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Kinetics of Rheological Properties of Acacia Solutions

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Abstract □ The kinetics of the rheological properties of acacia solutions prepared from two different lots of USP grade acacia were investigated with respect to preservative, temperature, and pH. A rotating viscometer was used to measure the viscosity of samples stored at 40, 50, 60, and 70° for up to 6 weeks. Solutions were prepared using benzoic acid as a preservative. Control solutions containing no preservative were also studied. An analog computer was used to analyze the viscosity and time. An Arrhenius-type relationship was established for the apparent first-order rate constants.

Keyphrases □ Acacia solutions—rheological properties □ Rheological properties, acacia solutions—kinetics □ Temperature, aging effects—acacia solutions, viscosity □ Preservative effects, acacia solutions—rheological properties

It was reported that solutions of acacia undergo a change in viscosity with time (1-4). Taft and Malm (1) found that bacterial growth lowered the viscosity of acacia solutions, while Osborne and Lee (2) reported that unpreserved acacia solutions exhibited a greater decrease in viscosity with aging than did acacia solutions preserved with 0.2% benzoic acid. Joslin and Sperandio (3) studied the effect of temperature and method of preparation on acacia solutions. They reported that the temperature of the water used to prepare the solutions affected the viscosity of the acacia solutions. They also reported that storage temperature affected the change in viscosity.

More recently, Araujo (4) studied the effects of certain preservatives on the aging characteristics of acacia solutions for a period of 1 year; he reported that acacia solutions, in a range of 10-25% by weight, behaved as Newtonian systems. He observed that the viscosity of all preserved and unpreserved acacia solutions decreased

with aging. After 6 weeks at room temperature, the reduction in viscosity of the acacia solutions appeared to follow a zero-order process.

The literature contains very few kinetic studies on change of viscosity of aqueous solutions of gums. Levy and Schwarz (5) characterized the viscosity reduction of tragacanth solutions as a zero-order process, while Tobolsky (6) reported that the degradation of most linear polymers followed a first-order process.

Acacia in solution can be hydrolyzed by using sulfuric acid (7) or by heating the solution for a period of time (8, 9).

One report indicated the possibility of a relationship between viscosity and molecular weight of acacia (10). An earlier investigation indicated that acacia with a molecular weight of 280,000 may be split into fragments with molecular weights of less than 10,000 after autohydrolysis for 1 day (11). This combined information seemed to imply that there might be a change in viscosity upon hydrolysis which may be related to the change in molecular weight. Therefore, it seemed reasonable that the rate of change in viscosity might be related to the rate of hydrolysis of acacia.

If bacterial growth affects the viscosity of acacia solutions, the rate of viscosity change might also be affected by the rate of bacterial growth. Araujo (4) speculated that the rate of bacterial decomposition of acacia solutions stored at room temperature appeared to decrease after a period of 6 weeks.

Since the greatest decrease in viscosity of acacia solutions appeared to occur in the first 6 weeks (3, 4), the kinetics of the rheological properties of acacia solutions over this initial time period warranted investigation,

Table I—Mean and Range of Nine Viscosity Determinations of Acacia Solutions

Lot	Weeks	0.2% Benzoic Acid at				No Preservative at			
		40°	50°	60°	70°	40°	50°	60°	70°
Mean and Range of η, cps.									
1	0	74.5	74.6	71.0	66.3	74.8	72.4	70.8	69.0
		72.5-76.7	73.3-75.8	70.0-72.7	65.2-67.5	72.6-77.5	70.7-74.1	69.0-72.3	66.9-71.0
	1	72.1	67.9	60.9	51.7	68.7	68.1	59.4	51.1
		70.4-73.6	66.4-69.3	59.4-61.9	51.0-52.3	67.5-70.1	66.8-69.3	58.2-60.5	50.1-52.3
	2	65.7	59.6	52.2	47.2	65.7	61.9	53.1	48.9
		64.9-66.6	57.1-61.6	50.5-53.4	46.2-47.9	64.3-67.5	61.0-62.7	51.8-54.0	47.5-50.3
	3	61.0	55.8	47.3	41.9	60.8	56.4	47.3	44.1
		60.1-62.1	54.5-56.8	45.3-48.2	40.9-43.4	59.7-62.1	54.0-57.5	45.7-48.5	42.5-45.5
	4	61.4 ^a	53.4 ^a	45.6 ^a	35.8	54.6	52.1	43.7	39.7
		60.4-62.3	52.6-54.0	45.0-46.0	32.7-38.6	51.4-56.6	49.2-53.8	40.5-45.3	38.3-41.4
	5	58.2 ^a	49.7	46.0	34.9	54.5 ^a	49.9	44.2	38.5
		57.4-58.8	49.2-50.1	44.1-47.7	33.3-36.2	54.0-54.7	49.4-50.5	43.0-45.7	36.4-39.9
6	55.0	49.4	41.5	31.8 ^a	50.1	48.7	43.2	36.1	
	54.3-55.5	48.6-50.1	40.7-42.3	30.5-33.3	49.2-50.8	47.9-49.9	42.3-43.9	34.3-37.9	
2	0	55.2	54.9	53.1	51.5	55.6	54.7	53.8	53.6
		54.2-57.1	53.6-56.2	51.8-54.2	49.2-52.9	54.3-57.1	53.6-56.2	52.9-54.9	53.0-54.5
	1	52.9	51.4	47.8	42.7	48.1	50.8	49.3	43.4
		52.4-53.6	51.0-52.1	47.5-48.1	41.8-44.4	47.5-49.2	50.1-52.1	48.8-49.8	43.1-43.7
	2	49.1	46.9	43.0	35.6	43.9	48.5	45.3	37.5
		46.6-50.4	44.9-48.2	42.5-43.6	34.4-36.2	42.9-44.9	47.7-49.1	44.2-46.2	35.7-38.9
	3	49.2	45.0	38.5	30.7	38.9	44.4	39.7	34.5
		47.9-50.3	43.6-45.7	34.8-39.5	27.4-33.4	37.9-40.1	43.1-45.2	37.0-41.4	30.5-36.6
	4	46.9 ^a	39.5	32.8	25.8	33.0	40.5	36.8	31.3
		46.2-47.5	34.4-43.6	26.6-37.3	21.8-28.3	30.1-35.6	38.3-43.3	32.7-39.6	28.6-33.5
	5	44.5	41.4	36.4	30.3 ^a	35.0 ^a	41.0	38.0	31.3 ^a
		43.7-45.3	40.9-41.8	35.6-37.5	28.9-31.9	34.6-35.3	40.3-41.6	37.4-38.8	30.5-31.8
6	44.5	40.2	34.0 ^a	25.8 ^a	31.9 ^a	41.6	36.1	28.9 ^a	
	42.7-45.7	39.2-40.9	33.5-35.0	25.4-26.1	31.4-32.2	40.8-42.0	35.4-36.4	28.5-29.0	

^a Six determinations of viscosity were made.

with the following objectives:

1. To determine the relationship between the change in viscosity of acacia solutions and storage time.
2. To determine the effect of preservative on the rate of change in viscosity of acacia solutions.
3. To determine the effect of storage temperature on the rate of change in viscosity of acacia solutions.
4. To determine the effect of lot variation on the parameters studied.

EXPERIMENTAL

Preparation of Acacia Solutions—All acacia solutions were prepared in the same manner. Distilled water (2400 ml.) containing the appropriate amount of preservative was heated until dissolution

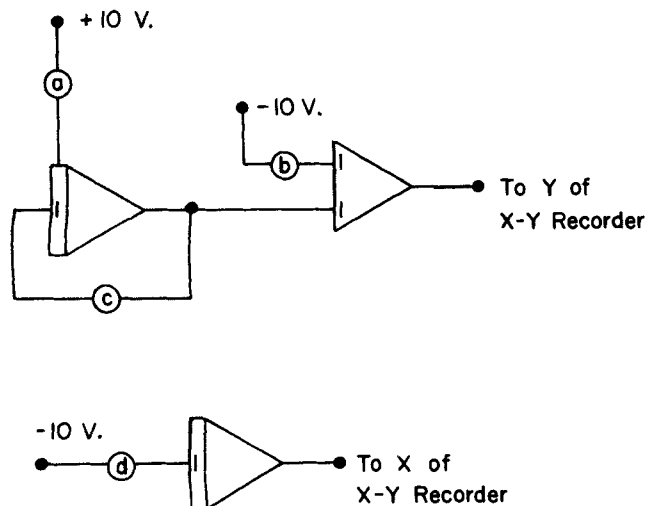


Figure 1—Analog computer program for fitting viscosity versus time data.

was effected. The preservative solution was cooled at 60° and placed in a blender¹. Eight hundred grams of acacia USP was added, and the mixture was blended at low speed for 1 min. in order to prepare a 25% by weight solution. The acacia solutions were allowed to stand for 1 day to permit complete hydration of the acacia. The solutions were then placed in 50-ml. serum vials. The vials were sealed, using rubber stoppers and aluminum closures.

All acacia used came from two lots which met the USP requirements for acacia powder; they are designated as Lots 1² and 2³.

Preservative Used—Two sets of acacia solutions with respect to preservative were prepared in this study. One contained no preservative, and the other contained 0.2% by weight of benzoic acid USP.

Temperature and Time Studies—The samples were divided and placed in four constant-temperature water baths set at 40, 50, 60, and 70°. These temperatures were maintained within ±0.5°. At given times, the samples were taken from the water baths, cooled, and measured rheologically; the pH was determined also.

Rheological Measurements—All rheological measurements were

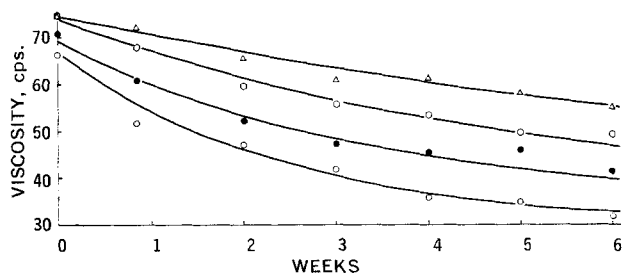


Figure 2—Viscosity stability at different temperatures of acacia solutions from Lot 1 containing benzoic acid. Key: Δ , 40°; \circ , 50°; \bullet , 60°; and \circ , 70°.

¹ Waring Blendor, model CB5.
² Fisher Scientific Co.
³ Stein Hall and Co.

Table II—Values of k and η_{∞} Calculated from Computer Data

Lot	Preservative	Temperature	k , weeks ⁻¹	η_{∞} , cps.
1	Benzoic acid	40°	0.104	32.8
		50°	0.184	33.1
		60°	0.296	33.6
		70°	0.418	29.7
	None	40°	0.146	33.5
		50°	0.170	33.5
		60°	0.308	35.0
		70°	0.436	34.1
2	Benzoic acid	40°	0.084	25.2
		50°	0.126	24.6
		60°	0.226	25.9
		70°	0.430	24.7
	None	40°	0.258	25.9
		50°	0.138	26.5
		60°	0.192	26.7
		70°	0.426	26.6

made with a rotational viscometer⁴ equipped with a dual measuring head which allows a greater range of viscosity measurements.

The temperature of the sample was maintained at $25 \pm 0.2^\circ$ using a constant-temperature circulator⁵. All samples were measured using rotary bob MV I and beaker MV supplied with the viscometer; either six or nine determinations were made for each sample, the number depending on the limitations of the viscometer.

Viscosity, η in cps., was calculated from Eq. 1:

$$\eta = K \times U \times S \quad (\text{Eq. 1})$$

where K is an instrumental constant dependent on the rotary bob and the measuring heat setting, U is the instrument setting which controls the revolutions per minute of the rotary bob, and S is the normal scale reading of the instrument. The mean and the range of the six or nine determinations of viscosity were used for analog computer analysis and are given in Table I.

pH Measurements—All pH measurements were made on a research pH meter⁶ immediately after the viscosity determination.

Data Analysis—An analog computer⁷ equipped with an X-Y recorder⁸ was used to analyze the rheological data. An output of 1 v. on the ordinate was equivalent to 10 cps. of actual data, and 1 v. on the abscissa was equivalent to 1 sec. of computer time which was equivalent to 1 week of actual data.

RESULTS AND DISCUSSION

Time Studies—In this study, as seen in Table I, the viscosity of acacia solutions was determined at intervals up to 6 weeks for all samples. In all cases, the viscosity appeared to decrease with increasing time. However, in some samples, the viscosity decreased to a lesser extent than in others.

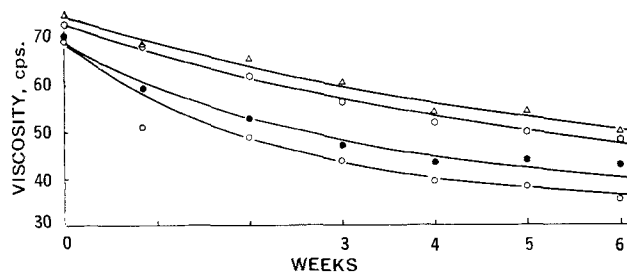


Figure 3—Viscosity stability at different temperatures of acacia solutions from Lot 1 containing no preservative. Key: Δ , 40°; \circ , 50°; \bullet , 60°; and \circ , 70°.

⁴ Haake Rotovisko, instrument 67-369, Polyscience Corp., Evanston, Ill.

⁵ Haake constant-temperature circulator, model Fe.

⁶ Corning model 12-B.

⁷ Pace TR-48, Electronic Associates, Inc.

⁸ Mosely Autograt model 2D-2 X-Y, Hewlett-Packard, Inc.

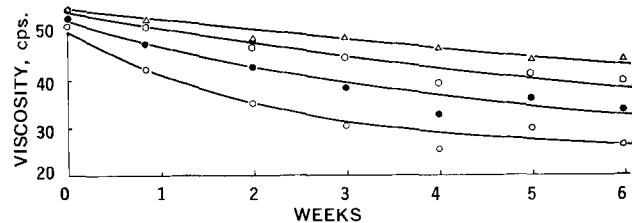


Figure 4—Viscosity stability at different temperatures of acacia solutions from Lot 2 containing benzoic acid. Key: Δ , 40°; \circ , 50°; \bullet , 60°; and \circ , 70°.

In Lot 1, the greatest decrease in viscosity was exhibited by the sample containing benzoic acid stored at 70°. It decreased a total of 34.5 cps. over 6 weeks, while the sample containing benzoic acid stored at 40° exhibited the smallest decrease, 19.5 cps.

In Lot 2, the sample containing the preservative stored at 70° also exhibited the largest decrease in viscosity, 25.7 cps. over 6 weeks, while the sample containing preservative at 40° again had the smallest decrease, 10.7 cps., over the same time period.

However, the overall change in viscosity does not provide information as to the path the change takes, *i.e.*, whether the change is slow and then fast or vice versa. By sampling at given times and using appropriate methods, the rate of the decrease may be measured.

If the viscosity decrease is due to the decrease in molecular weight of acacia, then it would appear that after complete hydrolysis of acacia, the viscosity measured would be the viscosity of a solution of the end-products of the hydrolysis. This would then mean that the viscosity would eventually become constant.

An analog computer was programmed for the model:

$$(\eta - \eta_{\infty}) = (\eta_0 - \eta_{\infty})e^{-kt} \quad (\text{Eq. 2})$$

where η_0 is the initial viscosity, η_{∞} is the viscosity at infinite time, k is the specific rate constant, and t is time in weeks. The program used to simulate Eq. 2 is shown in Fig. 1. The variable potentiometers, a, b, and c, correspond, respectively, to $\eta_0 - \eta_{\infty}$, η_{∞} , and k . Potentiometer d remained constant and corresponds to a constant change in time.

The rheological data were plotted on graph paper, and the graph paper was placed on the X-Y recorder. By adjusting potentiometers a, b, and c, a curve was drawn to fit the viscosity data. The potentiometer readings were recorded and used to calculate η_0 , η_{∞} , and k . The calculated values of η_{∞} and k are given in Table II. The computer-drawn curves for each set of viscosity *versus* time data are shown in Figs. 2-5 and appear to fit the experimental data reasonably well.

The pH of the acacia solutions remained fairly constant, with two exceptions which will be noted later.

The specific rate constants are relatively small, indicating a slow change in viscosity. Since it appears that a first-order relationship exists between viscosity and time, future studies might determine a definite relationship between the rate of hydrolysis of acacia and the rate of viscosity change.

Lot Effects—The most significant difference between the two lots is in the initial viscosities. The average initial viscosity of Lot 1 was 17.5 cps. greater than the average initial viscosity of Lot 2. This difference could possibly be accounted for by differences in the average molecular weight of the acacia due to variation in the natural source of the gum. The variation in molecular weight may be attributed to the composition of the acacia molecule itself. Studies have indicated that the acacia molecule contains D-ga-

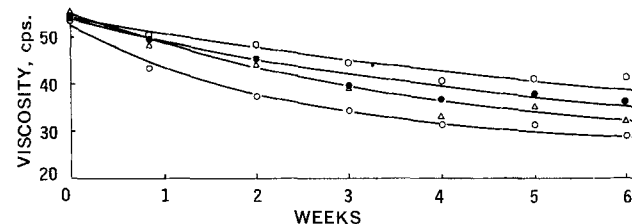


Figure 5—Viscosity stability at different temperatures of acacia solutions from Lot 2 containing no preservative. Key: Δ , 40°; \circ , 50°; \bullet , 60°; and \circ , 70°.

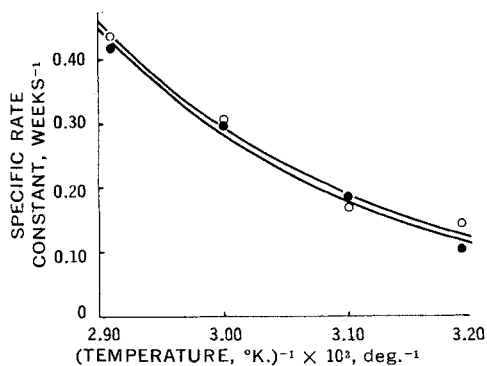


Figure 6—Arrhenius-type plots for specific rate constants of acacia solutions from Lot 1. Key: ●, 0.2% benzoic acid; and ○, no preservative.

lactose, L-arabinose, L-rhamnose, and D-glucuronic acid in varying proportions, depending upon the source of the gum (12–15).

Lot 1 also had a greater η_{sp} than Lot 2, with the average difference being 7.4 cps., which might be explained by the varying proportions of major constituents of the acacia molecule.

Effect of Preservative—When the pH of the acacia solutions was measured, it was noted that the solutions with benzoic acid had an initial pH of 0.15–0.20 pH units lower than the corresponding solutions prepared without benzoic acid. This difference of pH might be attributed to the acidic nature of the preservative.

An unusual result, possibly due to preservative effect, involved the unexpectedly high value of the rate constant for Lot 2 at 40° with no benzoic acid. Since bacterial growth might be favored at 40°, it was thought that the unusually large rate constant could have been caused by bacterial hydrolysis. The pH of this group decreased from 4.14 to 3.67 over the 6-week period. Araujo (4) observed a sharp pH decrease for the first 6 weeks of his study at room temperature, which he attributed to bacterial attack.

However, if bacterial attack caused the inconsistency in the rate constant, then it appears that there would have been a disagreement in the rate constant for Lot 1 at 40° with no benzoic acid. This discrepancy is not evident by comparing the rate constants in Table II. However, a similar decrease from 4.11 to 3.69 pH units was also observed for this group. Therefore, no definite conclusion can be drawn to account for the inconsistency of the rate constant for Lot 2

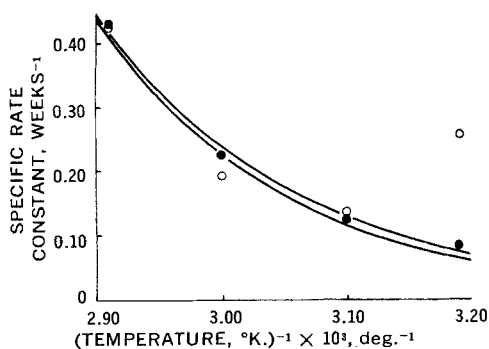


Figure 7—Arrhenius-type plots for specific rate constants of acacia solutions from Lot 2. Key: ●, 0.2% benzoic acid; and ○, no preservative.

Table III—Values of E_a Calculated from Computer Data

Lot	Preservative	E_a , kcal./mole
1	Benzoic acid	9.4
	None	8.7
2	Benzoic acid	12.4
	None	13.2

at 40° with no benzoic acid. However, an analysis of variance of the rate constants shows no significant effect of preservative on the rate of change in viscosity of the acacia solutions.

Effect of Temperature—The effect of temperature on the specific rate constants is highly significant. Therefore, an analysis of the effect was made using an Arrhenius-type equation:

$$k = Ae^{-E_a/RT} \quad (\text{Eq. 3})$$

where T is the absolute temperature, R is the gas constant, E_a is the energy of activation, and A is a preexponential factor. The rate constant–temperature data were analyzed by the analog computer. The computer plots are shown in Figs. 6 and 7.

The values for E_a were calculated for the rate constant change and are given in Table III. At the present stage of rheological scientific development, it is difficult to interpret the significance of this Arrhenius-type plot. Thus, E_a may or may not be related to the energy of activation for the hydrolysis of acacia. However, the fact that an Arrhenius-type relationship seemed to exist cannot be overlooked. It seems plausible to assume that the first-order rate for viscosity change may have a definite relationship to the rate of hydrolysis of acacia.

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