Citrates and the Viscosity of Pectin Solutions[1]

BY HUGO P. KORTSCHAK

The fact that citric acid will lower the viscosity of pectin solutions was first shown by Ohn,[2] who was, however, mostly interested in the jellying properties of such solutions. This investigation was made to determine more exactly the interrelationships involved over a larger concentration range, and to evaluate the respective influences of pH and citrate concentration.

Experimental

Measurements were made with an Ostwald viscosimeter. As it is hardly possible to make pectin solutions reproducibly, and as it was the change in viscosity which was of interest, no effort was made to obtain exact values for the absolute viscosity. The viscosimeter was surrounded by a water-bath at about 27.5°. During each separate series of measurements, the temperature did not vary more than 0.05°. Values reported are viscosities relative to water at 27.5°.

Pectin.—Most of the measurements were made with lemon pectin (Practical) from the Eastman Kodak Company. A purified apple pectin from Braun–Knecht–Heimann Company and a preparation from sugar cane bagasse were also used. No measurable difference could be found when the pectin was heated with water for a short time, to facilitate dispersion, but most of the solutions were prepared without heating.

Citric Acid.—Baker c. p. analyzed and Merck c. p. were used. Sodium salts were made by the addition of the calculated amount of sodium hydroxide solution. Solid $2Na_3C_6H_5O_7 \cdot 11H_2O$ was also prepared. The required concentrations were obtained by progressive dilution of a stock solution, which was never allowed to stand for more than twenty-four hours.

As the use of different samples of pectin, citric acid, and citrates showed no detectable differences in behavior, it is unnecessary to state which particular preparation was used in each case. The sugar cane pectin was too impure for quantitative results, so that values obtained with it are not reported. Qualitatively, this preparation behaved in the same manner as the other pectins.

(1) The work presented in this paper was done as part of Project ST-P-5 of the H. S. P. A. Experiment Station.
(2) Ohn, Ind. Eng. Chem., 22, 635 (1930).

All citrate concentrations are reported as grams of anhydrous $C_6H_8O_7$ per 100 cc. of solution.

TABLE I

RELATIVE VISCOSITY OF 0.1% PECTIN SOLUTIONS WITH CITRIC ACID AND ITS SODIUM SALTS

$c_{H_3Cit.}$	H_3Cit. pH[a]	Vis.	NaH$_2$Cit. pH[a]	Vis.	Na$_2$HCit. pH[a]	Vis.	Na$_3$Cit. pH[a]	Vis.
0	3.95	1.300	3.95	1.300	3.95	1.300	3.95	1.300
0.0005	3.88	1.300	3.94	1.300	4.00	1.304		
.001	3.82	1.294	3.94	1.295	4.04	1.305	4.15	1.304
.002	3.72	1.286	3.95	1.289	4.09	1.304	4.50	1.307
.004	3.60	1.277	3.94	1.285	4.25	1.300	4.87	1.313
.006	3.50	1.270	3.95	1.277	4.35	1.299	5.28	1.312
.008	3.38	1.268	3.89	1.277	4.50	1.297	5.65	1.311
.010	3.37	1.264	3.90	1.273	4.59	1.290	5.92	1.308
.020	3.16	1.249	3.89	1.264	4.86	1.282	6.40	1.292
.050	2.92	1.227	3.87	1.247	5.09	1.262	6.86	1.261
.080	2.82	1.225	3.86	1.241	5.15	1.250	7.01	1.250
.10	2.73	1.221	3.79	1.241	5.15	1.246	7.06	1.245
.25	2.57	1.222	3.79	1.232	5.15	1.234	7.29	1.244
.50	2.42	1.223	3.79	1.232	5.15	1.233	7.38	1.255
1.00	2.40	1.232	3.79	1.244	5.18	1.246	7.47	1.278

[a] pH measured with glass electrode.

Discussion

An unexpected feature of these curves is the rise in viscosity at low citrate concentrations (Table I, Fig. 1a). The maximum occurs at lower concentrations, and becomes less pronounced, with decreasing sodium content of the salt.
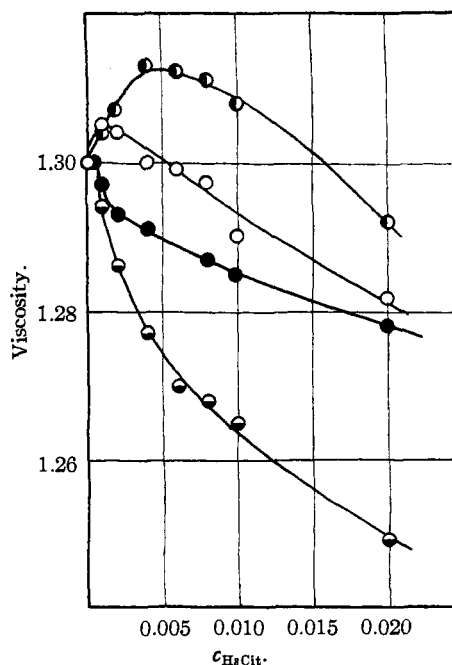

Fig. 1a.—Relative viscosity of 0.1% pectin sols. Symbols as in Fig. 1b.

At higher citrate concentrations, the viscosity falls until a minimum is reached (Fig. 1b). This minimum is rather flat, and is the region which caused Ohn to say that "further addition has little effect." The position of the minimum is approximately the same for the acid and acid salts, at between 0.25 and 0.50% citric acid, in 0.1% pectin solution. For the neutral salt it occurs at about 0.15%. At higher citrate concentrations than this, the viscosity increases linearly, with no further pronounced effect due to the presence of pectin.
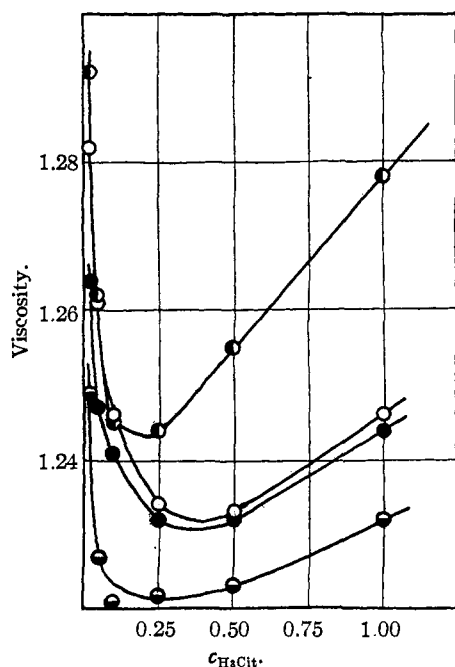
An increase in the pectin concentration (Table III) shifts both maximum and minimum to higher citrate concentrations. In each case the minimum occurs when pectin and citric acid are present in equal quantity by weight. This behavior is not explained by the hypothesis of Ohn, who
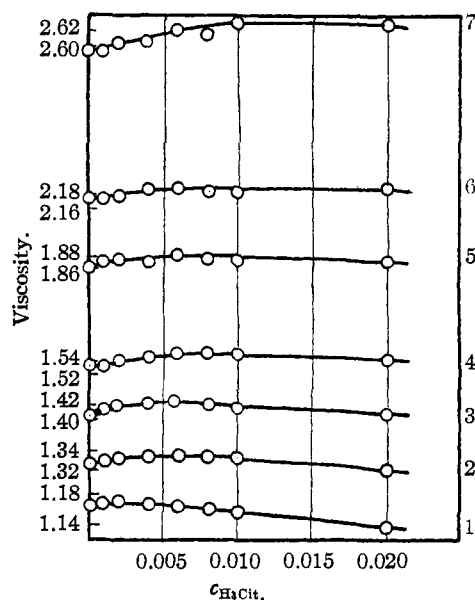

Fig. 2a.—Effect of sodium citrate on the viscosity of pectin sols. Legend as in Fig. 2b.

Fig. 1b.—Relative viscosity of 0.1% pectin sols: ◐, Na₃Cit.; ○, Na₂HCit.; ●, NaH₂Cit.; ◒, H₃Cit.

Fig. 1b shows that at citrate concentrations above 0.5% the curves become linear. The increase in viscosity in this region is due only to the increasing citrate concentration, any effect of the pectin being negligible. The fact that the curves are not parallel, the slope increasing with increasing sodium content of the salt, is not due to the pectin, for this is also the case when pectin is absent (Table II).
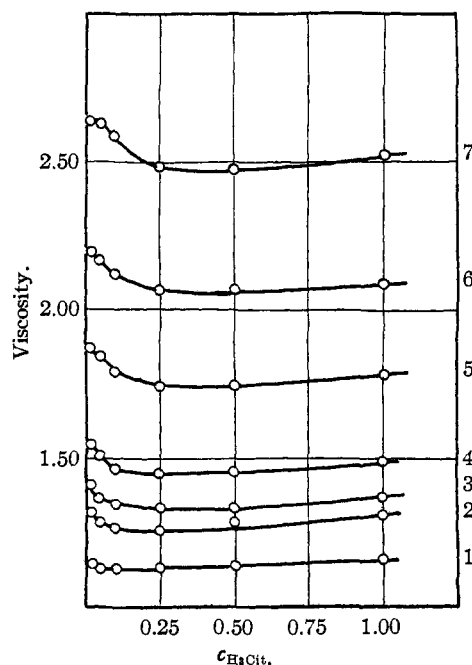

Fig. 2b.—Effect of sodium citrate on the viscosity of pectin sols: 1, −0.05, 2, −0.10, 3, −0.15, 4, −0.20, 5, −0.30, 6, −0.40, 7, −0.50 % pectin.

TABLE II

VISCOSITY OF CITRATE SOLUTIONS

$c_{H_3Cit.}$	H₃Cit.	H₂NaCit.	HNa₂Cit.	Na₃Cit.
0.1	1.004	1.005	1.006	1.006
1.0	1.021	1.021	1.030	1.039
10.0	1.205	1.272	1.365	1.480

considered the viscosity lowering a result of the "breaking up of the fibrils of the pectin," *i. e.*, as due to a change in the properties of the solvent. However, this behavior becomes predictable if we assume a combination between the citrate and the pectin, containing equal parts of each, and less hydrated than the pectin itself.

TABLE III

RELATIVE VISCOSITY OF PECTIN SOLUTIONS WITH SODIUM CITRATE

$c_{H_3Cit.}$	0.05	0.10	0.15	0.20	0.30	0.40	0.50
0	1.166	1.300	1.409	1.534	1.863	2.178	2.593
0.001	1.169	1.304	1.413	1.536	1.871	2.177	2.595
.002	1.173	1.307	1.421	1.539	1.874	2.179	2.603
.004	1.168	1.313	1.422	1.543	1.872	2.188	2.607
.006	1.164	1.312	1.424	1.548	1.881	2.191	2.622
.008	1.160	1.311	1.424	1.550	1.877	2.186	2.617
.010	1.157	1.308	1.417	1.548	1.876	2.184	2.630
.020	1.138	1.292	1.409	1.542	1.873	2.192	2.628
.050	1.122	1.261	1.367	1.503	1.846	2.168	2.626
.080	1.122	1.250	1.348	1.477	1.803	2.133	2.593
.10	1.122	1.245	1.341	1.469	1.788	2.120	2.577
.25	1.128	1.244	1.333	1.451	1.747	2.053	2.481
.50	1.137	1.255	1.341	1.457	1.752	2.059	2.468
1.00	1.160	1.278	1.368	1.489	1.786	2.084	2.509

The accuracy of the measurements is not sufficient to permit a quantitative discussion of the maximum which occurs at low citrate concentrations. With increasing pectin content, the maximum shifts to higher citrate concentrations, but this relationship does not appear to be linear. It may be assumed tentatively that the citrate concentration for maximum viscosity is proportional to the square root of the pectin concentration.

The behavior described above is not specific for pectin and citric acid. Qualitative measurements have shown that aconitic acid may replace the citrates, agar or gum acacia (not starch or the hexose sugars or sucrose) the pectin. Further investigation along these lines is planned.

Summary

1. The viscosities of pectin solutions containing citric acid or citrates have been measured.

2. The viscosity reaches a maximum at low citrate concentrations, a minimum at higher concentrations.

3. Minimum viscosity occurs when equal concentrations of pectin and citric acid are taken, indicating combination of some kind.

4. The position of the maximum is shifted to higher citrate concentrations by increased pectin content, or by decreased acidity.

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Synthesis of Aliphatic *t*-Butyl Ketones

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The reaction of trimethylacetamide with ethylmagnesium bromide has been reported to give good yields of ethyl *t*-butyl ketone.[1] Since ketones containing the *t*-butyl group are important in the work of this Laboratory, the reaction has been extended to include other aliphatic Grignard reagents. Normal Grignard compounds gave good yields of ketones. With branched Grignard reagents the yield of ketone was low, the predominating product being trimethylacetonitrile. With *t*-butylmagnesium chloride, the yield of trimethylacetonitrile was 73%.

Experimental

Reaction of Trimethylacetamide with Grignard Reagents.—The following describes a typical reaction. Two moles of the Grignard reagent were prepared in 700 cc. of anhydrous ether. The addition of 50.5 g. (0.5 mole) of trimethylacetamide, m. p. 152.5–153.5°, required from one-half to one hour. The reactants were stirred and heated to reflux temperature for sixteen hours. The mixture was decomposed with ice and the ether layer separated. The aqueous layer was acidified with hydrochloric acid and extracted several times with ether. The ether extracts and ether layer were combined and carefully distilled through a fractionating column until the ether was removed. The residual solution was dried with anhydrous sodium sulfate and fractionated through an efficient column.[2] The results are tabulated.

All of the compounds listed have been prepared previously, except those for which analytical data are reported.

(1) Ramont, Laclotre and Anagnostopoulos, *Compt. rend.*, **185**, 282 (1927).

(2) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932); Wilson, Parker and Laughlin, *ibid.*, **55**, 2795 (1933).