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Solubility of Dialdehyde Starch in Various Dilute Solutions

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HARRY C. ROBERTS¹

Abstract. The solubilities of 93%, 62%, and 5% dialdehyde starch in 0.5% and 1.0% sodium hydroxide; 0.5%, 1.0% and 5.0% borax; and in 0.5%, 1.0% and 5.0% sodium acetate solutions at 55°C for solution times of 15, 30, 60, and 120 minutes were determined as a part of an overall study of DAS-wheat gluten reaction products designed for adhesives. A method for determining the DAS content of solutions from apparent densities was developed.

The results indicate that while any dilute inorganic alkaline solution will probably dissolve DAS the choice of reagent will depend upon what is desired in solution time, chain length of the DAS in solution, and viscosity of the solution.

Dialdehyde starch is formed by the selective oxidation of 1,2 glycol groups in starch by periodate ion. It was developed through the pilot plant stage by the Northern Utilization Research and Development Division, U.S.D.A., Peoria, Illinois, (1) (3) (5) as part of their studies on the utilization of agricultural products. The current studies on the solubility of dialdehyde starch (DAS) are a part of a project on reacting DAS and wheat gluten to form adhesives. While the solubility data are necessary for this project they are also needed for other studies utilizing DAS.

The formula for DAS is shown in Figure 1. Three oxidation levels of DAS were available: 93%, 62%, and 5%. The percent oxidation refers to the number of dialdehyde units per 100 repeating units. The experimental work was in two parts: development of a method for determining the amount of DAS in

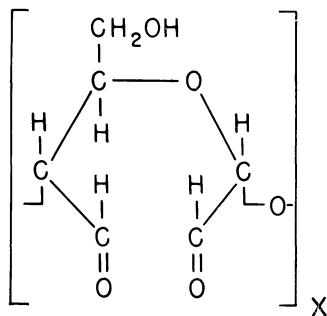


Figure 1. Dialdehyde Starch Formula.

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a solution and the determination of the solubility of DAS in dilute solutions of sodium hydroxide, borax, and sodium acetate.

SOLUTION ANALYSIS

Four published techniques for the determination of oxidation levels of DAS were considered as possible methods for determining the DAS contents of solutions. These methods were:

(1) Complete oxidation of the sample with periodate and determination of periodate consumed (6). This method cannot be applied to solutions since the unoxidized portion of the starch may not be soluble to the same extent as the oxidized portion.

(2) Quantitative reduction of carbonyl groups by sodium borohydride (6). This method is adaptable but very time consuming.

(3) Conversion of p-nitrophenyl hydrazine to insoluble p-nitrophenyl hydrazone by the carbonyl groups (7). This method is adaptable but also very time consuming.

(4) Quantitative alkali consumption (4). This method is fast and can be applied but can give misleading results since the consumption of alkali is in the ratio of one mole of alkali to one mole of dialdehyde for only a short period of the reaction. The relation between temperature and reaction time is very critical.

It should be possible to calculate the amount of DAS in a solution from density data using the apparent molal volume concept. The apparent molal volume (2) is defined by the relation

$$\theta_v = \frac{v - n_1 v_0}{n_2} \quad (\text{T,P constant}) \quad (1)$$

where

θ_v = apparent molar volume; v = volume of solution containing n_1 moles solvent, n_2 moles solute; v_0 = volume of pure solvent at given T,P. When molal concentrations are used it is defined (2) by the equation

$$\theta_v = \frac{1}{m} \left[\frac{(1,000 + mM_2)}{d_3} - \frac{1000}{d_2} \right] \quad (2)$$

when $n_2 = m$, the molality, and n_1 is the number of moles of solvent in 1000g. of solvent, $d_2 =$ density of pure solvent, $d_3 =$ density of solution.

If there is essentially no heat of reaction and the partial molal enthalpy is constant, the partial molal volume is constant. This is true for the sodium acetate and the sodium borate solutions

used and for very dilute sodium hydroxide solutions. The apparent density of dialdehyde starch in solution is

$$d_1 = \frac{161}{\theta_v} \tag{3}$$

The following equations are solved simultaneously

$$v_1 d_1 + v_2 d_2 = 100 d_3 \tag{4}$$

$$v_1 + v_2 = 100 \tag{5}$$

giving
$$v_1 = \frac{100 d_3 - 100 d_2}{d_1 - d_2} \tag{6}$$

The concentration of the solution is

$$\% \text{ DAS} = \frac{d_1 v_1}{100 d_3} \times 100 \tag{7}$$

Six samples each of 62 and 93% DAS were dissolved in water to produce solutions of known DAS contents covering a range of approximately 2 to 21%. Densities were determined by a pycnometer. The apparent density was then calculated using Equations 2 and 3. The average apparent density was 1.6442 g. per cc and the average deviation was ± 0.0342 . A representative cross section of checks made on this method by the alkali consumption method is shown by the data in Table 1.

Table 1. DAS Concentrations by the Apparent Density and Alkali Consumption Methods*.

DAS Oxidation Level %	DAS Concentration, %	
	Density Method	Alkali Method
62	9.34	10.99
	12.95	12.19
	18.20	19.68
	18.50	18.78
93	5.62	5.99
	5.98	5.98
	8.03	8.73
	8.62	9.41
	14.84	14.71
93	15.79	16.85
	18.83	19.42
	19.59	19.95
	19.66	18.24
	21.18	22.22
	21.25	21.85

* Random checks on DAS in various solvent solutions.

SOLUBILITY DETERMINATIONS

One hundred milliliter amounts of solvent solution were added to weighed amounts of DAS in 250 ml beakers. The mixtures were stirred by hand to insure complete wetting of the sample.

They were then placed in a constant temperature water bath and stirred mechanically at a constant rate for a definite time. Water was added at the end of the time interval to compensate for evaporation and pH readings taken. After centrifuging, viscosity and density analysis data were made on the solution. DAS content was determined by the density method with random sample checks by the alkali consumption method.

The following aqueous solutions were used as solvents: 0.05% and 0.10% sodium hydroxide; 0.05% 1.0%, and 5.0% borax; and 0.5%, 1.0%, and 5.0% sodium acetate. Solubility data for 93% DAS in 0.05% sodium hydroxide are shown in Table 2.

Table 2. Solubility of 93% DAS in 0.05% Sodium Hydroxide Solutions.

DAS added gr./100ml	Solution time, min.	Solution Properties			DAS Content %
		pH	Density g/cc	Viscosity cp	
5	15	7.0	1.0140	0.886	4.43
10		6.7	1.0307	1.034	8.47
15		6.6	1.0431	1.199	11.39
20		6.5	1.0503	1.418	13.05
25		6.3	1.0540	1.563	13.89
30		5.8	1.0501	1.689	13.00
5	30	6.2	1.0141	0.899	4.45
10		6.0	1.0303	1.038	8.37
15		5.9	0.0446	1.239	11.73
20		5.7	0.0568	1.638	14.53
25		5.5	1.0615	1.979	15.59
30		5.1	1.0554	2.009	14.21
5	60	6.1	1.0147	0.896	4.60
10		5.7	1.0311	1.047	8.56
15		5.6	1.0451	1.248	11.85
20		5.6	1.0600	1.750	15.25
25		5.5	1.0650	2.315	16.37
30		5.0	1.0542	2.040	13.93
5	120	5.8	1.0165	0.916	5.04
10		5.6	1.0320	1.063	8.78
15		5.3	1.0455	1.249	11.94
20		5.3	1.0624	1.854	15.79
25		5.2	1.0616	2.394	15.61
30		5.0	1.0621	2.625	15.72

DAS dissolves rapidly in dilute sodium hydroxide solutions. The general pattern followed by both 0.5% and 0.10% sodium hydroxide for the three oxidation levels of DAS is very similar to that for 0.05% solution and 93% DAS shown in Table 2. Very little additional solubility was gained by a longer solution time than 15 minutes. Apparently solution occurred after the alkali degraded a small part of the starch producing acids, such as glycolic and formic, which are the actual solvents. If the concentration of alkali is kept small the degradation is not sufficient to

break down the starch chains enough to lower the viscosity appreciably.

When sodium acetate solutions were used as solvents the DAS dissolved more slowly going through a definite gel stage. As the result of the slow reaction there was apparently less breakdown of the starch chain with resulting higher viscosities than with sodium hydroxide. Under some conditions solid cakes rather than solutions were obtained with sodium acetate solutions. These tended to break up and go into solution with increased solution time. When borax solution was used the solubility pattern fell between sodium hydroxide and sodium acetate solutions.

The type of reagent solution best suited for dissolving DAS depends upon the type of DAS solution desired. If a product of minimum degradation and high viscosity is needed a reagent such as sodium acetate is indicated. If more rapid solution and a lower viscosity with accompanying degradation are desired sodium hydroxide solutions are good solvents. Apparently the amount of degradation can be controlled by the concentration of sodium hydroxide used. Probably any inorganic alkaline solution of proper concentration can be used as a solvent for DAS.

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