Determination of Molar Solubility and Swelling Degree mole of the Polyster Polyols in Water, Saline, Cu(II) and Urea Solution as Swelling Agents

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Previous works on poly(vinyl alcohol) (PVA) has effect on its swelling. Its hydroxyl groups have been studied as swollen elastic networks and as water sorbents. Various polymers have been prepared from PVA and different acids such as anthranilic acid, amino acetic acid and *p*-amino benzoic acid and studied for their solubility and swelling properties to correlate them with various structural factors. These polyster-polyols have been studied for solubility and swelling in water, saline, Cu(II) and urea solutions for the purpose of comparing solubility with structural characteristics. Molar solubility decreases with increase in hydroxyl groups. The swelling degree mole (g/g) is calculated, It was observed that, these values are increasing with increase in hydroxyl groups.

Key Words: Poly(vinyl alcohol), Anthranilic acid, Amino acetic acid, *p*-Amino benzoic acid, Solubility, Swelling degree.

INTRODUCTION

Various polymer have been prepared from poly(vinyl alcohol) and studied for their solubility and swelling in different swelling agents[1-5]. Poly(vinyl alcohol) (PVA) hydro gels have been studied as swollen elastic networks and as water sorbents[6,7]. Vasno and Ichiro[8] prepared a wide range of poly(vinyl alcohol) films and studied their solubility and swelling properties and correlated them with various structural factors. Previous work on PVA has effect on its swelling property[9]. Such study can help in evaluating the utility of products in soil, lenses, lubricants, *etc*. Cross-linked poly(vinyl alcohol) gets exhibited increase in swelling with reticulation degree up to a certain limit after which higher reticulation degree decreases swelling capacity[10]. Swelling studies performed at room temperature using water, dilute solutions of NaCl (saline), Cu(II) and urea as swelling agents[11]. The effect of sorption, repeated sorption and desorption on solubility and swelling properties of polyster resins was studied[12]. Determination of degree of

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swelling is used in practice for testing finished polymer articles intended for service in liquid and gaseous media. It also serves as promising method of assessing the degree of cross linking, the degree of hydration, *etc*. Degree of swelling can be determined only for polymers with limited swelling, because upon unlimited swelling, the polymer itself begins to dissolve. Naito *et al.*[13] studied the relation between swelling and solubility of PVA films and evaluated limited degree of swelling at zero concentration of dissolved film.

EXPERIMENTAL

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 anthranilic acid (ANA), amino acetic acid (AAA) and *p*-amino benzoic acid (4-ABA) chlorides. These products were studied for swelling and solubility in water and dilute solution of sodium chloride, Cu(II) and urea. The solubility (g/mL) and the swelling degree (g/g) were studied in each solvent as swelling agent. The result obtained for solubility (g/mL) and swelling degree (g/g) of each swelling agent are presented in Tables 1 and 2, respectively. It has been observed that the values of degree of swelling and solubility show gradation in each service in general. The relation between the degree of swelling and solubility was studied for PVA films and evaluated. Further, molar solubility (g mol/mL) and swelling degree mole (g/g) are calculated.

TABLE-1
SOLUBILITY (g/mL) OF THE POLYSTER-POLYOLS IN DIFFERENT SWELLING AGENTS

Product	Water	NaCl solution	Urea solution	Cu(II) solution
K-P-ANA(1)	0.0367	0.0278	-	0.1170
K-P-ANA(2)	0.0411	0.0241	-	0.0120
K-P-ANA(3)	0.0399	0.0231	0.0280	0.0100
K-P-ANA(5)	0.0380	0.0172	0.0255	0.0150
K-P-ANA(10)	0.0378	0.0181	0.0186	0.0840
K-P-AAA(1)	0.0625	0.0236	-	0.0854
K-P-AAA(2)	0.0482	0.0237	-	0.0670
K-P-AAA(3)	0.0510	0.0259	0.0310	0.110
K-P-AAA(5)	0.0410	0.0213	0.0258	0.0680
K-P-AAA(10)	0.0431	0.0210	0.0230	0.0640
K-P-4-ABA(1)	0.0377	0.0171	-	0.0940
K-P-4-ABA(2)	0.0430	0.0261	-	0.0992
K-P-4-ABA(3)	0.0373	0.0232	0.0250	0.0182
K-P-4-ABA(5)	0.0398	0.0234	0.0183	0.0954
K-P-4-ABA(10)	0.0340	0.0193	0.0293	0.0879

TABLE-2
SWELLING DEGREE (g/g) OF THE POLYSTER-POLYOLS IN DIFFERENT SWELLING AGENTS

Product	Water	NaCl solution	Urea solution	Cu(II) solution
K-P-ANA(1)	3.76	2.60	-	1.71
K-P-ANA(2)	4.10	2.40	-	1.24
K-P-ANA(3)	3.80	2.65	2.50	1.05
K-P-ANA(5)	3.90	2.00	1.82	1.20
K-P-ANA(10)	3.75	1.85	1.72	1.55
K-P-AAA(1)	6.49	3.08	-	2.90
K-P-AAA(2)	3.06	2.97	-	2.06
K-P-AAA(3)	3.16	2.36	3.01	2.19
K-P-AAA(5)	3.03	2.23	2.62	1.74
K-P-AAA(10)	3.36	2.66	2.45	1.98
K-P-4ABA(1)	1.79	1.33	-	1.81
K-P-4-ABA(2)	2.96	2.22	-	3.24
K-P-4-ABA(3)	2.87	1.99	2.41	4.23
K-P-4-ABA(5)	2.16	2.28	2.44	3.47
K-P-4-ABA(10)	2.03	1.75	2.10	2.04

RESULTS AND DISCUSSION

The polymeric alcohol-esters in each series have varying proportions of alcohol and ester groups and hence can sorbs water to varying extents[14,15]. But as increasing esterification takes place, solubility in water decreases and polymer swells in water. The cross-linked K-P-ANA, K-P-AAA and K-P-ABA samples containing PVA were prepared. 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_{AS} indicating that salt was not sorbed by the sample during the sorption process. The exclusion of the salt by product can be of technological importance. It also observed that the presence of salt lowers degree of swelling and solubility of the sample[16]. Sorption studies of some of these polyster-polyols from urea and Cu(II) solution have been carried out. The solubility in different solution in general observed in decreased order.

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

The degree of swelling (DS) is usually calculated by the relation

$$\text{Degree of swelling (DS)} = \frac{W_{As} - W_{BS}}{W_{BS}}$$

where W_{AS} is the weight of the sample after sorption and W_{BS} is the weight of the sample before sorption. The values so obtained are presented in Table-3.

TABLE-3
MOLAR SOLUBILITY (g mol/mL) OF THE POLYSTER-POLYOLS IN DIFFERENT SWELLING AGENTS

Product 10^{-5}	Water 10^{-5}	NaCl 10^{-5}	Urea 10^{-5}	Cu(II) 10^{-5}	X
K-P-ANA(1)	18.91	14.32	-	6.03	0.5
K-P-ANA(2)	15.80	9.26	-	4.61	2.0
K-P-ANA(3)	9.95	5.76	6.98	2.49	5.0
K-P-ANA(5)	6.58	2.98	4.45	2.59	9.0
K-P-ANA(10)	3.50	1.67	1.72	1.72	20.0
K-P-AAA(1)	45.12	17.03	-	6.17	0.5
K-P-AAA(2)	39.83	19.58	-	5.54	0.25
K-P-AAA(3)	38.63	19.62	2.35	8.33	0.5
K-P-AAA(5)	20.70	10.75	1.30	3.43	2.0
K-P-AAA(10)	11.55	5.63	6.16	1.72	6.0
K-P-4-ABA(1)	19.43	8.81	-	4.85	0.5
K-P-4-ABA(2)	13.19	8.00	-	3.04	3.5
K-P-4-ABA(3)	9.30	5.78	6.23	4.53	5.0
K-P-4-ABA(5)	6.89	4.05	3.17	1.65	9.0
K-P-4-ABA(10)	3.15	1.78	2.71	0.81	20.0

In present studies, 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

$$\text{Molar solubility (g mol/mL)} = \frac{\text{Solubility (g/mL)}}{W_{F(a)}} \quad (1)$$

where $W_{F(a)}$ = formula weight of product.

These values of molar solubility are presented in Table-3 for each series of products. It was observed that, molar solubility decreases with increase in hydroxyl groups (X). The value of swelling degree mole are calculated using formula and are presented in Table-4.

TABLE-4
SWELLING DEGREE (g/g mol) OF THE POLYSTER-POLYOLS IN DIFFERENT SWELLING AGENTS

Product	Water	NaCl	Urea	Cu(II)	X
K-P-ANA(1)	729.44	504.40	-	332.00	0.50
K-P-ANA(2)	1066.00	624.00	-	322.40	2.00
K-P-ANA(3)	1523.80	1062.65	1824.55	421.10	5.00
K-P-ANA(5)	2250.30	1154.00	1050.14	692.40	9.00
K-P-ANA(10)	4046.25	1996.15	1856.00	1673.00	20.00
K-P-AAA(1)	898.87	426.60	-	402.00	0.50
K-P-AAA(2)	370.26	359.37	-	249.10	0.25
K-P-AAA(3)	417.25	311.52	397.00	277.00	0.50
K-P-AAA(5)	599.94	441.54	518.80	345.00	2.00
K-P-AAA(10)	1523.28	992.18	914.00	739.00	6.00
K-P-4-ABA(1)	621.60	258.00	-	351.00	0.50
K-P-4-ABA(2)	965.00	724.00	-	1056.00	3.50
K-P-4-ABA(3)	1150.87	798.00	966.41	1996.00	5.00
K-P-4-ABA(5)	1246.32	1315.56	1408.00	2003.00	9.00
K-P-4-ABA(10)	2190.40	1888.30	2266.00	2201.20	20.00

$$\text{Swelling degree mol (g/g)} = \text{Swelling degree (g/g)} \times W_{F(a)} \qquad (2)$$

It was observed that these values are increasing with increase in (X). This is in accordance with conclusion that increase in hydrophilic group would increase swellable site and hence swellability of these polyster-polyols. It was observed that simultaneous occurrence of swelling and solubility take place in sorption process. It has also been observed that the degree of swelling is lower in salt solution than in water. Swelling in its broader sense is consideration an either limited or unlimited. Swelling by sorption takes place up to a certain limit when further sorption takes place beyond this limit, the substance will solubilize. Another limit would be reached when the substance would get totally dissolved.

From the studies of swelling and solubility of the sample in water, we can evaluate (I) A: number of moles of water required to cause maximum swelling of one of mole of the sample and (II) B: minimum number of 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 formula weight of the sample in anhydrous form.

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