# Viscosity-Concentration Relations of Cellulose Acetate

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The determination of intrinsic viscosity is important in the cellulose and cellulose derivative industries as a practical measure of average degree of polymerization or molecular weight. Concentrated solution viscosities are also important in the industry, to determine flow properties of commercial solutions. Some work has been reported on the relationship of concentrated solution viscosities to intrinsic viscosities of cellulose and some of its derivatives. Davis and Elliott (*7*) discuss the effect of concentration on viscosity of several cellulose derivatives. Kauppi and Bass (*4*) have shown that the Philippoff type of equation defines the behavior of ethylcellulose in 80/20 toluene-ethyl alcohol over a concentration range from 5 to 25%. Very few of the viscosity formulas relating concentration, viscosity, and intrinsic viscosity predict well over a wide concentration range as most of them were derived for use with dilute solution data to predict intrinsic viscosity.

This work was undertaken to determine the relationship of concentrated solution viscosities of secondary cellulose acetate over a wide range of both concentration and intrinsic viscosity.

## PROCEDURE

The intrinsic viscosities were determined by measuring the relative viscosities of dilute solutions of each sample in acetone at 25 °C. Relative viscosities were determined for concentrations of 0.25, 0.50, and 0.75 gram per 100 ml. of solution. A Wagner pipet and auxiliary apparatus to ensure temperature control within ±0.1 °C. were used (*9*). The intrinsic viscosities were determined from the relative viscosities by use of the Martin equation (*7*).

$$\log \eta_{sp}/C = \log [\eta] + k[\eta]C$$

where

$\eta_{sp} = \eta_r - 1$

$\eta_r = \dfrac{\text{time of flow of solution}}{\text{time of flow of solvent}}$

$C$ = concentration in grams/100 ml. of solution

$[\eta]$ = intrinsic viscosity

$k$ = constant = 0.178 for cellulose acetate in acetone

A plot of log $\eta_{sp}/C$ *vs.* $C$ when extrapolated to zero concentration gives the intrinsic viscosity. No corrections for rate of shear were applied to these data, as no significant effect of shear rate on intrinsic viscosity is encountered in the molecular weight range of these samples (*3*). A second method of determining intrinsic viscosities was the combination of the Baker (2) and Philippoff (*8*) equations

$$\eta_r = \left(1 + \frac{[\eta]C}{a}\right)^a$$

where $a$ is a constant which for cellulose acetate in acetone is 8. A plot of $\eta_r^{1/8}$ *vs.* $C$ is used to determine $[\eta]$. The intrinsic viscosity, $[\eta]$, is equal to eight times the slope of the line.

The determinations of the concentrated solution viscosities were made by the ASTM method (*1*). Time of fall was determined in a standard square bottle using a ⅛-inch stainless steel ball. The solutions which had viscosities of less than 15 poises were determined by the Hoeppler viscometer method (*6*), using the appropriate ball for each solution. Viscosities were determined at 25 °C. at concentrations of 5, 10, 15, 20, 25, and 30% by weight in acetone containing 2.5% of water. The effect of varying rate of shear on these concentrated solution viscosities was not studied. The viscosities reported are the direct measurements obtained by the relatively low shear conditions of the ASTM viscosity method.

## DATA

Five samples of secondary cellulose acetate of 39.7% acetyl having a wide intrinsic viscosity range were used. These cellulose acetates were made from purified wood pulp by the solution process in acetic acid and acetic anhydride (*5*).

The relative viscosities were determined at 0.25, 0.50, and 0.75 gram per 100 ml. of solution concentration on each of the five samples in acetone at 25 °C. (Table I).

**Table I. Relative Viscosities and Intrinsic Viscosities of Five Samples of Cellulose Acetate in Acetone at 25 °C.**

| Sample | Concentration, G./Dl. | Relative Viscosity | Intrinsic Viscosity by Martin Equation | Intrinsic Viscosity by Baker-Philippoff Equation |
|---|---|---|---|---|
| A | 0.246 | 1.156 | 0.60 | 0.59 |
| | 0.492 | 1.333 | | |
| | 0.742 | 1.520 | | |
| B | 0.248 | 1.267 | 0.96 | 0.95 |
| | 0.497 | 1.577 | | |
| | 0.744 | 1.963 | | |
| C | 0.253 | 1.499 | 1.50 | 1.50 |
| | 0.499 | 2.083 | | |
| | 0.746 | 2.837 | | |
| D | 0.256 | 1.690 | 2.15 | 2.10 |
| | 0.497 | 2.638 | | |
| | 0.741 | 4.149 | | |
| E | 0.251 | 1.890 | 2.65 | 2.64 |
| | 0.495 | 3.363 | | |
| | 0.740 | 5.813 | | |

The concentrated solution viscosities for each sample were determined in duplicate at 25 °C. (Table II). It was impossible to measure the viscosities of the higher molecular weight samples at the higher concentrations by this procedure.

## DISCUSSION OF RESULTS

A plot of log $\eta_{sp}/C$ *vs.* $C$ for the data in Table I is shown in Figure 1. The extrapolated values at zero concentration are the intrinsic viscosities, determined by the Martin equation, given in Table I. These values for intrinsic viscosities are used as the basis of calculations in this paper.

**Table II. Concentrated Solution Viscosities in Duplicate of Five Cellulose Acetate Samples at 25 °C. in Acetone Containing 2.5% of Water**

| Concn., Wt.% | ASTM Viscosity, Centipoises A | B | C | D | E | Solution Av., Sp. Gr. | Concn., G./Dl. |
|---|---|---|---|---|---|---|---|
| 5 | 2.47 | 6.36 | 21.8 | 76.6 | 173 | | |
| | 2.42 | 6.46 | 22.6 | 75.8 | 173 | | |
| | Av. 2.44 | 6.41 | 22.2 | 76.2 | 173 | 0.803 | 4.02 |
| 10 | 11.5 | 51.2 | 304 | 1480 | 4480 | | |
| | 11.5 | 51.6 | 308 | 1510 | 4780 | | |
| | Av. 11.5 | 51.4 | 306 | 1500 | 4630 | 0.822 | 8.22 |
| 15 | 44.5 | 279 | 1930 | 16,100 | 51,800 | | |
| | 44.8 | 287 | 2000 | 16,100 | 53,000 | | |
| | Av. 44.6 | 283 | 1960 | 16,100 | 52,400 | 0.843 | 12.6 |
| 20 | 155 | 1240 | 11,900 | 105,000 | 441,000 | | |
| | 151 | 1270 | 11,900 | 104,000 | 431,000 | | |
| | Av. 153 | 1260 | 11,900 | 104,000 | 436,000 | 0.864 | 17.3 |
| 25 | 527 | 4410 | 53,400 | 658,000 | Gel | | |
| | 530 | 4270 | 54,000 | 651,000 | Gel | | |
| | Av. 529 | 4340 | 53,700 | 654,000 | ... | 0.885 | 22.1 |
| 30 | 2130 | 20,700 | 331,000 | Gel | Gel | | |
| | 1990 | 21,300 | 340,000 | Gel | Gel | | |
| | Av. 2060 | 21,000 | 335,000 | ... | ... | 0.907 | 27.2 |

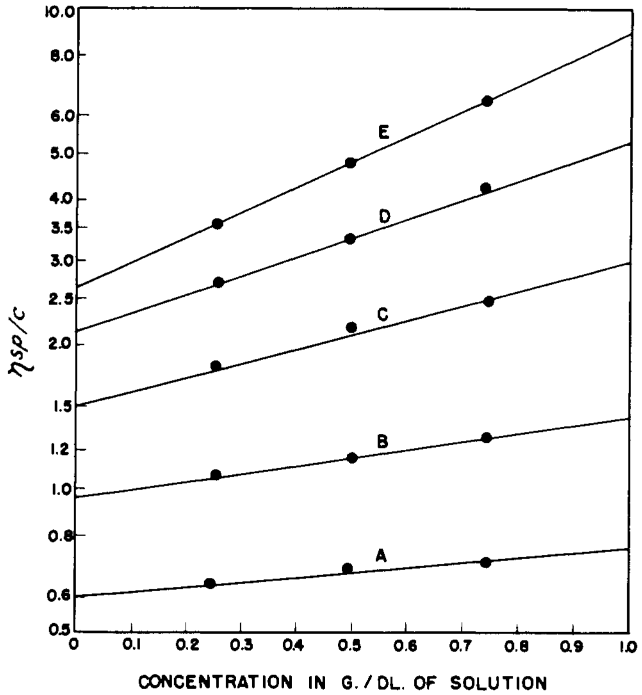

**Figure 1. Determination of intrinsic viscosities by Martin equation**

Log $\eta_{sp}/C$ vs. concentration in grams per deciliter for dilute solutions of five cellulose acetate samples in acetone at 25 °C.

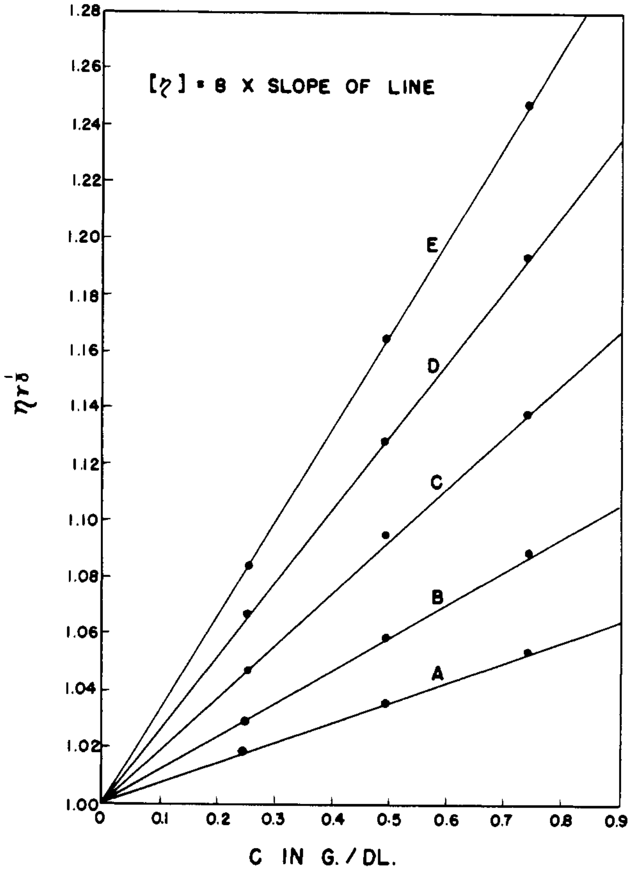

**Figure 2. Determination of intrinsic viscosities by Baker-Philippoff equation**

$\eta_r^{1/8}$ vs. concentration in grams per deciliter for dilute solutions of five samples of cellulose acetate in acetone at 25 °C.

A plot of $\eta_r^{1/8}$ vs. $C$ for the data in Table I is shown in Figure 2. The slope of the line for each sample times the constant 8 gives the intrinsic viscosity of the sample. The two equations give approximately the same value of intrinsic viscosity for each sample.

The concentrated solution viscosities obtained for the five samples (Table II) were analyzed by applying both the Martin equation and the Baker-Philippoff equation. Only the latter equation is quoted in literature as being applicable over wide concentration ranges. As a matter of interest, the Martin equation was investigated to determine its deviation from the experimental data at higher concentrations. A plot of log $\eta_{sp}/C$ vs. $C$ for the concentrated solution viscosities is shown in Figure 3. The continuous lines in the plot show the actual experimental curves obtained for the five samples. The dotted lines show a calculated line using the determined intrinsic viscosity and a $k$ of 0.178. The Martin equation agrees with the experimental data only up to an $\eta_{sp}/C$ of 10 or a concentration of 4 grams per deciliter.

In applying the Baker-Philippoff equation to the data it was necessary to determine the power constant, $a$, by rearranging the equation to the following expression:

$$\frac{\eta_r^{1/a} - 1}{C} = \frac{[\eta]}{a}$$

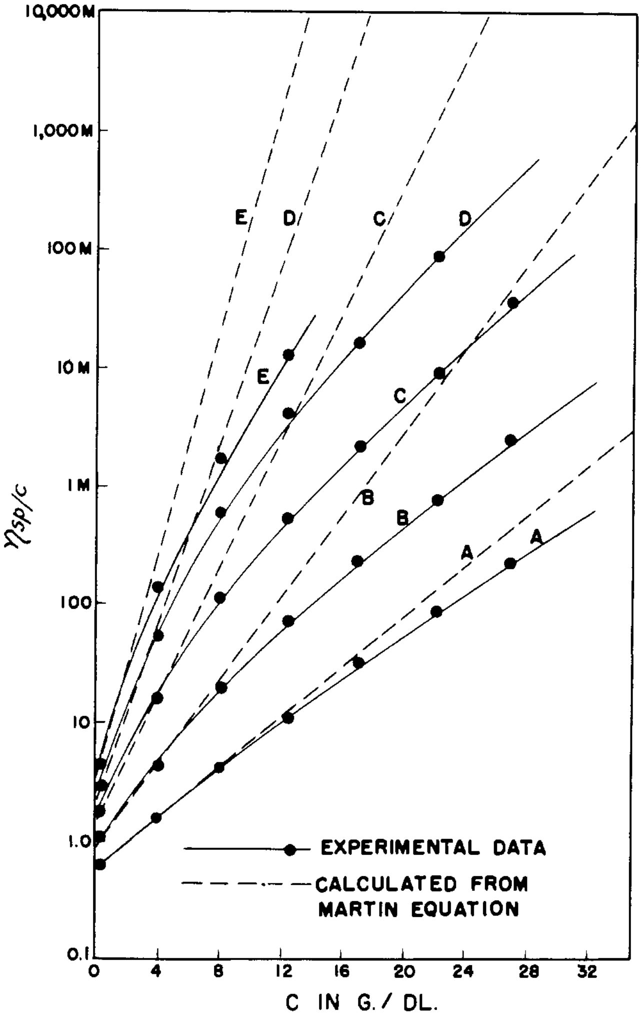

**Figure 3. Comparison of experimental and calculated viscosity data by Martin method**

Log $\eta_{sp}/C$ vs. concentration for concentrated solutions of cellulose acetate at 25 °C. in acetone containing 2.5% of water

The desired value of $a$ is the one which gives the most nearly constant $[\eta]/a$ over the range of concentration investigated. The relative viscosities were determined from the viscosities in Table II by dividing them by the viscosity of the solvent. The determined viscosity of the solvent was 0.338 centipoise at 25 °C. The $[\eta]/a$ values determined for $a = 7$, 8, and 9 are given in Table III. It is seen by the range of the values given that $a = 8$ gives the most constant $[\eta]/a$. Using $a = 8$ the Baker-Philippoff equation becomes the original Philippoff equation.

$$\eta_r = \left(1 + \frac{[\eta]C}{8}\right)^8$$

$\eta_r^{1/8}$ vs. C should give a straight line. As $\eta_r$ is equal to the viscosity of the solution divided by the viscosity of the solvent, the latter being a constant at constant temperature, the absolute viscosity should give a straight line when plotted on a $1/8$ power scale against concentration. This latter relationship is given for each sample in Figure 4. For acetone solutions of a given cellulose acetate the absolute viscosity on a $1/8$ power scale vs. concentration in grams per deciliter approximates a straight line for the range of concentration tested. The straight lines extrapolate to the viscosity of the solvent at zero concentration.

**Table III. Determination of Best Value of $a$ for Baker-Philippoff Equation**

Values of $\frac{[\eta]}{a}$ for different values of $a$.

$\frac{[\eta]}{a}$ calculated for $a = 7$, 8, and 9.

| | | Concentration, Grams/Dl. of Solution | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample | $a$ | 4.02 | 8.22 | 12.6 | 17.3 | 22.1 | 27.2 | Range |
| A | 7 | 0.0812 | 0.0798 | 0.0797 | 0.0808 | 0.0840 | 0.0910 | 0.0113 |
| | 8 | 0.0697 | 0.0677 | 0.0665 | 0.0665 | 0.0668 | 0.0726 | 0.0061 |
| | 9 | 0.0610 | 0.0585 | 0.0569 | 0.0563 | 0.0570 | 0.0600 | 0.0047 |
| B | 7 | 0.1305 | 0.1280 | 0.1278 | 0.1302 | 0.1288 | 0.1410 | 0.0132 |
| | 8 | 0.1108 | 0.1066 | 0.1043 | 0.1039 | 0.1018 | 0.1094 | 0.0090 |
| | 9 | 0.0964 | 0.0910 | 0.0880 | 0.0865 | 0.0838 | 0.0887 | 0.0126 |
| C | 7 | 0.2035 | 0.2008 | 0.1945 | 0.2005 | 0.2050 | 0.2275 | 0.0330 |
| | 8 | 0.1711 | 0.1557 | 0.1546 | 0.1563 | 0.1568 | 0.1699 | 0.0165 |
| | 9 | 0.1475 | 0.1378 | 0.1282 | 0.1277 | 0.1260 | 0.1340 | 0.0215 |
| D | 7 | 0.291 | 0.283 | 0.289 | 0.295 | 0.312 | ... | 0.029 |
| | 8 | 0.241 | 0.227 | 0.225 | 0.223 | 0.231 | ... | 0.018 |
| | 9 | 0.203 | 0.188 | 0.183 | 0.178 | 0.180 | ... | 0.025 |
| E | 7 | 0.358 | 0.355 | 0.356 | 0.374 | ... | ... | 0.019 |
| | 8 | 0.294 | 0.277 | 0.273 | 0.278 | ... | ... | 0.021 |
| | 9 | 0.249 | 0.230 | 0.219 | 0.219 | ... | ... | 0.030 |
| Averages for all samples | | | | | | | | |
| | 7 | | | | | | | 0.0211 |
| | 8 | | | | | | | 0.0141 |
| | 9 | | | | | | | 0.0187 |

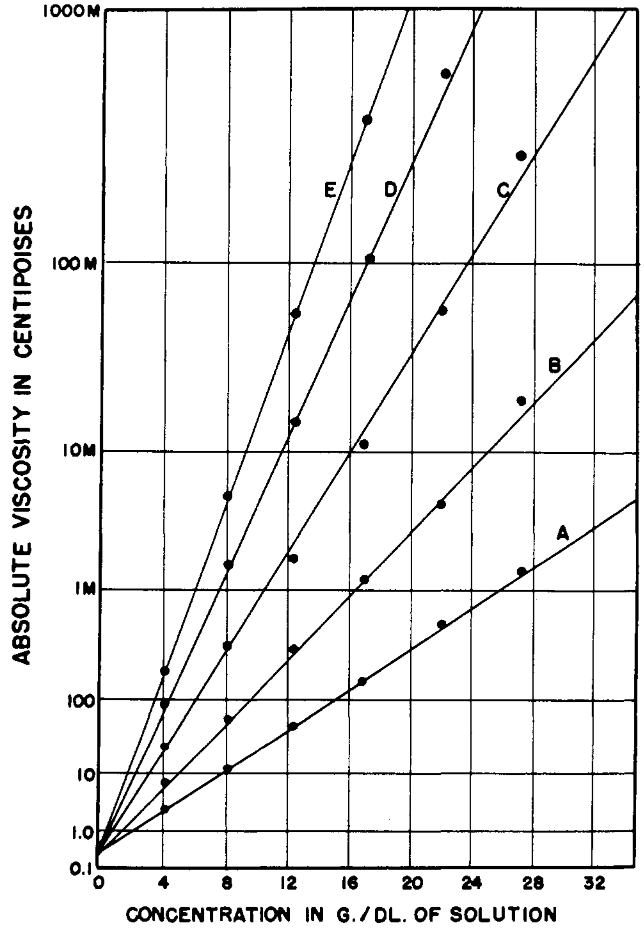

**Figure 4. Viscosity of concentrated solutions of cellulose acetate at 25 °C. in acetone containing 2.5% of water vs. concentration in grams per deciliter**

Plotted on $1/8$ power scale

**Table IV. Experimental and Calculated Relative Viscosities and Their Ratios, Z**

| Sample | | Concentration, Grams/Dl. of Solution | | | | | |
|---|---|---|---|---|---|---|---|
| | | 4.02 | 8.22 | 12.6 | 17.3 | 22.1 | 27.2 |
| A | Exptl. | 7.22 | 34.1 | 132 | 453 | 1560 | 6090 |
| | Calcd. | 8.26 | 43.4 | 208 | 772 | 2510 | 7310 |
| | $Z$ | 0.876 | 0.786 | 0.634 | 0.587 | 0.624 | 0.832 |
| B | Exptl. | 19.0 | 152 | 838 | 3720 | 12,800 | 62,000 |
| | Calcd. | 23.3 | 242 | 1620 | 7970 | 31,900 | 110,000 |
| | $Z$ | 0.815 | 0.628 | 0.520 | 0.467 | 0.402 | 0.567 |
| C | Exptl. | 65.7 | 906 | 5810 | 25,000 | 159,000 | 992,000 |
| | Calcd. | 85.6 | 1740 | 16,700 | 105,000 | 494,000 | 1,920,000 |
| | $Z$ | 0.768 | 0.522 | 0.348 | 0.336 | 0.322 | 0.516 |
| D | Exptl. | 225 | 4430 | 47,500 | 308,000 | 1,940,000 | |
| | Calcd. | 352 | 11,600 | 141,000 | 1,041,000 | 5,460,000 | |
| | $Z$ | 0.639 | 0.382 | 0.377 | 0.298 | 0.354 | |
| E | Exptl. | 512 | 13,700 | 155,000 | 1,290,000 | | |
| | Calcd. | 872 | 36,800 | 524,000 | 4,160,000 | | |
| | $Z$ | 0.587 | 0.373 | 0.296 | 0.310 | | |

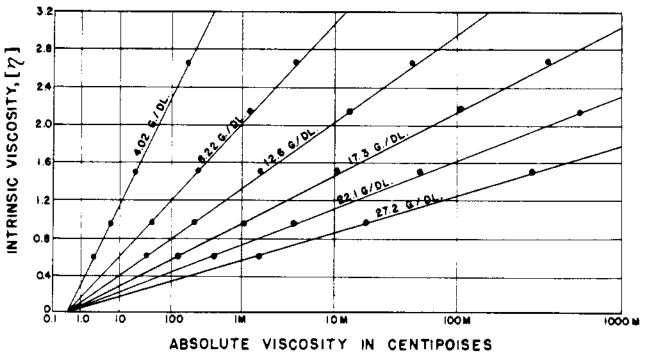

**Figure 5. Viscosity of concentrated solutions of cellulose acetate at 25° C. in acetone containing 2.5% of water vs. intrinsic viscosity**

Plotted on ⅛ power scale

The absolute viscosity data may also be plotted on a ⅛ power scale vs. the intrinsic viscosity. This should lead to straight lines for each concentration (Figure 5).

Figures 4 and 5 show that the ⅛ power of the viscosity of secondary cellulose acetate in acetone containing 2.5% of water varies directly with both intrinsic viscosity and concentration over the ranges of concentration and intrinsic viscosity investigated.

In Figure 6 the relative viscosities which were calculated from the Baker-Philippoff equation using the known intrinsic viscosities are plotted as dotted lines. The relative viscosities which were experimentally determined are plotted as solid lines. The calculated viscosities determined by the equation differ from the experimental points. A coefficient, $Z$, was introduced into the equation to make it fit the experimental points. $Z$ may be written mathematically as:

$$Z = \frac{\eta_r}{\left(1 + \frac{[\eta]C}{8}\right)^8}$$

$Z$ was calculated for each experimental point and is given in Table IV along with the experimental and calculated relative viscosities. It was observed that this coefficient was a function of concentration and intrinsic viscosity as is shown by the plot of $Z$ vs. concentration (Figure 7). As the concentration increases from zero the value of $Z$ decreases, the decrease being more rapid as the intrinsic viscosity is increased. After a concentration of 20 to 25% is passed, $Z$ becomes larger again, approaching and even exceeding 1.

Several theories may be given for the viscosity behavior indicated by the variation of $Z$ over the concentration range.

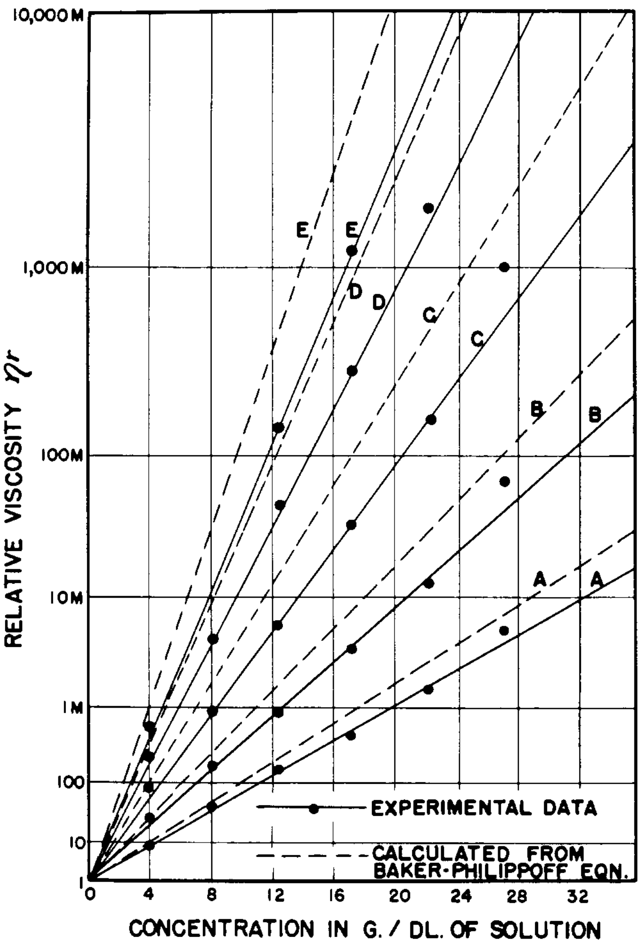

**Figure 6. Comparison of experimental and calculated viscosity data by Baker-Philippoff equation**

Correlation of relative viscosity with concentration for cellulose acetate of different intrinsic viscosities at 25°C. in solvent of acetone containing 2.5% of water

At concentrations of less than 1% $Z$ is close to unity. As the concentration is increased from 1 to 20%, $Z$ decreases, suggesting an imperfect solution with agglomeration of the molecules. At higher concentrations the $Z$ value increases, in some cases even exceeding 1; presumably the molecular agglomerates coalesce, producing gel-type solutions. The decrease of $Z$ as the concentration increases to 20% may be due simply to the fact that the Baker-Philippoff equation does not truly predict the concentrated solution viscosities of secondary cellulose acetate in 97.5% acetone under the conditions of these viscosity measurements.

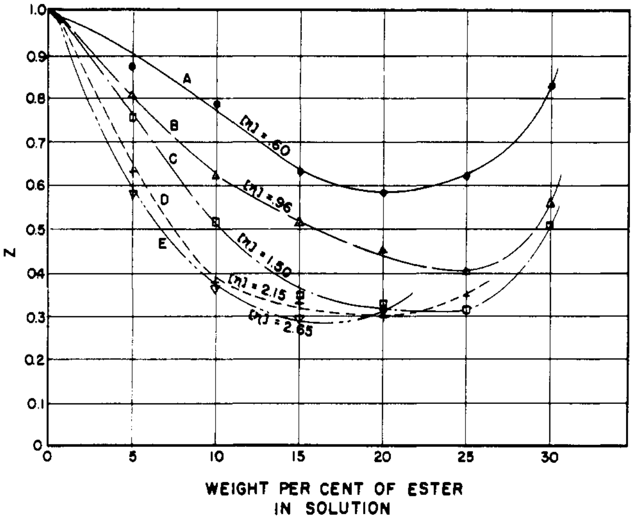

**Figure 7. Relationship of Z with concentration for samples of cellulose acetate of different intrinsic viscosities**

Using solvent of acetone containing 2.5% of water

There are factors which affect concentrated solution viscosities without affecting intrinsic viscosities. They would, of course, also affect *Z*. Some of these factors are methods of acetylation, salts in the product, or differences in raw materials. The relationship of *Z* to concentration is useful in comparing the viscosity behavior of different cellulose acetates in concentrated solutions. It may also point to the manufacturing variables which affect the viscosity properties of the product.

## CONCLUSIONS

The $^1/_6$ power of the concentrated solution viscosities of secondary cellulose acetate in acetone was found to be approximately a linear function of intrinsic viscosity and concentration. A coefficient was introduced into the Baker-Philippoff equation to give an equation which would approximate the experimental data. This coefficient varies with both intrinsic viscosity and concentration.

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Received for review September 13, 1956. Accepted April 25, 1957. Division of Cellulose Chemistry, 130th Meeting, ACS, Atlantic City, N. J., September 1956.

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# Viscosities of Solutions of Pine Wood Lignin from Kraft Black Liquor

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The lignin studied was a commercial pine wood lignin (Indulin A, Polychemicals Division, West Virginia Pulp and Paper Co.), recovered by acidification of kraft black liquor from the pulping of pine woods of the Southeast. A typical analysis as offered by the manufacturer is: moisture 4.3%, ash 0.4%, methoxyl 13.9%, and sulfur 1.4%. Four fractions of the lignin prepared by fractionation with acetone and with methanol, and a chemically modified form were also studied. The commercial lignin was fractionated according to the procedure outlined in Figure 1.

An oxidized lignin was prepared by passing oxygen gas through an aqueous alkaline solution of the commercial lignin. A solution containing 20% of the commercial lignin was prepared in which 4 moles of alkali were used to each 840 grams of the lignin. The solution was heated to 70° C. and oxygen gas was passed in for 11.5 hours at a rate of 0.04 cu. foot per minute per 1000 grams of lignin. When oxygen addition had been completed, the mixture was heated to 90° C. and 12*N* sulfuric acid was added with good stirring until a pH of 2.0 was obtained. The acidified mixture was allowed to cool to 70° C. and then filtered. The oxidized lignin cake was washed with water until the wash water had a pH of 4.5. The lignin was then dried to constant weight at 105° C.

## PREPARATION OF PYRIDINE SOLUTIONS FOR VISCOSITY TESTS

After being dried to constant weight, the lignin and lignin fractions were stored in ground-glass weighing bottles, which were kept in desiccators containing both concentrated sulfuric acid and sodium hydroxide pellets as desiccants. The pyridine used to make the test solutions was Baker's analyzed reagent grade (J. T. Baker Chemical Co., Phillipsburg, N. J.).

## TESTS OF VISCOSITY OF LIGNIN-PYRIDINE SOLUTIONS

The viscometers used in the tests were the Cannon-Fenske-Ostwald Type 50 (Cannon Instrument Co., State College, Pa.), standardized by the instrument company under the direction of M. R. Cannon. They held a charge of approximately 7.0 ml. and had a driving head of approximately 9.0 cm., and the working diameter of the lower reservoir was 3.0 cm. Their suggested range of operation was 0.8 to 3 centistokes. The viscosities of the pyridine solutions were determined at 20.00° ± 0.01° C. by the testing procedure recommended by the Cannon Instrument Co.

The kinematic viscosity in centistokes for the pyridine solvent and the lignin solutions was obtained by multiplying the efflux time in seconds by the calibrated viscometer