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# Viscometric Determination of Molecular Weight of Cellulose Pulps in Zinc Ethylenediamine Solution*

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## INTRODUCTION

For process control or other purposes, the degree of polymerization (DP) of cellulose pulps is routinely determined by evaluating their intrinsic viscosities in cupriethylenediamine (CED) or cuprammonium solutions. However, these solutions are not so stable and exclusion of oxygen is necessary, during the course of measurements, to prevent appreciable degradation of cellulose molecules. Besides, owing to the intense blue color of these solvents, it is difficult to ascertain visually the complete dissolution of cellulose in them.

The use of an alternative, comparatively new, solvent, zinc ethylenediamine (ZED), which is colorless and stable, especially below 0°C., has shown several advantages over the solvents containing complexes of copper. The method of its preparation, reported by Jayme and Neuschaffer,[1] involves the time-consuming step of removing chloride ion from $Zn(OH)_2$ as it is obtained by precipitation from $ZnCl_2$. In the present communication, a preliminary report of a more convenient method of preparing zinc ethylenediamine solution and its use in the viscometric determination of molecular weight ($M_n$) and DP of rayon-grade pulps is described.

## EXPERIMENTAL

### Preparation of the Solvent

Analar ZnO (approximately in the proportion 50 g./kg. of ethylenediamine) was vigorously shaken with different concentrations of ethylenediamine in water at 0°C. Aliquots from the solutions were taken from time to time and filtered through a sintered-glass funnel, and the amounts of zinc in each solution were estimated volumetrically[2] with the use of a standard solution of the disodium salt of ethylenediaminetetraacetic acid and Eriochrome Black T indicator. Ethylenediamine concentrations in various mixtures were estimated potentiometrically by titrating against standard HCl. The attainment of the dissolution equilibrium took about 72 hrs. The amounts of zinc thus brought into ethylenediamine solution

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of different concentrations (on a weight basis) are shown in Figure 1. Although the solution corresponding to 25% ethylenediamine dissolved a maximum amount of zinc, it did not show any sign of dissolving cellulose. The solution containing 40% ethylenediamine and 0.255*M* zinc showed appreciable dissolving power. The rate of dissolution is increased by lowering the temperature below 0°C. Hence, the study was repeated at the concentration range 35–45% ethylenediamine for determination of the optimum composition. It was found that a solution containing 41.2% ethylenediamine and 0.25*M* zinc dissolves rayon-grade pulps to the extent of 5 g./l. at −8°C. in $^1/_2$ hr.

The following eight rayon-grade pulp samples, with their commercial names given in parentheses, were used in the present investigation: A (Tenacell), B (Hawkesburg Novocell), C (Kipawa Novocell I), D (Kipawa

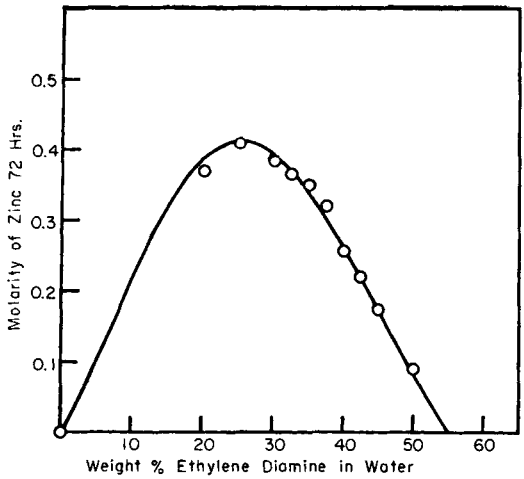


Fig. 1. Amount of zinc complexed versus concentration of ethylenediamine in water at −8°C. in 72 hrs.

Novocell II), E (Modosilk-special), F (Uddeholm Ultra), G (Borregaard-Super VS) and H (Rayonier-Hicolor). The first four were obtained through the courtesy of Riordon Sales Ltd., U.S.A., and the remaining were kindly supplied by National Rayon Corporation, India. The pulps were purified by the A.S.T.M. method D 539–53. For eliminating undissolved particles and obtaining reproducible flow times it was necessary to filter the pulp solutions through a sintered-glass funnel (No. 2) before use.

## Viscometric Measurements

*1.* Flow times for the solvent and pulp solutions of different concentrations were measured with an Ubbelohde viscometer and the use of the constants $A = 0.05935$ and $B = 1.13413$ in the equation $\eta = At + B/t$; $\eta_{sp}/c$ vs. $c$ plots were then made for intrinsic viscosity. Temperature

was regulated to within ±0.01°C. in a thermostated bath while flow measurements were carried out at the four temperatures 15, 20, 25, and 30°C. Figure 2 depicts the $\eta_{sp}/c$ vs. $c$ plots for sample A at the various temperatures and also indicates the range of concentrations used in the present work.

*2.* For shear dependence of viscosity of the cellulose solutions, a multigradient viscometer covering the shear rate range 10–100 sec.$^{-1}$ was used.

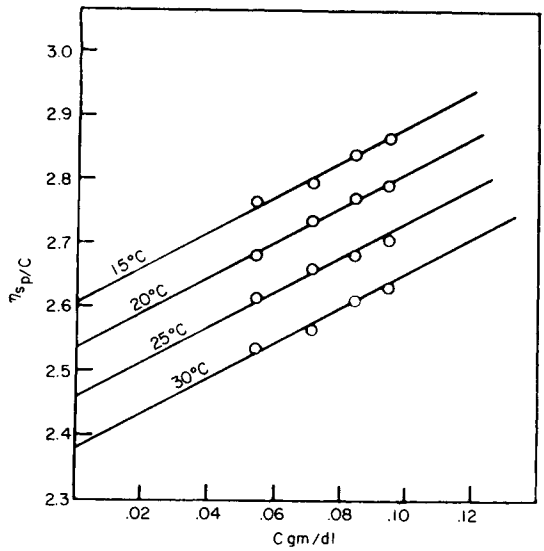


Fig. 2. Plots of $\eta_{sp}/c$ vs. $c$ at four temperatures for sample A.

*3.* The preparation of cupriethylenediamine and intrinsic viscosity determination of the cellulose pulp solutions in it were made according to the A.S.T.M. method D 539-53.

## RESULTS AND DISCUSSION

The intrinsic viscosities of eight samples in ZED solution at different temperatures are recorded in Table I. In the last column but one the temperature coefficients of intrinsic viscosity are recorded. The variation of $[\eta]$ with temperature is linear, and it can be seen from Figure 3 that there is very little scatter in the data. Pulps C and D are reported to be samples obtained from different batch preparations of the same (softwood) raw material. Figure 3 shows that they have the same intrinsic viscosity, indicating the reproducibility of the product obtained in different batches.

The ZED solvent is stable at and below 0°C. but at room temperature it tends to develop a faint yellow color on long standing in a glass (Pyrex) container. The decrease in flow time of dilute pulp solution on standing in air was found to be of the order of 0.1%/hr., which is much smaller than

TABLE I
Variation of Intrinsic Viscosity with Temperature

| Samples | $\eta$, dl./g. at ($T$°C.) | | | | $(d[\eta]/dT)$ × $10^2$ | $\overline{M}_n$ (25°), × $10^4$ |
|---|---|---|---|---|---|---|
| | 15° | 20° | 25° | 30° | | |
| A | 2.60 | 2.53 | 2.46 | 2.38 | 1.47 | 8.7 |
| B | 2.81 | 2.75 | 2.68 | 2.60 | 1.43 | 9.5 |
| C | 3.87 | 3.82 | 3.71 | 3.65 | 1.40 | 13.5 |
| D | 3.88 | 3.82 | 3.75 | 3.65 | 1.40 | 13.7 |
| E | 3.20 | 3.16 | 3.12 | 3.05 | 1.09 | 11.2 |
| F | — | 3.63 | 3.56 | 3.49 | 1.40 | 12.9 |
| G | 3.27 | 3.23 | 3.19 | 3.13 | 0.97 | 11.5 |
| H | 3.23 | 3.15 | 3.09 | 3.03 | 1.30 | 11.1 |

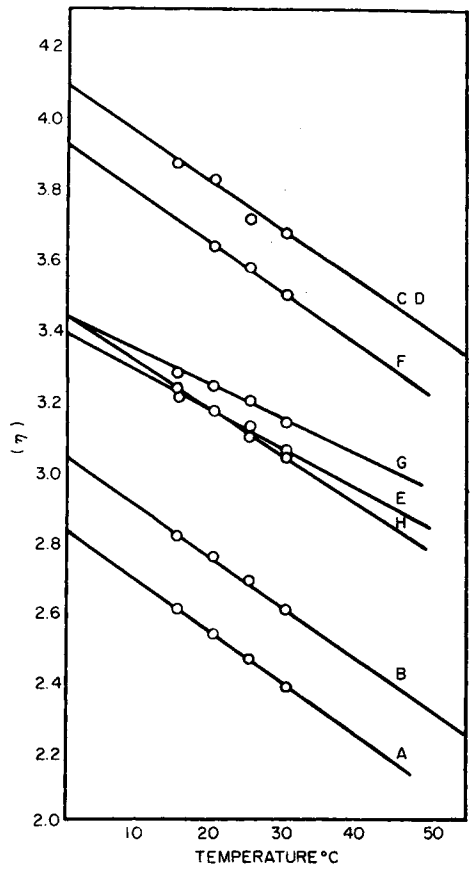


Fig. 3. Variation of intrinsic viscosity with temperature.

that in CED solutions. Therefore, exclusion of air during the measurement was not necessary in the present case. The study of shear dependence of intrinsic viscosity showed that the flow was Newtonian in the range 20–100 $sec^{-1}$.

The intrinsic viscosities in CED solution at 25°C. obtained by us are given in Table II (column 3), wherein are also recorded (column 2) the corresponding TAPPI values kindly supplied by Riordon Sales. The number-average molecular weight $\bar{M}_n$, calculated from our own values of $[\eta]_{CED}$ by use of the Mark-Houwink equation $[\eta] = K\bar{M}_n^a$ (where $K = 1.33 \times 10^{-4}$ and $a = 0.905$) are given in column 4, Table II. The validity of this equation relating intrinsic viscosity and number-average molecular weight and the values of $K$ and $a$ for cellulose CED system have been well established by Immergut et al.[3]

TABLE II
Intrinsic Viscosities and Molecular Weights

| Sample | $[\eta]_{CED}$ | $[\eta]_{CED}$[a] | $\bar{M}_n$ | $[\eta]^*_{ZED}$[a] | Calculd. $\bar{M}_n$ |
|---|---|---|---|---|---|
| A | 3.5 | 4.00 | 88,760 | 2.46 | 86,940 |
| B | 4.1 | 4.19 | 93,440 | 2.68 | 95,410 |
| C | 5.9 | 5.88 | 135,800 | 3.71 | 136,000 |
| D | 5.9 | 5.90 | 136,400 | 3.75 | 136,700 |

[a] Present investigation.

The $M_n$ values obtained for samples A to D were used in calculating, by the method of least squares, the corresponding $K$ and $a$ values for the cellulose–ZED system from the intrinsic viscosity data at 25°C. given in Table I values.

$K = 5.85 \times 10^{-5}$ and $a = 0.936$ are arrived at, and thus a viscometric relationship with CED can be seen, where $K$ is considerably higher in the latter system. The corresponding $\bar{M}_n$ in ZED are given in the last column of Table II. The molecular weights of samples D, G, and H, calculated from our ZED viscosity data, are 136,000, 114,900, and 111,400, which are comparable to the values 155,000, 149,500, and 151,000 obtained from reported, approximate DP values of cellulose pulps of the same trade name.

In a practical determination of intrinsic viscosity, if the measurements are carried out at any temperature in the range 15–30°C., the values could be readily converted to those at 25°C. by making use of the temperature coefficient of intrinsic viscosity as 1.3 dl./g./degree. The error in $[\eta]$ likely to be introduced in this way does not exceed ±1%.

In conclusion, the results of this investigation suggest that the use of ZED as solvent for cellulose pulps for viscometric determination of their molecular weights is preferable to the commonly used CED or cuprammonium solvents.

The authors are indebted to Mr. P. R. Chinchole for assistance in this work.

## References

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## Synopsis

A convenient method of preparing zinc ethylenediamine complex (ZED) solution for use as solvent for cellulose pulp is described, and the advantages in using this solvent (0.25*M* zinc in 41% ethylenediamine in water) over cupriethylenediamine (CED) or cuprammonium solutions for viscometric determination of molecular weight of cellulose are indicated. Intrinsic viscosities of eight rayon-grade pulp solutions have been determined at four temperatures: 15, 20, 25, and 30°C. The constants $K = 5.85 \times 10^{-5}$ and $a = 0.936$ of the Mark-Houwink equation $[\eta] = K\overline{M}_n^a$, required for evaluating the molecular weight of cellulose pulps in ZED solution, have been determined by using the molecular weight values obtained from CED solutions.

## Résumé

On décrit une méthode facile pour préparer une solution de complexe zinc-éthylènediamine (ZED) destinée à servir de solvant de la pâte de cellulose; on souligne les avantages de ce solvant (0.25*M* de zinc dans 41% d'éthylène diamine dans l'eau) sur les solutions de cuprié thylène-diamine (CED) ou de cuprammonium, pour la détermination viscosimétrique des poids moléculaire de la cellulose. On a déterminé les viscosités intrinsèques de huit solutions de pâte qualité rayonnejà quatre températures différentes: 15°, 20°, 25° et 30°C. Les constantes $K = 5.85 \times 10^{-5}$ et $a = 0.936$ de l'équation de Mark-Houwink, $[\eta] = K\overline{M}_n^a$ requise pour la détermination du poids moléculaire de pâtes de cellulose en solution ZED, ont été déterminées à partir des valeurs du poids moléculaire obtenu en solutions CED.

## Zusammenfassung

Eine einfache Methode zur Darstellung einer Lösung des Zink-Äthylendiaminkomplexes (ZED) als Lösungsmittel für Cellulosepulp wird beschrieben und die Vorteile dieses Lösungsmittels (0,25 M Zink in 41% Äthylendiamin in Wasser) gegen Cupriäthylendiamin- (CED) oder Cuprammoniumlösungen zur viscosimetsischen Molekulargewichtsbestimmung von Cellulose werden gezeigt. Die Viskositätszahl von acht Rayonpulplösungen wurde bei vier Temperaturen, nämlich 15°, 20°, 25° und 30°C, bestimmt. Die Konstanten der Mark-Houwinkgleichung, $[\eta] = K\overline{M}_n^a$, $K = 5{,}85 \times 10^{-5}$ und $a = 0{,}936$, die zur Ermittlung des Molekulargewichts von Cellulosepulps in ZED-Lösung benötigt werden, wurden mit den aus CED-Lösungen erhaltenen Molekulargewichtswerten bestimmt.

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