MASTER

DETERMINATION OF ABSOLUTE MOLECULAR WEIGHTS
OF
NITROCELLULOSE BY GEL PERMEATION CHROMATOGRAPHY

B. J. Jacobs
R. A. Blythe
C. S. MacDougall
A. C. Teter

QUALITY DIVISION

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Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 647
AMARILLO, TEXAS 79177
806-335-1581

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SUMMARY

Vapor pressure osmometry was used to determine absolute molecular weights of three different grades of nitrocellulose. Nitrocellulose samples of 250 - 750 mg were weighed into 10 ml volume flasks and dissolved in tetrahydrofuran. The solutions were run against tetrahydrofuran solvent and the molar concentrations were determined by comparing values of ΔR for the samples with a calibration curve. The molecular weight of each of the nitrocellulose samples was then calculated from the sample weight and molar concentrations. These results were then correlated with GPC measurements to obtain a correct "Q factor."

INTRODUCTION

As deterioration of the nitrocellulose binder in PBX 9404 is critical in estimating useful shelf lives of units, a thorough investigation of the aging of nitrocellulose (NC) has been initiated. One of the parameters of particular interest is the molecular weight. Gel Permeation Chromatography (GPC) is a relatively rapid, accurate technique for measuring molecular weights. It relies, however, on calibration with standards of known molecular weights. At present, polystyrene standards are employed. Analyses of nitrocellulose molecular weights therefore include a "Q factor," or polystyrene equivalent, in all calculations. This is satisfactory for comparative data on NC molecular weights. However, as packing density and molecular configurations are dissimilar for NC and polystyrene, use of the polystyrene equivalent does not yield an absolute molecular weight. As vapor pressure osmometry measurements depend only on concentration of standard, three NC samples were analyzed for absolute molecular weights. These results were then correlated with GPC measurements in order to determine a correct "Q factor."

EXPERIMENTAL

APPARATUS

Vapor Pressure Osmometry

Analyses were carried out with a Beckman Model 301A Vapor Pressure Osmometer. Standards used in calibrating the osmometer were prepared by dissolving polystyrene of known molecular weight in tetrahydrofuran (THF).

Gel Permeation Chromatography

All GPC analyses were performed on a Waters Model 200 GPC using an RI detector.

SAMPLE PREPARATION

Vapor Pressure Osmometry

Nitrocellulose samples of 250 - 750 mg were accurately weighed into 10 ml volumetric flasks. Approximately 5 ml of THF were added to each flask and the flasks were placed on a shaker until the NC went into solution. THF was then added to the flasks to the 10 ml mark.

Gel Permeation Chromatography

A 0.018 g portion of each nitrocellulose sample was weighed into 20 ml of THF and dissolved with frequent manual shaking.

DISCUSSION

PRINCIPLE OF VAPOR PRESSURE OSMOMETRY

The operating principle of vapor pressure osmometry will be only briefly described. A solution of any solvent will have a lower vapor pressure than the pure solvent. When a drop of solvent and a drop of solution are placed on thermister probes, a differential mass transfer will occur between the two drops, resulting in lower evaporation from the solution drop. This transfer causes a temperature difference between the two drops which is proportional to the vapor pressure lowering, and hence proportional to the solute concentration. It is emphasized that measurements depend only on solute concentration, not on solute (or standard) type. Fig. 1 shows the standardization of the equipment.

VAPOR PRESSURE OSMOMETRY MEASUREMENTS OF NITROCELLULOSE

Three different grades of nitrocellulose were analyzed for absolute molecular weights. It is to be emphasized that all syringes were rinsed very thoroughly with THF as a very slight contamination of the samples would vitiate results. Table I shows the results of the analyses. Measurements on materials of known molecular weight indicate these values are accurate at least within $\pm 10\%$.

CHROMATOGRAPHIC MEASUREMENTS OF NITROCELLULOSE

The same grades of nitrocellulose were then examined by gel permeation chromatography. Fig. 2 shows the chromatograms of NC, which clearly shows the shifts indicative of varying molecular weights. However, using the polystyrene equivalent ($Q = 41.3$), molecular weights of 15,635 to 24,180 were obtained. As these values did not agree with the absolute values as measured by vapor pressure osmometry, further work was performed to determine an accurate "Q" value and thus permit measurement of absolute molecular weights by the more rapid GPC method.

P-4

Fig. 1. Calibration of Vapor Pressure Osmometer

5-d

Fig. 2. GPC Chromatograms of Nitrocellulose

CALCULATION OF "Q" CALIBRATION FACTOR

The number molecular weight average ($\bar{M}_n$) is directly measured by vapor pressure osmometry. Further, the definition of $\bar{M}_n$ is given by Equation 1.

$$\bar{M}_n = \bar{A}_n Q \quad (1)$$

$$\text{Where } \bar{A}_n = \frac{\sum H_i}{\sum \left(\frac{H_i}{A_i}\right)} \quad (2)$$

The height of the i^{th} count (H_i) is measured from the GPC chromatograms. Since separation of species by GPC is by molecular size, the Angstrom size of the i^{th} count fraction (A_i) can be measured from a calibration curve (Fig. 3). Table II gives the data for NC (Sample A) and a sample calculation. Table I gives the values of Q as calculated from data on each of the NC samples. The "Q" factors determined from three different analyses are essentially equal. Segal, et. al., have reported(1) a "Q" value of ~ 56 for NC using polystyrene columns. However, the total nitrogen in the nitrocellulose used for his study was about 13.6%. A shift to lower "Q" values is expected with lower total nitrogen due to solute - solvent interaction.

CONCLUSION

Vapor pressure osmometry was used to determine the absolute molecular weights of several samples of nitrocellulose. These values were in turn employed in the calculation of a "Q" factor for nitrocellulose. This constant allows the determination of absolute molecular weights by the more rapid method of gel permeation chromatography.

(1) L. Segal, J. D. Timpa, and J. I. Wadsworth, "Gel Permeation Chromatography and Cellulose .I. Effect of Degree of Nitration of Cellulose on Molecular Weight Distribution Data, *Journal of Polymer Science: Part A-1*, Vol. 8, 25-35 (1970).

P-7

Fig. 3. Relationship Between Angstrom Length and Elution Counts

Table I. Measurement of Molecular Weights of Nitrocellulose

<u>Sample</u>	<u>$\bar{M}_n$</u>	<u>% N in NC</u>	<u>Q</u>
A	5,674	11.98	14.81
C	8,710	12.23	14.70
B	12,058	12.19	13.85

Table II. Calculation of "Q" for Nitrocellulose

<u>Counts</u>	<u>H_i</u>	<u>A_i</u>	<u>H_i/A_i</u>
21	0	37,000	0
22	0.02	14,000	0.0000014
23	0.13	7,700	0.0000169
24	0.44	4,600	0.0000956
25	1.18	2,800	0.0004214
26	2.25	1,700	0.0013235
27	3.13	980	0.0031939
28	3.26	600	0.0054333
29	2.69	365	0.0073699
30	1.76	200	0.0088000
31	0.91	110	0.0082727
32	0.36	50	0.0072000
33	<u>0</u>	<u>0</u>	<u>0</u>

$$\Sigma H_i = 16.13$$

$$\Sigma (H_i/A_i) = 0.0421286$$

$$\bar{A}_n = \Sigma H_i / \Sigma (H_i/A_i) = 383$$

$$Q = \bar{M}_n / \bar{A}_n = 5674 / 383 = 14.81$$