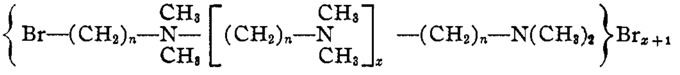
Summary

1. ω-Bromoalkyldimethylamines of the series $Br(CH_2)_nN(CH_3)_2$, where n has the value 7, 8, 9 or 10, have been prepared.

2. These amines have been found to polymerize readily to give products of the type



$$\left\{ Br-(CH_2)_n-\overset{CH_3}{\underset{CH_3}{N}}-\left[(CH_2)_n-\overset{CH_3}{\underset{CH_3}{N}}\right]_x-(CH_2)_n-N(CH_3)_2 \right\}Br_{x+1}$$

The polymers are basic to methyl orange in water solution. The molecular weights calculated from the ratio of non-ionic to total bromine vary from 3350 to 28,000 for different samples. The polymers are hygroscopic substances which vary in physical state from resinous gums through glass-like products to amorphous solids.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE NORTH DAKOTA AGRICULTURAL EXPERIMENT STATION AND THE DEPARTMENT OF AGRICULTURE, UNIVERSITY OF MINNESOTA]

Relation of Concentration to Action of Gelatinizing Agents on Starch[1]

BY C. E. MANGELS AND C. H. BAILEY

Aqueous solutions of certain substances are known to have the power of swelling or gelatinizing starch granules at ordinary temperatures. This property of alkalies, strong acids and other reagents has long been known.

Reychler[2] studied qualitatively the gelatinizing effect of a number of reagents on starches, but more recently Ostwald and Frankel[3] have followed the reaction by means of viscosity determinations. There is comparatively little or no information on record, however, regarding the action of starch gelatinizing reagents over a wide range of concentration. This paper presents a contribution in that field.

Experimental

The swelling or gelatinizing effect of different reagents over a series of concentrations was followed by means of viscosity determinations supplemented in some cases by microscopic examinations. An Ostwald pipet, similar in design to that used by Ostwald and Frankel[3] and having a capillary 3.0 mm. in diameter, was used for the determinations. A starch, prepared in the laboratory from a hard red winter wheat patent flour, was used in all cases. Solutions of strong bases, neutral salts and urea were used as cold gelatinizing agents.

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(1) Joint contribution from North Dakota Agricultural Experiment Station and Minnesota Agricultural Experiment Station. Condensed from one section of a thesis presented by C. E. Mangels to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Paper No. 1177, Journal Series, Minnesota Agricultural Experiment Station.

(2) Reychler, *Bull. soc. chim. Belg.*, **29**, 118, 309 (1920).

(3) Ostwald and Frankel, *Kolloid-Z.*, **43**, 296 (1927).

Procedure.—The equivalent of 1 g. of moisture-free starch was weighed into a 200-cc. Erlenmeyer flask. The flask containing the starch was placed in a cabinet maintained at 30 ± 0.5°. For weaker concentrations, 50 cc. of reagent solution of desired strength was added to the starch at 30°. When the concentration was likely to produce immediate gelatinization, the requisite amount of distilled water necessary to dilute a concentrated stock solution of the reagent was added to the flask. The water and starch were shaken together and the requisite amount of stock reagent added from a buret. This procedure gave a uniform paste free from lumps for the strong concentrations. The flasks were replaced in the 30° cabinet, and then removed at the end of three hours for a viscosity determination.

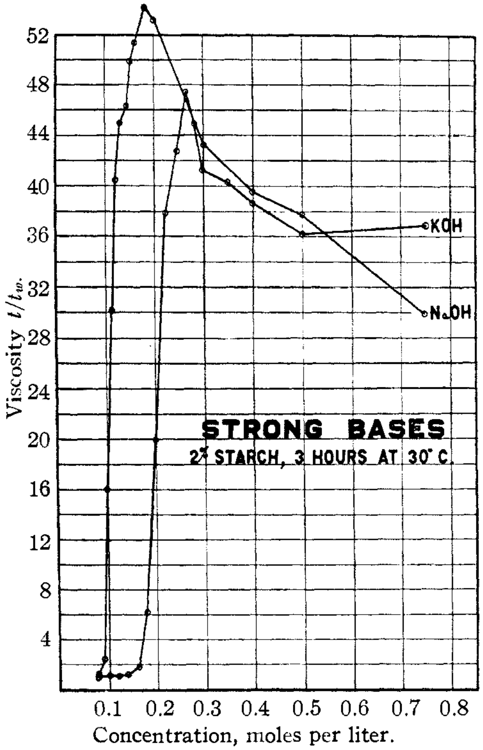

Fig. 1.

The viscosity was determined by means of the Ostwald pipet at 30°. Viscosity is expressed in all cases as t/t_w, where t is the time of flow of the starch preparation and t_w the time of flow for water at 30°. The viscosities of the solutions used varied slightly with concentration, but were of low order as compared to viscosity of the starch preparations. Sodium salicylate was the most viscous of the reagents used but a 3 molar solution of sodium salicylate has a t/t_w value of approximately 2.3 at 30°, while a 2% starch preparation with this reagent shows a value of 42+.

Sodium Hydroxide and Potassium Hydroxide.—The strong bases act upon starch at much lower concentrations than neutral salts. The results are shown in Fig. 1. It will be noted that the sodium hydroxide curve lies to the left of the potassium hydroxide curve. The ascending curve in both cases is almost perpendicular and very small increases in concentration produce a relatively large increase in viscosity. In the case of sodium hydroxide, complete gelatinization occurs between molar concentrations of 0.12 and 0.15. With potassium hydroxide, complete gelatinization occurs between 0.20 and 0.22 mole concentration, but the change is not as sharp as in the case of sodium hydroxide. There is a change in direction of the sodium hydroxide curve between molar concentrations of 0.13 and 0.14 and a similar change in the potassium hydroxide curve at molar concentration of 0.22. These changes in direction become more noticeable in case of other reagents.

Sodium Salicylate (Fig. 2).—The sodium salicylate curve lies between the strong base curves and the thiocyanate curves. An increase in viscosity is noticeable at 0.6 mole per liter and is significant at 0.8 mole. The ascent of the curve is very steep between concentrations of 0.8 and 1.0 molar, but after 1.0 molar a distinct break is found in the direction of the curve. Above a concentration of 1.4 moles, the curve is approximately a straight line until a concentration of 2.8 moles is reached when another break occurs.

Thiocyanates.—The data for thiocyanates are shown in Fig. 3. The thiocyanates used give three very interesting curves. Sodium salicylate required a higher order of concentration for gelatinization than the strong bases, and the concentrations necessary for thiocyanates lie distinctly above the salicylate concentrations.

Increase in viscosity is very gradual with all three thiocyanates until the concentration reaches 2 moles per liter. The swelling effect of the three salts at lower concentration is of the following order: $NH_4 < Na < K$. The difference between Na and K is small, and the Na curve crosses the K curve between 2.0 and 2.2 moles per liter. The NH_4 curve which is distinctly below the K curve at lower concentrations crosses the K curve at approximately 3 moles per liter and would apparently cross the Na curve if extended.

The interesting features of the thiocyanate curves are the relations between the three ions and the distinct break or constant point in the K and NH_4 curves. The Na curve shows a distinct break in direction at 2.2 moles per liter, but both the K and NH_4 curves show a practically constant viscosity for a small range of concentration. This constant viscosity is apparently an accentuating of the break in direction which has been noted with other reagents.

Both the Na and K curves reach a maximum and then decrease, but the NH_4 curve has apparently not reached a maximum. The maximum t/t_w of the Na curve is 35.9, while the maximum for the K curve is only 19.3. A similar relationship was noted between K and Na ions with the strong bases.

Iodides.—The data for iodides are shown in Fig. 4. The iodides require somewhat higher concentrations than the thiocyanates, but the order of concentration is similar. The maximum for these curves, however, is considerably lower.

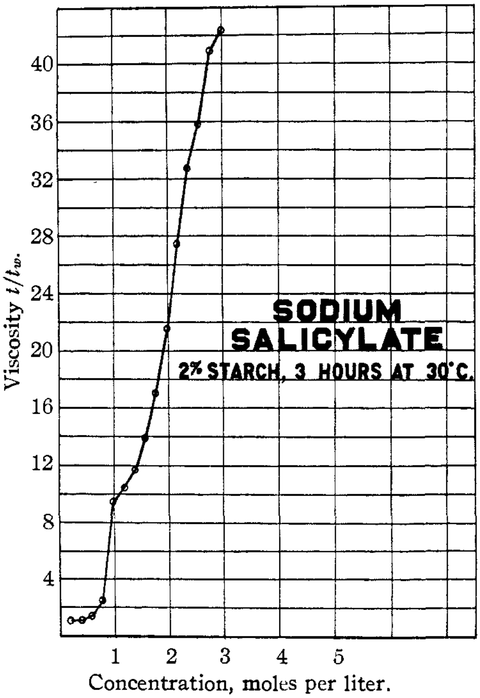

Fig. 2.

Increase in viscosity is noticeable at 1.5 moles per liter. Between concentrations of 2.2 and 2.4 moles, the potassium iodide preparation shows greater viscosity than the sodium iodide preparation, but between 2.4 and 2.6 moles, the Na curve crosses the K curve. The Na curve shows a distinct dip or break at 2.8 moles per liter, and the potassium iodide curve shows merely a change of direction. The relation between K and Na salts is, therefore, similar to that observed with the thiocyanates.

Bromides.—The effect with bromides is considerably less than that obtained with iodides. None of the bromide preparations became completely gelatinized. The Na salt apparently has slightly greater swelling power than the K salt, but the difference is small.

Chlorides.—The solubility of potassium chloride is comparatively low and no observations were made with this reagent. A 5 molar solution of sodium chloride, however, had apparently no swelling effect on starch even after standing for a week or more at 30°.

The alkaline earth chlorides, however, do cause some swelling. Of the three alkaline earth chlorides used, the order was Mg < Ca < Sr, if the viscosity after three hours at 30° is considered.

If the alkaline earth chloride preparations are allowed to stand for twenty-four hours, the order becomes Mg < Sr < Ca. Calcium chloride solutions above 2.4 molar concentration cause pronounced swelling of starch granules if allowed to act for a sufficient length of time.

Urea.—The results with urea, a non-electrolyte, are shown in Fig. 5.

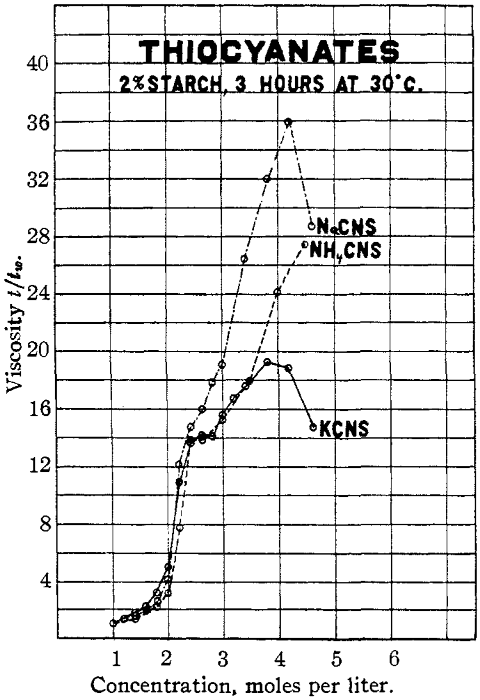

Fig. 3.

The urea concentration curve is quite different from that of strong bases, thiocyanates, salicylates or iodides. The urea curve has apparently not reached a maximum at a concentration of 10 moles per liter. The increase in viscosity with increasing concentration is relatively very gradual. The curve does not show a decided break in direction at any point and is not as steep as other curves at the range where complete gelatinization occurs.

Hofmeister Series or Lyotropic Effect.—Since comparatively high concentrations are necessary to gelatinize starch, not many comparisons of different anions and cations can be made. Figure 6 shows that for the sodium compounds examined, the lyotropic series is Cl < Br < I < CNS < salicylate < OH. The Cl ion was without measurable effect at any concentration.

The difference due to cations does not appear to be a strictly lyotropic effect. When comparing strong bases, sodium hydroxide is distinctly more effective than potassium hydroxide at concentrations less than 0.3 molar. At concentrations of 0.3 to 0.5 molar, the difference is small, but at 0.75 molar, K exceeds Na.

A comparison of three cations is made in the case of thiocyanates and the effect of the cations varied with the concentration used. At molar concentrations of 1.4 to 2.0, the series is NH_4 < Na < K. At molar concentrations ranging from 2.2 and up to about 4.0, the series would be NH_4<K< Na. At higher concentrations, the series becomes K<NH_4<Na. If still higher concentrations than 4.6 molar were used, the curves indicate that

the order would probably be K<Na<NH_4. The comparison of the two iodides is interesting because the relation between K and Na ions is similar to that noted in the case of thiocyanates. At concentrations up to 2.4 molar, Na<K, but above this concentration, K<Na.

The results with strong bases, thiocyanates and iodides would indicate that the K ion at high concentrations apparently has a destructive effect on the starch which decreases viscosity. With strong bases, the potassium hydroxide curve never reaches the high point reached by the sodium hydroxide curve.

Microscopical Examination.—At lower concentrations of the reagents, the starch preparations were opaque suspensions. As the concentration of the reagent was increased, the preparations tended to become translucent. This change in appearance was gradual with neutral salts and urea but quite abrupt with the strong bases. A microscopical examination of the starch preparation indicates not only the reason for this change of appearance, but also serves to explain some peculiar variations noted in the viscosity–concentration curves.

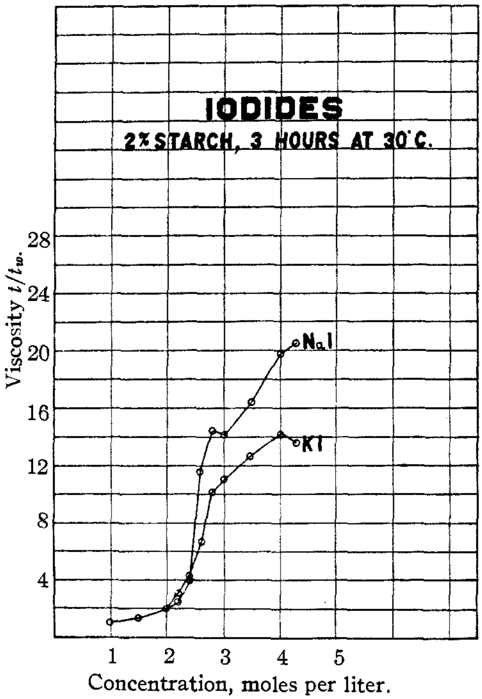

Fig. 4.

Potassium Thiocyanate Preparations.—A preparation with 1.25 molar potassium thiocyanate after twenty-four hours appeared to be made up entirely of slightly swollen granules when examined under a low power microscope (100X). This preparation is an opaque suspension.

As the concentration of potassium thiocyanate is increased, the starch preparations become more and more translucent and the viscosity greatly increases. Under the microscope, the swelling of the granules increases as the potassium thiocyanate concentration increases. These swollen granules were sac-like structures apparently filled with liquid and had very clearly defined edges. The highly hydrated granules are translucent and the preparation, therefore, has a translucent appearance.

With a potassium thiocyanate concentration of 2.0 molar, the granules were enormously swollen and a few burst granules were noted. As the concentration was further increased, more fragments of burst granules were observed until at a concentration of 2.4 moles, only the fragments of the burst sac-like bodies were noted.

With a still further increase in potassium thiocyanate concentration, the fragments of burst granules are peptized or dissolved until at a concentration of 3.0 molar, the microscope shows a clear field.

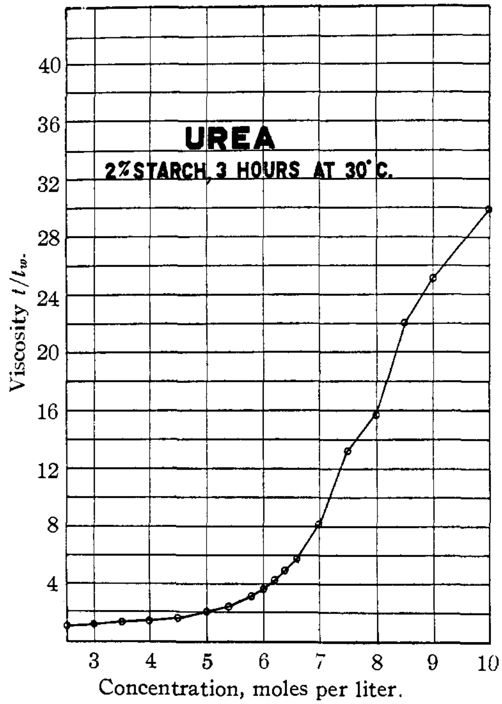

Fig. 5.

The starch preparations at lower concentrations are pseudo-colloidal in nature since the viscosity is evidently due to jostling of swollen granules. The granules swell further and finally burst as the concentration increases. The dip or break in the direction of viscosity–concentration curves is evidently due to the bursting of the swollen granules and the discharge of the relatively non-viscous amylose solution from the interior of the granule. The decrease in concentration due to bursting of the granules is offset, however, by a dispersion or peptization of the amylopectin material. Depending on the rapidity of dispersion of amylopectin, the viscosity will (1) decrease, (2) remain constant, or (3) increase. As the amylopectin becomes more completely dispersed, the viscosity increases at a rapid rate. The preparations with concentration of 3 molar potassium thiocyanate and above are probably true colloidal dispersions. Other neutral salts and urea gave preparations which, microscopically, were similar to potassium thiocyanate preparations.

Sodium Hydroxide.—A preparation with 0.10 molar sodium hydroxide when examined under the microscope (low power) appeared to be a mixture of unchanged granules and swollen granules. The swollen granules appeared as rather large, jelly-like masses in which the unchanged granules were imbedded.

If the concentration of sodium hydroxide solution is increased from 0.10 molar to 0.12 molar, complete gelatinization occurs, and no unchanged granules are visible under the microscope. The appearance of the material is similar to that of the swollen masses present in the 0.10 molar sodium hydroxide suspension.

The appearance of the sodium hydroxide and potassium hydroxide preparations under the microscope is distinctly different than that of potassium thiocyanate and other neutral salt preparations.

Alsberg[4] postulates that swelling of the starch granule in water is prevented by the rigidity of the outer or amylopectin layer of the starch granule. This outer layer must act as a semipermeable membrane. The amylose in the interior of the granule is evidently unable to diffuse into the medium, but the membrane is permeable to water and electrolytes. The dispersing agents, therefore, must have a softening effect on the rigid outer layer. As this layer is rendered partially elastic, the amylose of the interior of the granule takes up water.

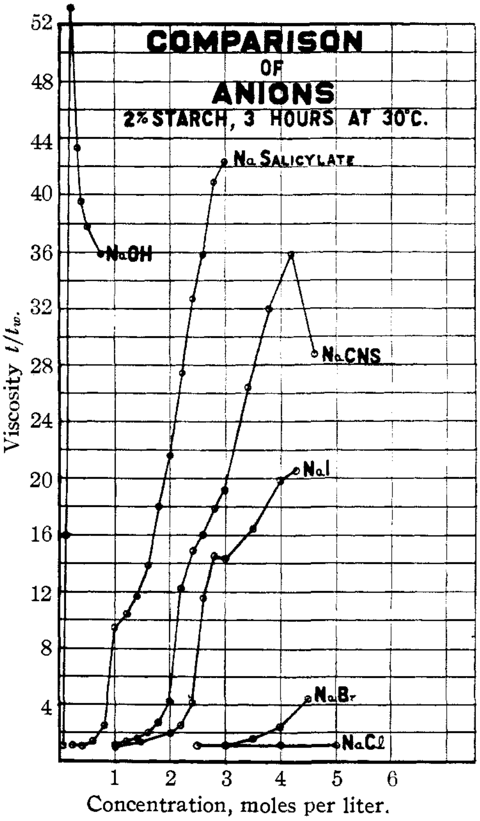

Fig. 6.

Summary

1. Studies were made of the swelling or gelatinizing effect of aqueous solutions of reagents on wheat starch over a range of concentrations. The reagents used were (1) strong bases (sodium hydroxide and potassium

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(4) Alsberg, *Ind. Eng. Chem.*, **18**, 190 (1926).

hydroxide), (2) sodium salicylate, (3) thiocyanates (Na, K and NH_4 salts), (4) iodides (Na and K salts), (5) bromides (Na and K salts), (6) alkaline earth chlorides, and (7) urea. Viscosity, determined by means of an Ostwald pipet, was used as a measure of swelling or gelatinization of the starch.

2. Viscosity or swelling power of the reagents, in general, increased with concentration. Considerable variation in swelling or gelatinizing power of different reagents was noted. A Hofmeister series or lyotropic effect of anions was noted in the concentration–viscosity studies as follows: Cl < B < I < CNS < salicylate < OH. The relations of different cations indicated some effect other than a lyotropic series.

3. Microscopical examination indicates that viscosity at lower concentrations of reagents is due to jostling of swollen granules. As concentrations are increased, the granules burst, and the amylopectin is dispersed, forming a true colloidal dispersion.

MINNEAPOLIS, MINNESOTA

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

The Methylation and Constitution of Inulin

BY JAMES COLQUHOUN IRVINE AND TERENCE NEIL MONTGOMERY

The application of the methylation method to the elucidation of the constitution of inulin is due to Irvine and Steele,[1] who showed that the polysaccharide could be converted into a trimethyl derivative which on hydrolysis yielded a trimethyl-γ-fructose as the essential product. This result, which was confirmed in various ways[2] and characterized inulin as the only known natural compound composed exclusively of γ-fructose residues, was followed by the observation that the hydrolysis sugar referred to above is 3,4,6-trimethylfructose.[3] It then appeared that the constitution of inulin was in large measure solved, but subsequent developments have shown that such is not the case. It is known, for example, that under certain conditions small quantities of glucose are formed when inulin is hydrolyzed and the isolation from inulin of one or more anhydro-difructoses showing greater resistance to hydrolysis than the major portion of the polysaccharide has added further complications to the problem.[4] Obviously, if these products are not adventitious but represent fractions of the inulin molecule, the constitution must be adjusted to accommodate

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[1] Irvine and Steele, *J. Chem. Soc.*, **117**, 1474 (1920).

[2] Irvine, Steele and Shannon, *ibid.*, **121**, 1060 (1922).

[3] Haworth and Learner, *ibid.*, 619 (1928).

[4] Jackson, *Bur. Standards J. Research*, **3**, 27 (1929); **6**, 709 (1931); Irvine and Stevenson, THIS JOURNAL, **51**, 2197 (1929); Pringsheim and Hensel, *Ber.*, **64**, 1431 (1931).