Countercurrent Fractionation of Cellulose Derivatives with Porous Charcoal II

HAROLD A. SWENSON* and AGNETA ROSENBERG

*Paper Technology Department, Swedish Forest Products Research Laboratory,
Stockholm, Sweden*

The effect on the resulting cumulative integral and differential DP weight distribution curves, of altering the uptake to the charcoal stages is investigated. This is accomplished through variation of the concentration of the polymer charge and the number of charcoal stages.

In an earlier paper by Swenson¹ it was shown that secondary cellulose acetates could be fractionated with a countercurrent procedure of the Craig type² in which porous charcoal was used as the stationary phase.

The separations were shown to occur by the preferential diffusion and adsorption of the lower, in preference to the higher weight molecules, by the charcoal stages, the unadsorbed polymer of higher DP advancing to later stages. The fractionation method and the fifty stage countercurrent apparatus designed for the experiment were also described.

In the present paper, the effect on the resulting integral and differential DP weight distribution curves, of altering the uptake to the charcoal stages is investigated. This is accomplished through variation of the concentration of the polymer charge and the number of charcoal stages.

The fractionation of a high DP secondary cellulose acetate and a cellulose nitrate are also reported and the osmotically determined molecular weights of the original samples and of a limited number of the fractions are given.

The low concentration, fifty stage fractionation of
cellulose acetate 1.62

Two grams of the sample — the samples are identified in the text by their intrinsic viscosity values — in 30 ml acetone, were introduced to the first of the 50 stages, each containing 8 g of charcoal saturated with solvent. 5 min. shaking periods were used.

The concentration of the polymer charge was chosen so that the removal of a high percentage of the sample to the charcoal would be obtained while also

* Present address: The Institute of Paper Chemistry, Appleton, Wisc., USA.

taking advantage of all the charcoal stages. It was known that 49 additions of following solvent to the first stage would have resulted in the fractionation effect of no more than 42 of the stages, because of the detaining, countercurrent effect of the charcoal on the polymer¹. Consequently, 59 additions of 25 ml acetone were made, between the successive shaking and transfer operations which served to spread the polymer to further stages. The 10 extra additions of the solvent, free of polymer, were decanted from the last charcoal stage of the apparatus.

At the conclusion of the run, after the routine removal of the solvent from the transfer reservoirs and the charcoal tubes with a syringe, elution was done by shaking the charcoal stages twice with 25 ml dioxan. The run was then duplicated and the respective fractions combined to afford more material for analyses. The accuracy of the duplication was checked by separate determinations of the amounts and intrinsic viscosities of the unadsorbed polymer found at the later stages in the two runs.

Of the sample 74 % was recovered, 9 % was not taken up by the charcoal. The average intrinsic viscosity of the recovered fractions was 1.47. Correction for irreversible precipitation effects (see Experimental) increased this figure to 1.53.

This run is compared to an earlier fractionation of the same sample¹ in which the amount of polymer charge appreciably exceeded the uptake capacity of the charcoal stages. 5 g of sample 1.62 was introduced in this run in 70 ml acetone to the first two stages followed by 50 additions of 25 ml acetone to the first stage. To elute the adsorbed polymer, two shakings with 25 ml dioxan were used. Of the sample 25 % was in the decanted acetone which, when added to the eluted material accounted for a total recovery of 60 %. The average intrinsic viscosity of the recovered fractions, uncorrected, was 1.53.

Fig. 1. Eluted and free material expressed as mg/g charcoal found at each stage in fifty stage fractionations of cellulose acetate sample 1.62. Upper figure: Five grams of sample followed by 50 solvent additions. Lower figure: Two grams of sample followed by 60 solvent additions. Open symbols: the eluted fractions. Solid symbols: the material not taken up by the charcoal.

Fig. 2. The cumulative integral fractionation curves from the cellulose acetate fractionations. a. 0.5 g of sample 0.95; 20 stages and 19 additions of solvent. b. 5 g of sample 0.95; 50 stages and 50 solvent additions. c. 2 g of sample 1.62; 50 stages and 60 solvent additions. d. 5 g of sample 1.62; 50 stages and 50 solvent additions. e. 3.6 g of sample 2.24; 50 stages and 60 solvent additions.

In this and subsequent fractionations reported, the amounts eluted from the charcoal are corrected to 100 % recovery assuming, following an earlier finding¹, in which the amounts and intrinsic viscosities from successive elutions were determined, that representative elution of like proportions of the polymer regardless of DP were recovered.

Fig. 3. The differential weight distribution curves of cellulose acetate samples 1.62 and 2.24. A. 5 g, 50 stage fractionation of sample 1.62. B. 2 g, 50 stage fractionation of sample 1.62. C. 3.6 g, 50 stage fractionation of sample 2.24.

The quantities of adsorbed and unadsorbed polymer found at each apparatus stage in the two fractionations are shown in Fig. 1. It can be seen in the lower part of the figure how the polymer has been spread to further charcoal stages in the lower concentration run as a result of the extra additions of solvent.

The integral fractionation curves from the two runs are shown in Fig. 2, curves *c* and *d*. The DP weight distribution curves, obtained by graphical differentiation of the integral curves, are given in Fig. 3, the latter closely reflecting the amounts found at each apparatus stage as shown in Fig. 1.

In the DP weight distribution curve resulting from the high concentration fractionation, Fig. 3 A, the first peak from the right derives from the decanted, unadsorbed material of highest DP and the peak next to the left, the material eluted from the corresponding underlying charcoal stages.

In the lower concentration run, Fig. 3 B, the material in these peaks of less fractionated higher DP polymer have largely been taken up by the charcoal stages resulting in a single maximum distribution curve, an extension of the DP range of the fractions and higher apparent homogeneity of the fractions.

Twenty stage fractionation of cellulose acetate 0.95

To determine how the fractionation is influenced by using fewer stages in combination with high uptake of sample to the charcoal, the low DP sample was run at low concentration. 0.5 g of the sample in 25 ml acetone was introduced to the first of 20 stages, each containing 9 g of charcoal, the effective charcoal capacity of the apparatus.

Nineteen 25 ml additions of acetone were made between successive 5 min. shaking periods. Elution was done by shaking twice for two or more hours with dioxan. Total recovery was 59 %. Less than 4 % of the sample was not taken up by the charcoal. The average intrinsic viscosity of the recovered fractions, which required no correction for irreversible precipitation effects, was 0.94.

This run is compared to an earlier¹ 50 stage fractionation of the same sample in which the amount of sample again exceeded the uptake capacity of the charcoal. 5 g was introduced in 70 ml acetone, in two 35 ml portions to the first two stages of the apparatus followed by fifty additions of acetone. 9 g of charcoal per stage and 5 min. shaking periods were used. Recovery after three elutions with 25 ml dioxan was 92 %, 15 % of the sample was unadsorbed. The average intrinsic viscosity of the recovered fractions, uncorrected, was 0.95.

The experimental integral curves which resulted from the two runs are shown in Fig. 2, curves *a* and *b*, and the differential weight distribution curves in Fig. 4. In the latter figure, curve A, from the high concentration 50 stage fractionation, the two peaks from right to left, the unadsorbed material and the material later eluted from the corresponding underlying charcoal stages, respectively, have again resulted from exceeding the uptake capacity of the 50 charcoal stages. More stages or more charcoal per stage were needed to adsorb and further fractionate the free material.

Fig. 4. The differential weight distribution curves of cellulose acetate 0.95. Upper figure: 5 g, 50 stage fractionation. Lower figure: 0.5 g, twenty stage fractionation.

Little polymer material was found in the transfer reservoirs following the 20 stage run and no polymer was found in the first 25 reservoirs after the 50 stage run. This shows, since little or no transfer of polymer was occurring between stages, that the lower DP peaks in the two distribution curves have largely been stabilized by irreversible adsorption. As a result, extending the runs to further stages could not be expected to effect appreciable further fractionation of this lower DP material.

Fractionation of cellulose acetate 2.24

The fractionation of a high DP secondary cellulose acetate was of particular interest since it appeared from earlier fractionations of the lower DP acetate 1.62 that a limit was being approached in the DP of the polymer sample which could be effectively fractionated. In the fractionation run, 3.6 g of acetate 2.24 was introduced in 60 ml acetone in two 30 ml portions to the first stage followed by sixty 25 ml additions of acetone between the successive shaking and transfer operations. 9 g of charcoal were used in each of the 50 apparatus stages and 5 min. shaking periods.

Total recovery, after two 25 ml dioxan elutions was 73 %, 21 % of the sample remaining free of the charcoal. The average intrinsic viscosity of the fractions was 2.00, before correction, and 2.20, after correction for the irreversible precipitation effect.

The experimental integral fractionation curve is given in Fig. 2, curve e, and its graphical differentiation in Fig. 3, curve c. The peak to the right is again the apparent result of too high sample concentration for the uptake capacity of the charcoal stages. The peak contains, however, in contrast to earlier runs with lower DP acetates, both unadsorbed decanted polymer and a smaller amount of adsorbed polymer which was eluted with dioxan. The latter adsorbed material was found in the charcoal stages over the entire DP range of the fractions to DP ca. 450 in comparison to the runs with acetate sample 1.62 (*cf.* Fig. 3, A, B), in which the highest DP fractions removed from the charcoal had a DP of ca. 300.

A further indication that the experiment shows no apparent limit in the DP of the polymer which can be fractionated, is indicated by the percentage of the sample not taken up by the charcoal, 21 % from 3.6 g of sample 2.24 compared to 25 % not taken up by the charcoal in a similar 50 stage fractionation of 5 g of sample 1.62.

Osmotic pressure determinations

Measurements were made on the original cellulose acetate samples and on the lower DP fractions, Nos. 4, 6 and 8, from the 2 g, 50 stage fractionation of sample 1.62, Fig. 3 B. The small amounts in the fractions were insufficient to allow determinations on more of the fractions from the run.

The measurements were made in Schulz type osmometers at $25^\circ\text{C} \pm 0.02$. The osmotic pressure molecular weight of the original acetate 2.24 and of additional samples not included in the paper were determined at the Institute of Physical Chemistry, Uppsala University, Uppsala, Sweden. Zimm-Myerson osmometers³ were used in the latter measurements. "Ultracellafilter, allerfeinst" membranes from Membran-Gesellschaft, Göttingen, were used in the determinations with both types of osmometers.

The osmotically determined M_n values and K_m values calculated from the intrinsic viscosities by means of the Staudinger relation $[\eta] = K_m \cdot (\text{DP})$, are listed in Table 1. $K_m = 7 \times 10^{-3}$ was chosen in the present paper to convert the intrinsic viscosity values to DP.

Table 1.

Sample	(η) exp	M_n	$K_m \times 10^3$	M_w ($K_m 7.0 \times 10^{-3}$)	DP
0.95	0.95	30 000	8.3	35 300	136
1.63	1.62	62 000	6.8	60 000	230
2.24	2.24	78 000	7.3	83 000	320
Fractions					
4	1.04	38 000	7.1	38 700	149
6	1.09	43 800	6.5	40 500	156
8	1.14	48 000	6.2	42 300	163

It is seen from the table that the M_n of the three fractions rises with the corresponding increase in intrinsic viscosity and fraction number. Because so few analyses on limited amounts from a narrow band of the total distribution could be made, the drop in the K_m value from fraction 4 to fraction 8 cannot safely be interpreted to be due to a corresponding decrease in polydispersity.

The substitution degree of secondary cellulose acetate fractions

Duplicate acetyl analyses were obtained on the eluted fractions 1, 3, 5, 7 and 9 and on combined contiguous eluted fractions Nos. 10 to 44 from the 1.62 fractionation (cf. Fig. 3 B) and single analyses on both combined contiguous,

Fig. 5. The acetyl substitution of the fractions versus their DP. Upper: Fractions from 3.6 g fifty stage fractionation of sample 2.24. Lower: fractions from 2 g fifty stage fractionation of sample 1.62.

eluted and unadsorbed fractions from the fractionation of sample 2.24 (cf. Fig. 3 C).

A plot of the percent acetyl of the fractions *versus* their respective DP values is given in Fig. 5. The original samples 1.62 and 2.24 had 39.1 and 40.1 % acetyl while the average of the analyses on the fractions were 41.0 % and 41.5 %, respectively. The higher average acetyl content of the fractions appears to have been due either to the presence of non-acetyl contaminants or to analytical reasons since the fractions analyzed were largely representative of the entire sample.

No significant variation of acetyl content with DP is apparent from Fig. 5. The variation in acetyl content between fractions, however, is roughly ten times as great as that reported by Staudinger and Eicher⁴ following the fractional precipitation of a commercial secondary cellulose acetate of similar DP and substitution degree from acetone with water. The higher apparent non-uniformity shows that the countercurrent fractionation is relatively free of substitution effects. This would be expected since the counter-current separations depend primarily on variations in diffusion rates. Rosenthal and White⁵ found variations in substitution of a similar order to those in Fig. 5 by the fractional cross precipitation of secondary cellulose acetates from acetone with water. The variations they reported were also apparently independent of DP.

The five stage fractionation of cellulose nitrate

1.5 g of a cellulose nitrate with intrinsic viscosity 1.95 (see Experimental) was introduced in 25 ml acetone to the first of 5 charcoal stages followed by four 25 ml additions of acetone between 5 min. shaking periods. 9 g of charcoal were used per tube. To elute, the charcoal was shaken twice with 25 ml dioxan.

Fig. 6. The amounts of eluted and free material in the fractions from the five stage fractionation of cellulose nitrate 1.95. Circles: the eluted fractions. Triangles: the unadsorbed fractions. The intrinsic viscosities are inscribed for each fraction.

The fractions, in both acetone and dioxan, were precipitated in water, evaporated and further dried under vacuum at room temperature before redispersing in acetone for the viscosity measurements. The total recovery was 95 %, 69 % of which was unadsorbed, decanted, material.

The average intrinsic viscosity of the recovered fractions was 1.62. This low value evidently resulted from degradation of the fractions since the high recovery apparently precluded unrepresentative elution as the cause for the low average intrinsic viscosity of the recovered fractions.

Fig. 6 shows the amounts taken up by each charcoal stage, the amounts decanted at each stage and the intrinsic viscosity of the fractions. The figure, which shows how rapidly and effectively the fractionation begins, also illustrates how the peak of free material appears at an early stage when the uptake capacity of the five charcoal stages is far exceeded. If the run were extended to more charcoal stages the peak of free material would gradually lessen as more material is removed to the charcoal stages. The higher polydispersity of the large fractions in the peak of free material is indicated by their viscosity values which, although the degradation effect must be taken into consideration, are close to that of the original sample.

The result of a 50 stage fractionation of the cellulose nitrate sample is not reported due to the degradation of the fractions which apparently occurred primarily during the precipitation and drying of the fractions. Erratic drops in viscosity were found when some of the fractions in acetone, which had not

Fig. 7. The intrinsic viscosity of the original cellulose acetate samples after precipitation from dioxan versus the intrinsic viscosity of the samples dispersed directly in acetone. The figure was used to correct the intrinsic viscosity of some of the eluted fractions.

altered in viscosity after standing for a week, were reprecipitated in water, dried below 55° C and redispersed in acetone. The viscosity efflux time of the original cellulose nitrate sample in acetone dropped only very slightly after six weeks at room temperature. In dioxan the sample did not change in efflux time after six weeks following an initial drop due to the formation of a slight haze of precipitate which formed after a few days.

EXPERIMENTAL

Materials. The cellulose acetates are Hercules Powder Company products. The samples with intrinsic viscosities of 0.95, 1.62 and 2.24 are substituted to the extent of 2.45, 2.39 and 2.48 respectively. The cellulose nitrate sample from Nitroglycerin AB, Gyttorp, Sweden, had a nitrogen content of 12.02%, an intrinsic viscosity of 1.95.

The acetone had analytical purity and the dioxan, of ca. 99% purity was used without further treatment. The charcoal, a Norit Company product, is a rather soft, extruded carbon with particle diameter 0.7 mm and with ca. 10% ash content, half of which could be removed with concentrated hydrochloric acid. The untreated charcoal, except for drying, was used in the experiments.

The characteristics sought for in choosing the charcoal were maximum uptake capacity, adequate adsorptive capacity and a particle size from which the polymer solution could be readily decanted. Hard charcoals would be desirable to minimize the charcoal fines that develop from abrasion of soft charcoals during the shaking. Since the uptake capacity was found to increase with increasing softness and porosity, however, the rather soft charcoal was chosen for the experiments. Prior screening and washing of the charcoal was done to minimize the fines. Centrifuging the fraction solutions was necessary¹.

Irreversible precipitation. Evidently due to variations in the purity of the dioxan, it was found that when the cellulose acetates in dioxan were precipitated in water on a steam bath and dried in vacuum at 105° C, theoretical recoveries, on which the concentration values were based were difficult to obtain. Further, the very dry precipitates would not disperse completely in acetone and low viscosity values resulted.

The dioxan fractions were, thereafter, precipitated in water, dried and evaporated at room temperature. The precipitates, containing some moisture, were then dispersed in acetone. The concentration of the latter solutions, used for the viscosity measurements,

was determined on a part of this solution by precipitating in water on the steam bath and drying at 105° C, under vacuum. Theoretical recoveries were obtained in this way but the viscosity values were still low.

To determine the degree of the insolubility effect on the viscosity, varying concentrations of the 0.95, 1.62 and 2.24 cellulose acetates in dioxan were precipitated without heat and the viscosity of the precipitates, redispersed in acetone, determined. The insolubility was found to be independent of the concentration of the solutions precipitated.

In Fig. 7 is shown a plot of the viscosity values on the redispersed precipitates *versus* the viscosity of the original samples dispersed directly in acetone. The graph which was used to correct the viscosity values illustrates that the insolubility increases with increasing DP.

Viscosity measurements. A single measurement method described in the earlier paper¹ was used for the cellulose acetates. The intrinsic viscosity of the cellulose nitrate samples were made by extrapolation of plots of the reduced viscosity *versus* concentration at three or more concentrations below 0.5 g/dl. Ostwald pipettes requiring 2 ml of solution recommended⁶ for a range between 0.3 and 5.0 centipoises were used at 25° C $\pm$ 0.02.

DISCUSSION

When complete uptake to the charcoal stages was approached in the fractionations of secondary cellulose acetate, single maximum positively skewed, DP weight distribution curves were obtained of the theoretical type to be expected from the random degradation of an original high DP polymer.

While a peak of lower DP material may be expected on theoretical grounds, it is also in the first stages of the apparatus that the highest concentration gradient as well as diffusion rate can be expected to combine in greatest uptake to the charcoal, both effects diminishing as the polymer solution advances to later stages.

Since the fractions in the charcoal stages are held by irreversible adsorption as the runs proceed, the adsorbed material is not further fractionated and the percentage of the sample held by the charcoal stages will determine in part their relative polydispersity. It is important, in consequence, to choose the amount of sample to be fractionated in relation to the uptake capacity, as well as the number, of charcoal stages.

In the countercurrent fractionations, too small a sample in relation to the adsorptive capacity resulted in detention of a higher proportion of lower DP material (*cf.* Fig. 4 B). Too large a sample, on the other hand (*cf.* Fig. 3 A) resulted in the apparent finer fractionation of the lower DP material in the distributions, while higher DP material of consequently higher polydispersity was left unadsorbed since more stages were needed to fractionate the latter material.

The uptake to the charcoal which has been varied in the present experiments by altering the polymer concentration and number of stages while keeping the charcoal capacity and shaking times constant, could also be varied by altering the shaking times, by using a diffusion medium of different porosity and adsorptive capacity or by altering the polarity of the solvent.

Comparison of the first fractions in the two runs in which 0.5 and 5.0 g of acetate 0.95 were introduced to the stages with 9 g charcoal, illustrates the effect of variation in the percentage of sample in the fraction on the selectivity of the separation. The percentages recovered, for example, in the first fraction stage, in the two fractionations, were 10.3 % and 2.6 %, respectively. The

higher apparent polydispersity to be expected of the higher percentage fraction is shown by the intrinsic viscosity, 0.63, compared to that of the low percentage fraction 0.53. The larger percentage fractions from the low concentration 20 stage run also appear to be less sharp when comparison is made of the intrinsic viscosity 0.63 of the single fraction containing 10.3 % of the sample, with the average intrinsic viscosity 0.57 of the first four fraction stages from the high concentration 50 stage run which contained 11.4 % of the sample.

It should be stressed that the solid phase counter-current fractionations are rigorously reproducible, this has been confirmed repeatedly in the course of the experiments. The method, in consequence, is useful for comparative determinations of polymolecularity pending the time when the comparative accuracy of the DP weight distribution curves can be established by determination of the M_w/M_n ratios of the fractions or by other means.

The upper and lower limits in DP which can be fractionated with the method also remain to be established since with the samples investigated, no apparent limit was found. Fractions varying in DP from *ca.* 70 to 500 were obtained in the experiments.

Acknowledgements. The authors wish to express their appreciation to Docent Bengt Rånby, Institute of Physical Chemistry, Uppsala University, Uppsala, Sweden, for the osmotic pressure analyses and also thank Dr. Bertil Enoksson of Nitroglycerin AB, Gytting, Sweden, for kindly providing cellulose nitrate samples with accompanying analyses.

The authors are also indebted to Dr. Per Olof Betghe and Miss Rose Marie Persson of the analytical department of this laboratory for the acetyl analyses and to Miss Maj-Britt Eriksson for her assistance in the experiments.

REFERENCES

1. Swenson, H. A. *Acta Chem. Scand.* **9** (1955) 572.
2. Craig, L. C., Hausmann, W., Ahrens, E. H. Jr. and Harfenist, E. J. *Anal. Chem.* **23** (1951) 1236.
3. Zimm, B. H. and Myerson, I. *J. Am. Chem. Soc.* **68** (1946) 911.
4. Staudinger, H. and Eicher, T. *Makromol. Chem.* **10** No. 1 (1953) 235.
5. Rosenthal, A. J. and White, B. B. *Ind. Eng. Chem.* **44** (1952) 2693.
6. Cannon, M. R. and Fenske, M. R. *Ind. Eng. Chem. Anal. Ed.* **10** (1938) 297.

Received July 6, 1956.