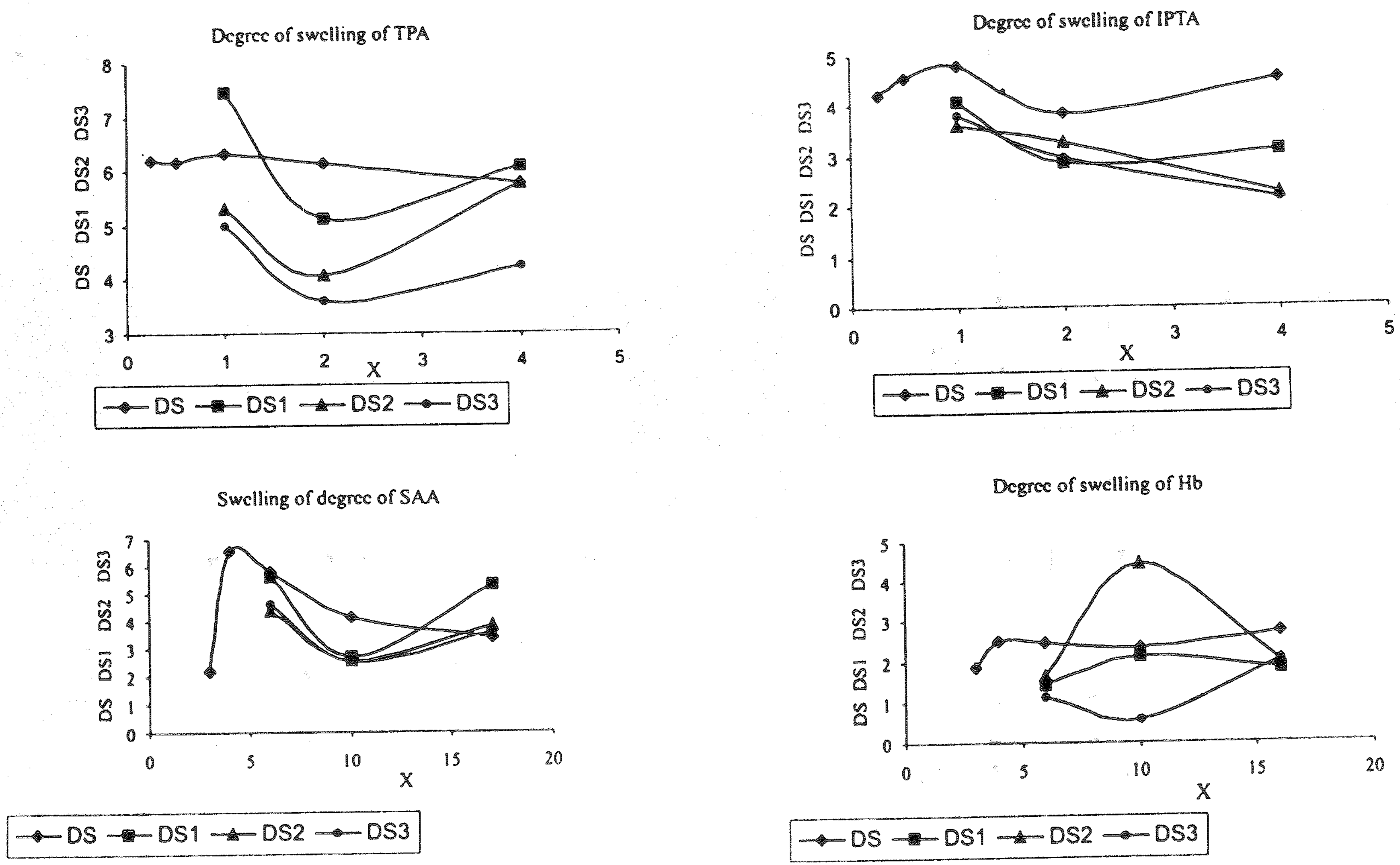
Degree of swelling of TPA
DS DS1 DS2 DS3
8
7
6
5
4
3
0
1
2
3
4
5
X
DS
DS1
DS2
DS3
Degree of swelling of IPTA
DS DS1 DS2 DS3
5
4
3
2
1
0
0
1
2
3
4
5
X
DS
DS1
DS2
DS3
Swelling of degree of SAA
DS DS1 DS2 DS3
7
6
5
4
3
2
1
0
0
5
10
15
20
X
DS
DS1
DS2
DS3
Degree of swelling of Hb
DS DS1 DS2 DS3
5
4
3
2
1
0
0
5
10
15
20
X
DS
DS1
DS2
DS3

Fig. 12

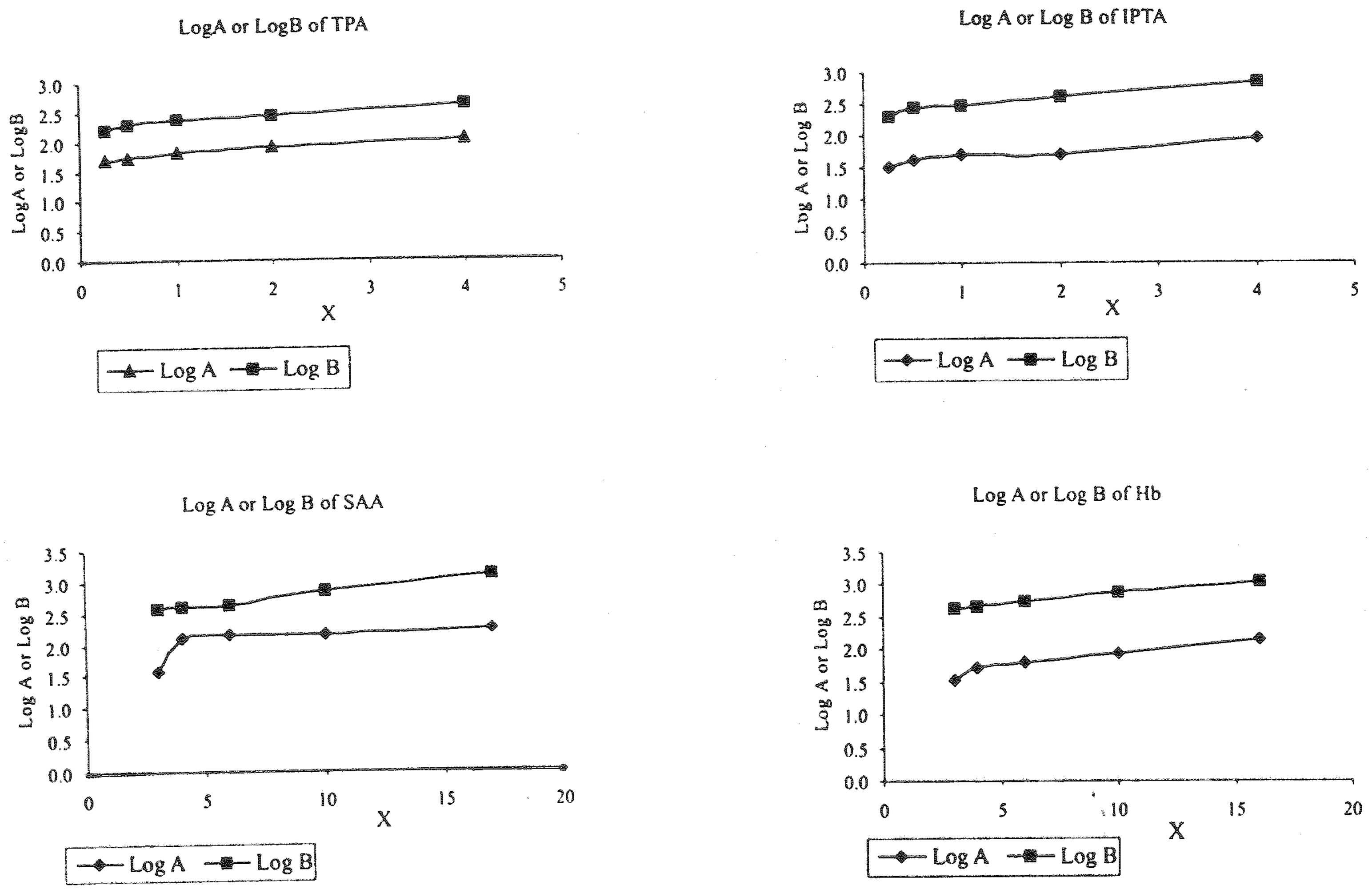
LogA or LogB of TPA
LogA or LogB
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
1
2
3
4
5
X
Log A
Log B
Log A or Log B of IPTA
Log A or Log B
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
1
2
3
4
5
X
Log A
Log B
Log A or Log B of SAA
Log A or Log B
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
5
10
15
20
X
Log A
Log B
Log A or Log B of Hb
Log A or Log B
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
5
10
15
20
X
Log A
Log B

Fig. 3

TABLE-2
WATER SORPTION

S. No.	Product	Formula	X	Solubility (g/mL)	Degree of swelling DS (g/g)	A	B
01	K-P-TPA(1)	$C_{6.5}H_8O_{3.5}$	0.25	0.051	6.20	49.621	154.648
02	K-P-TPA(2)	$C_7H_{10}O_{14}$	0.5	0.044	6.15	53.983	199.494
03	K-P-TPA(3)	$C_8H_{12}O_{4.5}$	1.0	0.042	6.33	63.330	238.095
04	K-P-TPA(5)	$C_{10}H_{17}O_6$	2.0	0.048	6.13	79.349	269.675
05	K-P-TPA(10)	$C_{14}H_{26}O_{8.5}$	4.0	0.044	5.75	105.416	416.666
06	K-P-IPTA(1)	$C_{6.5}H_8O_{3.25}$	0.25	0.039	4.22	32.353	196.581
07	K-P-IPTA(2)	$C_7H_{14}O_{10}$	0.5	0.031	4.57	40.114	283.154
08	K-P-IPTA(3)	$C_8H_{12}O_{4.5}$	1.0	0.033	4.81	48.101	303.031
09	K-P-IPTA(5)	$C_{10}H_{17}O_6$	2.0	0.031	3.85	49.830	417.562
10	K-P-IPTA(10)	$C_{14}H_{27}O_9$	4.0	0.027	4.53	85.314	697.530
11	K-P-SAA(1)	$C_{15}H_{21}O_{6.5}$	3.0	0.044	2.20	37.227	385.101
12	K-P-SAA(2)	$C_{17}H_{25}O_{7.5}$	4.0	0.049	6.57	127.385	395.691
13	K-P-SAA(3)	$C_{21}H_{33}O_{9.5}$	6.0	0.056	5.80	140.811	433.532
14	K-P-SAA(5)	$C_{29}H_{50}O_{14}$	10.0	0.047	4.13	142.714	735.220
15	K-P-SAA(10)	$C_{43}H_{77}O_{20.5}$	17.0	0.040	3.38	172.943	1279.166
16	K-P-Hb(1)	$C_{15}H_{23}O_{7.5}$	3.0	0.042	1.86	33.376	427.248
17	K-P-Hb(2)	$C_{17}H_{28}O_9$	4.0	0.045	2.51	52.431	464.197
18	K-P-Hb(3)	$C_{21}H_{36}O_{11}$	6.0	0.047	2.44	62.897	548.463
19	K-P-Hb(5)	$C_{29}H_{54}O_{16}$	10.0	0.050	2.34	85.540	731.111
20	K-P-Hb(10)	$C_{41}H_{80}O_{23}$	16.0	0.047	2.71	141.521	1111.111

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(*Received*: 8 March 2005; *Accepted*: 26 September 2005) AJC-4422