[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

Viscosities of Pectin Solutions

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More information on the physical properties of pectin (primarily a long chain, partially esterified polymer of galacturonic acid) is desired to assist in its evaluation for new uses to which it may be adapted, particularly in the field of pharmaceuticals. Among these properties, viscosity is one of the more important. In recent years perception of the relation of viscosity to the relative weight, size, and shape of dissolved molecules has been greatly increased. In addition, many practical applications, such as formation of gels, are directly related to viscosity.

An examination of the factors that influence the viscosity of aqueous pectin solutions has been considered necessary because the data in the literature are conflicting. Many of the pectins used have been contaminated with mineral matter and the purification procedures applied have degraded the material. Furthermore, data on some of the factors, such as the influence of temperature, are lacking. No complete examination of the viscosity behavior of solutions of a single, purified pectin has been published. This report is concerned with the effects of (1) concentration, (2) change of *p*H, (3) presence of sodium chloride or urea, and (4) temperature changes, on the viscosities of aqueous solutions of purified apple and citrus pectins. A further purpose is to attempt to establish conditions useful for the determination of the molecular weights of pectins in aqueous solutions by the viscometric method.

Experimental

Pectins.—The pectins used were a commercial citrus pectin,[1a] a commercial apple pectin,[2] and a degraded citrus pectin. The two commercial pectins were de-ashed in this Laboratory before use. This was accomplished by means of ion exchange resins[3] rather than by electrodialysis since the latter was found to be slow and to alter the pectin. Pectins were recovered from the de-ashed solutions by precipitating with 4 volumes of ethanol, dehydrating in ethanol, and drying *in vacuo* overnight at 70°. The dried pectin was ground in a Wiley mill to pass a 60-mesh screen and redried before use. The degraded citrus pectin was obtained by autoclaving a 3% solution of de-ashed citrus pectin for twenty minutes at 119°. The cooled solution was filtered through a coarse Mandler filter, and the pectin was precipitated and dried as just described.

Analytical data on the pectins, including the unmodified commercial citrus pectin, are given in Table I. The methoxyl content was determined by the saponification method of Hinton.[4] Equivalent weights were obtained by electrometric titration with standardized sodium hydroxide. The difference in equivalent weight values for the commercial pectin before and after de-ashing emphasizes the important influence of mineral constituents on such determinations. Anhydrogalacturonic acid contents, calculated from the equivalent weights and methoxyl contents, showed about 10% of the pectin unaccounted for as ester groups and anhydrogalacturonic acid residues in the de-ashed samples. No attempt was made to determine the nature of this material.

TABLE I

ANALYTICAL DATA ON THE PECTINS USED

Pectin	Ash, %	Me O, %	Anhydrogalacturonic acid, %	Equivalent weight	$[\alpha]^{25}\text{D}$
Commercial citrus	0.7	10.7	..	1100	230
De-ashed citrus	.2	10.7	85	720	230
Degraded citrus	.8	10.7	..	740	246
De-ashed apple	.2	10.9	84	830	233

Spectroscopic examination of the ash of the commercial citrus pectin showed that it contained mainly silicon, calcium, aluminum and sodium but was free of arsenic and practically free of lead. The ash from the degraded pectin was similar except that the silicon content was greatly reduced while the magnesium content was increased. Apparently, the Mandler filters removed siliceous materials but contributed metallic ions to the degraded pectin. Analyses of the ashes from pectins passed only through the ion exchange resins showed 75% siliceous material.

Viscosity Measurements.—Ostwald-Cannon-Fenske[5] pipets and an Ostwald pipet were used. The pipet for each solution was chosen so that the kinetic energy correction was less than 0.1% and the time of efflux was less than four hundred seconds. The pipets were calibrated with water, oils from the National Bureau of Standards, glycerol[6] and sucrose[7] solutions of known compositions. The introduction of equal volumes of solution into the viscometers maintained consistent hydrostatic heads. Time intervals were measured with stopwatches or electric timers reading to one-tenth of a second.

Pectin solutions were prepared by pouring water upon the weighed sample in a weighed beaker or by sprinkling the sample on water while stirring. After the mixture had been stirred from one to three hours, water was added to bring the solution to its desired weight. The solution was stirred vigorously for a short time and then its viscosity was determined in a water thermostat at 25 ± 0.05°. Viscosities at other temperatures known within 0.1° were measured in thermostats or in constant temperature rooms. Values having a maximum deviation of 0.5% of the relative viscosity (η_r) were readily obtained with pectin solutions having concentrations not exceeding 0.3%.[8] Citrus pectin solutions having concentrations between 0.3 and 0.5% gave reproducible results when allowed to stand six to twenty-four hours; at 0.8% concentration the maximum deviation increased to 7%. With apple pectin the maximum deviation increased to 5% as the concentration was increased to 0.7%. Results with different pectin solutions

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[1a] Pectinum, N. F. VII, California Fruit Growers Exchange, Ontario, Calif.

[2] Certo No. 1, General Foods, Inc., Hoboken, N. J.

[3] Amberlite IR-4 and IR-100, Resinous Products and Chemicals Co., Inc., Philadelphia, Pa.

[4] C. L. Hinton, "Fruit Pectins," Chemical Publishing Co., 1940, p. 33.

[5] M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

[6] M. L. Sheely, *Ind. Eng. Chem.*, **24**, 1060 (1932).

[7] E. C. Bingham and R. F. Jackson, *Bull. U. S. Bur. Standards*, **14**, 59 (1917).

[8] Because of statements by H. P. Kortschak [THIS JOURNAL, **61**, 681, 2312 (1939)] and G. Schneider and U. Fritschi [*Ber.*, **69B**, 2537 (1936)] casting doubt on the reproducibility of pectin solutions, considerable attention was paid to this point.

TABLE II

EFFECT OF PECTIN CONCENTRATIONS AND *p*H ON RELATIVE VISCOSITIES OF PECTIN SOLUTIONS

	Relative viscosity at 25°C.						
		De-ashed citrus pectin					
Concentration, g./100 g.	De-ashed apple pectin; *p*H unadjusted	*p*H unadjusted	*p*H 1.5	*p*H 5.5	*p*H 7.5	Degraded citrus pectin *p*H unadjusted	*p*H of unadjusted citrus pectin solutions[a]
0.005	1.089	1.044	..	..	..	1.019	4.30
.01	1.276	1.146	..	..	..	1.028	4.00
.025	1.501	..	1.114	1.361	1.257	1.051	3.70
.05	1.783	1.447	..	..	..	1.089	3.55
.1	2.363	1.738	1.501	2.028	1.918	1.159	3.35
.3	6.498	3.345	3.058	3.880	3.767	1.460	3.00
.5	..	6.272	5.889	6.756	6.604	1.816	2.88
.8	..	13.3	12.9	13.3	13.0	..	2.73

[a] The K_i for citrus pectin varies from 1.6 to 3.0 × 10^{-4} with a change in concentration from 0.025 to 0.8%.

at higher concentrations could not be duplicated within less than 10%, however measurements on a single solution did not have a maximum deviation greater than 0.5% of the relative viscosity. The deviation for the specific viscosity values ($\eta_r - 1$) was within 0.5% for values above 1 but increased to 20% with decreasing concentration of pectin.

When solutions stood for periods longer than three hours, they were placed in a refrigerator to inhibit bacterial action. Addition of substances other than pectin was made during the final dilution. Corrections were made for changes in volume resulting from the addition of other solutes so that viscosities could be compared at similar volume concentrations. The relative viscosities are ratios of the viscosities of pectin solutions to that of the solvent whether the solvent is water or a water solution of sodium chloride or urea.

As a further check on the accuracy of the measurements made on dilute pectin solutions, some observations were made with a Couette viscometer. The design was similar to one by Gurney[9] except that the outer cylinder rotated in a water-bath through which water at constant temperature was circulated. The instrument was calibrated with glycerol solutions.[6] Flow gradients used were from 4.5 to 66.5 sq. cm./sec. which are so low that there is little opportunity for orientation of the pectin molecules. The results agreed with those from the pipets within 0.5% showing that the flow gradients in the capillaries did not cause sufficient orientation of the pectin molecules to affect the results. They also show that the shape and size of the pipets did not influence the results.[10]

Other Tests.—Density determinations were made with a specific gravity bottle having a capacity of about 25 ml. of water at 25.0°. A Beckman *p*H meter was used. All chemicals were C. P. grade, and the ethanol was redistilled to free it from ash.

Results

Effect of Pectin Concentration.—Data for the relative viscosities at different concentrations for aqueous solutions of the de-ashed apple pectin, de-ashed citrus pectin, and the degraded citrus pectin are given in Table II and Fig. 1.

Comparison with pectins of known molecular weights is made in Fig. 1 where some of Säverborn's data[11] are plotted. Results of Baker and Goodwin[12] and of Kortschak[8] follow the same shape of curve which is more complicated than those expressed by the equations of Einstein[13] ($\eta_{sp} = kC$, where C is the concentration), Arrhenius[14] ($\ln \eta_r = kC$), Huggins[15] $\eta_{sp}/C = [\eta]\,(1 + k'\,\eta_{sp})$, where $[\eta]$ is the intrinsic viscosity, the ratio of η_{sp}/C as C approaches zero, and Bingham[16] ($1/\eta_r = kC$).

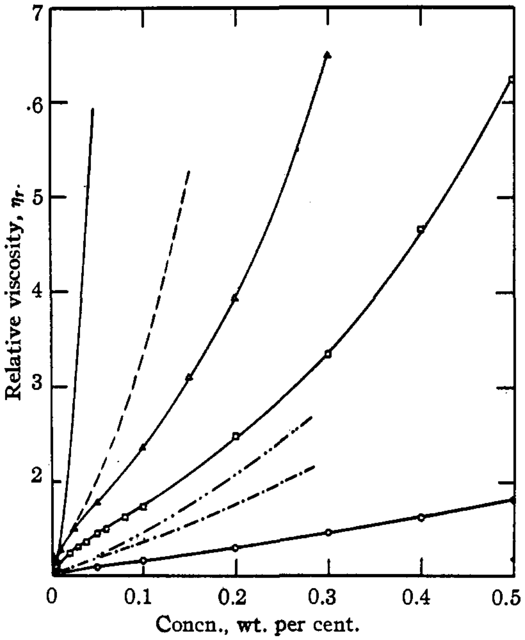

Fig. 1.—Relative viscosity *versus* concentration of various pectin solutions: △, de-ashed apple pectin, □, de-ashed citrus pectin, ○, degraded citrus pectin: ——— a lemon pectin having a molecular weight of 271,000; - - - - an apple pectin having a molecular weight of 99,000; —..—.. an apple pectin having a molecular weight of 55,000; —.—.— a lemon pectin having a molecular weight of 43,000. The data for the last four pectins were obtained from Säverborn's article, ref. 7.

The data for η_r as a function of concentration of the sodium salt of citrus pectin at a *p*H of 7.5 are given in Table II, 6th column. The data

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[9] L. E. Gurney, *Phys. Rev.*, **26**, 98 (1908).

[10] K. B. Rosen [*Bull. Natl. Formulary Com.*, **9**, 35 (1940)] stated that the size and shape of capillary viscometers affected viscosity measurements of pectin solutions. We found that pipets having the same shape but different efflux times, or different shapes and the same efflux time, gave the same results within 0.5%.

[11] S. Säverborn, *Kolloid-Z.*, **90**, 41 (1940).

[12] G. L. Baker and M. W. Goodwin, *Del. Agr. Expt. Sta. Bull.*, 216 (1931).

[13] A. Einstein, *Ann. Physik*, **19**, 289 (1906).

[14] S. Arrhenius, *Medd. Vetenskapakad, Nobel-inst.*, **4**, 13 (1916).

[15] M. L. Huggins, THIS JOURNAL, **64**, 2716 (1942); *Ind. Eng. Chem.*, **35**, 980 (1943).

[16] E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1923.

for the trimethylammonium, ethylenediammonium, 2,2-dihydroxymethylpropylammonium, and tetraethylammonium pectinates are practically identical with those obtained with the sodium pectinate.

Influence of Change in *p*H.—Viscosity results obtained with pectin solutions whose *p*H values were adjusted with hydrochloric or sulfuric acid were the same. Typical data given in Table II and Fig. 2 show that η_r of dilute pectin solutions is reduced to a low value which is nearly constant from *p*H 1 to 2. Sodium hydroxide forms the highly ionized sodium pectinate[17] increasing the viscosity to a maximum near *p*H 6. From *p*H 6 to 8, excess of sodium hydroxide decreases the relative viscosity. Above *p*H 8 the decrease becomes more pronounced and is probably due to alkaline degradation.[18]

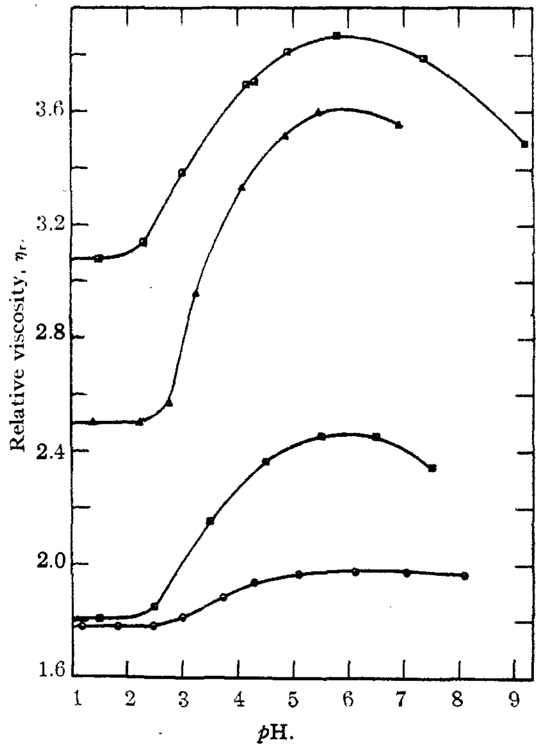

Fig. 2.—Effect of changing *p*H on the viscosity of pectin solutions: ◪, 0.3%; ◩, 0.15%; de-ashed citrus pectin, △, 0.15%; de-ashed apple pectin; ⊖, 0.5% degraded citrus pectin.

The η_r *versus p*H curves for dilute pectin solutions are similar to those obtained by Baker and Goodwin[12] for 0.25 and 0.125% apple pectin, by Edson[19] for 0.25% apple pectin, and by Kortschak[8] for citrus pectin solutions. Myers and Baker[20] and Glikman[21] report maxima at *p*H values other than 6. These results may be attributed to the ash content of the pectins used and to allowing insufficient time for conditions in the solution to reach equilibrium, which would mean that successive solutions were not strictly comparable.

Effect of Sodium Chloride or Urea.—Figure 3 shows the variation of log η_r with concentration for the pectins in 0.9% sodium chloride solution, and are practically identical with those obtained when the *p*H's of the pectin solutions were adjusted to 1.5 with acid. For comparison, curves of pectin solutions with *p*H unadjusted are included in Fig. 3. The curves with urea in concentrations up to 0.5 molal are the same as the latter and are not shown. With 6 molal urea solutions, the relative viscosity of 0.5% pectin is decreased about 9%.

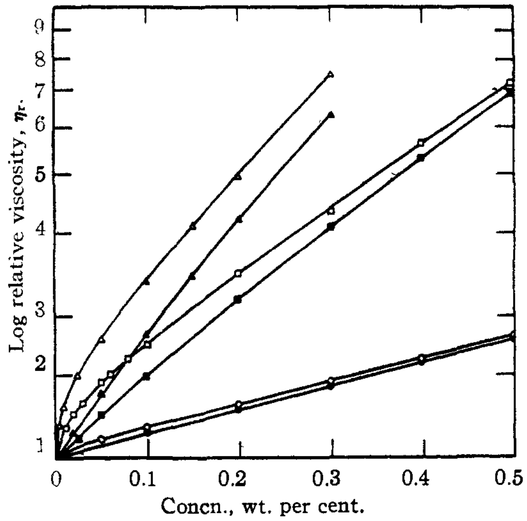

Fig. 3.—Log of the relative viscosity plotted against concentration of various pectins in the absence of salt and in the presence of 0.9% sodium chloride. △ de-ashed apple pectin; ▲, de-ashed apple pectin plus sodium chloride; □, de-ashed citrus pectin; ■, de-ashed citrus pectin plus sodium chloride; ○, degraded citrus pectin; ●, degraded citrus pectin plus sodium chloride.

Since the log η_r *versus C* plots are linear to 0.1% concentration of pectin, following the Arrhenius equation, when the *p*H is near 1.5 or when 0.9% or more sodium chloride is added, the intrinsic viscosity of pectin solutions can be calculated readily from the slopes of the lines.[22] These values can also be obtained by extrapolation of the linear log η_{sp}/C *vs. C* plots. The values calculated from the curves in Fig. 3 are 6.4, 4.2 and 1.2 for the de-ashed apple, the de-ashed citrus, and degraded citrus pectin, respectively. By comparing our results with Säverborn's,[11] the

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(17) R. F. Stuewer, *J. Phys. Chem.*, **42**, 305 (1938).

(18) R. M. McCready, H. S. Owens and W. D. Maclay, results to be published.

(19) L. E. Edson, Ph.D. dissertation, Columbia U., 1928.

(20) P. B. Myers and G. L. Baker, *Del. Agr. Expt. Sta. Bull.*, 149 (1927).

(21) S. Glikman (Glückmann), *Kolloid-Z.*, **60**, 52 (1932).

(22) L. Malsch [*Biochem. Z.*, **309**, 283 (1941); *C. A.*, **37**, 4280 (1943)] has found that viscosity curves for aqueous pectin-salt solutions can be described by the Staudinger equation ($\eta_{sp}/C = Km$, where K is a constant, m is the molecular weight, and C may be expressed in moles of repeating unit per liter).

molecular weights of our pectins appear to be between 70,000 and 80,000 for the apple pectin; between 50,000 and 60,000 for the citrus pectin; and between 20,000 and 30,000 for the degraded pectin. These molecular weights are being determined by independent methods and will be discussed in later papers.

The expanded form of Huggins' equation[15] expresses the data with sodium chloride–pectin solutions. The k' values calculated by the method of least squares are 0.43 for apple, 0.43 for citrus and 0.41 for degraded pectin.

Effect of Temperature Changes.—The variations of η_r with temperature for 0.05, 0.2, 0.5, 0.75 and 1.0% de-ashed citrus pectin and 0.2 and 0.75% de-ashed apple pectin solutions are shown in Fig. 4. At 0.05%, η_r does not vary with temperature; at higher concentrations the temperature coefficient of viscosity becomes increasingly negative. Similar results were obtained with de-ashed apple pectin at other concentrations and with the commercial citrus pectin. At 0.1% concentration and less for these pectins and their sodium or tetraethylammonium salts, η_r is practically independent of temperature from 0 to 50°. This constancy of η_r with temperature for low concentrations is an exception to the general rule that the η_r of hydrophilic colloids decreases with temperature.

Discussion

Knowledge of the structure of pectin and its state in solution is so inadequate that any hypothesis proposed to explain the viscosity behavior of pectin solutions must be considered tentative. A few facts, however, merit attention and will be discussed briefly in the following paragraphs.

The curves of η_r against concentration of pectin, which are shown in Fig. 1, are similar to those obtained with other ionizable hydrophilic colloids, such as gum arabic,[23] agar,[24] and polyacrylic acids,[25] and with certain salts.[26]

In the more dilute solutions, up to about 0.005% concentration of pectin, the slope of the η_r *versus* concentration curve is high and almost constant; in such dilute solutions, the pectinic acid is highly ionized. This could cause any or all of the following changes which would increase the viscosity above that expected for an un-ionized solute: (a) interaction between the solute and solvent, (b) an extension or unfolding of the molecule similar to that postulated by Meyer and Mark[27] for proteins removed from their isoelectric points, (c) an increase in the amount of work required to move one ion relative to another,[28] and (d) other factors comprising the electroviscous effect.

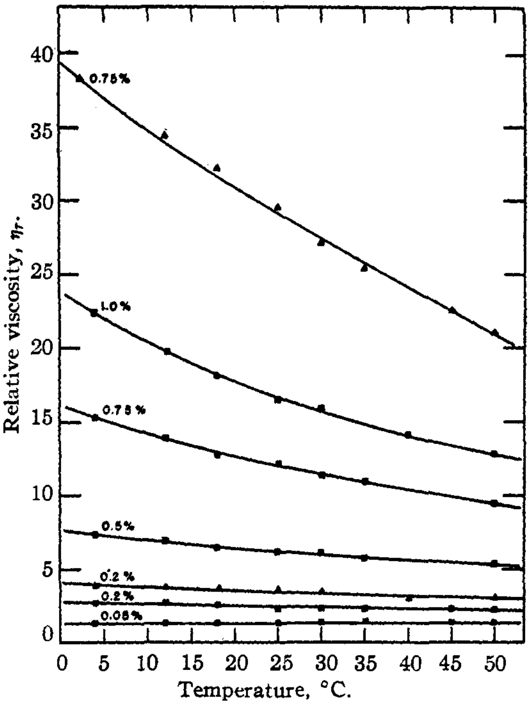

Fig. 4.—Relative viscosities of pectin solutions at various temperatures: ▲, de-ashed apple pectin; ■, de-ashed citrus pectin.

In the next region of concentrations, from 0.005 to approximately 0.1%, the slope of the η_r *versus* C curve decreases. In this region the proportion of ionized pectinic acid decreases. This decrease would be expected to cause a decrease in all of the factors just mentioned. In addition the decrease in the charge on the pectin molecule may permit formation of dimers and trimers in which the molecules are nearly parallel to each other as postulated by Snellman and Säverborn.[29] Association or an increase in folding would cause a decrease in the ratio of the length to the diameter of the dispersed material which would reduce its contribution to the viscosity of the solution.[30]

As the concentration is increased above 0.1%, the slope increases. This may be due to the formation of aggregates which enclose large quantities of solvent. The minimum slope appears at increasing concentration as the intrinsic viscosity of the pectin decreases. It is expected that aggregation would occur less readily with material of lower molecular weight.

The increase in viscosity as pectin is converted to its salt is similar to observations with solutions of other negatively charged hydrophilic colloids. As typical examples, gum arabic[31,32] and carboxy-

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(23) H. R. Kruyt and K. C. Winkler, *Kolloidchem. Beihefte*, **32**, 374 (1931).

(24) H. R. Kruyt and H. B. de Jong, *ibid.*, **28**, 1 (1928).

(25) W. Kern, *Z. physik. Chem.*, **181A**, 283 (1938).

(26) G. Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929).

(27) K. H. Meyer and H. Mark, "High Polymers," Interscience Publishers, Inc., New York, N. Y., **4**, 486–491 (1942).

(28) W. Kern[25] called this an "ionic" effect when explaining the viscosity curves he obtained with polyacrylic acids.

(29) O. Snellman and S. Säverborn, *Kolloid-Beihefte*, **52**, 467 (1941).

(30) For a review of the effect of particle shape on viscosity see M. Lauffer, *Chem. Rev.*, **31**, 561 (1942).

(31) A. W. Thomas and H. A. Murray, *J. Phys. Chem.*, **32**, 676 (1928).

(32) S. A. Schou and J. M. Olsen, *Dansk. Tids. Farm.*, **6**, 6 (1932).

methyl cellulose[33,34] may be cited. When a base is added to pectinic acid solutions the number of ionized carboxyl groups is increased just as it is on dilution. The reasoning applied to the more dilute solutions obtains in this case; that is, there would be an increase in the interaction of the solute and solvent, in unfolding, and in the ionic effect. It is noteworthy that hydroxides of cations as different as sodium and tetraethylammonium ions have practically the same effect on the viscosity. The *p*H effect increases with the intrinsic viscosity, but decreases when the concentration is sufficiently high to cause aggregation.

The decrease in viscosity on adding acid, sodium chloride, or salts of certain cations having hydroxides which do not precipitate in the *p*H range from 3 to 7[12] may be ascribed to a decrease in the charge on the pectin molecule. The factors which are influenced by such a change have already been discussed.

Urea and other organic compounds[35] appear to have little effect on the relative viscosity. If hydration of the pectin molecule is influenced by the presence of such compounds, the effect must be compensated by solvation with the added material so that the relative viscosity remains unchanged.

The decrease in relative viscosity of the more concentrated pectin solutions as the temperature is increased may be attributed to disaggregation and to release of enclosed water.

The weight intrinsic viscosity of pectin solutions is rather high (1.2 to 6.4 for the pectins reported), even when compared to tobacco virus in buffered solution which has a value of 0.6[36] and celluloses in cuprammonium solutions which have values between 3 and 5.[37] These high intrinsic viscosities can be explained on the assumption that pectin is a solvated, linear polymer.

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Summary

The relative viscosity of pectin solutions varies with concentration in a manner similar to that of other ionizable hydrophilic colloids and certain salts.

The viscosity of dilute pectin solutions increases to a maximum as the *p*H is adjusted to a value near 6. The viscosity can be reduced to a minimum value by the addition of acid or sodium chloride. As the concentration of pectin is increased above 0.5%, the relative viscosity is practically unaffected by changes in *p*H in the range of 1 to 7. Urea up to 0.5 molal concentration has little effect on the relative viscosity of pectin solutions.

The relative viscosity–concentration curve follows the Arrhenius equation to a concentration of pectin of about 0.1% or more, depending upon the value for the intrinsic viscosity, when the solution is at a *p*H of 1 to 2 or when 0.9% or more of sodium chloride is present. This makes it possible to calculate values for the intrinsic viscosity which may have some relationship to the molecular weight.

The viscosity–concentration curves for the pectinates of sodium, trimethylammonium, ethylenediammonium, 2,2-dihydroxymethylpropylammonium, and tetraethylammonium ions are practically identical.

Changing the temperature from 0–50° has little influence on the relative viscosity of pectin solutions at concentrations below 0.05%. Above that concentration the relative viscosity decreases with increase in temperature.

A tentative hypothesis is proposed to explain the results obtained.

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(33) C. J. Brown and A. A. Houghton, *J. Soc. Chem. Ind.*, **60T**, 254 (1941).

(34) S. L. Bass, A. J. Barry and A. E. Young, "High Polymers" (edited by E. Ott), Interscience Publishers, Inc., **5**, 785 (1943).

(35) S. Glikman, *Kolloid-Z.*, **55**, 64 (1931); *J. Phys. Chem.* (U. S. S. R.), **11**, 678 (1938).

(36) Calculated from data of J. W. Mehl, J. L. Oncley and R. Simha, *Science*, **92**, 132 (1940).

(37) E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).