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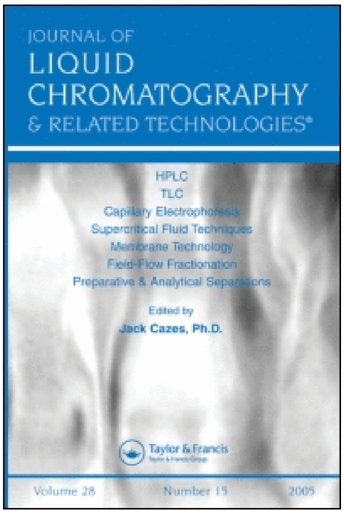

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UNIVERSAL CALIBRATION AND MOLECULAR WEIGHT AVERAGES IN GEL PERMEATION CHROMATOGRAPHY ILLUSTRATED BY CELLULOSE NITRATE AND POLY(OXYPROPYLENE)

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ABSTRACT

The nature of the averaging process in the analysis of gel permeation chromatograms was examined for cases where the molecules in the detector cell of the apparatus were of different molecular weight and of the same molecular weight. When the molecules have the same molecular weight, the hydrodynamic volume (1), $[\eta]M$, averaged across a chromatogram was found to become KM^{a+1} for any molecular weight average at the elution volume corresponding to that average. $[\eta]$ is intrinsic viscosity, M is molecular weight, and K and a are the appropriate Mark-Houwink constants. Thus when size separation is by molecular weight, the universal GPC calibration functions include KM_n^{a+1} where M_n is the number average molecular weight.

Cellulose nitrate and poly(oxypropylene) were analyzed using three sets of columns and two GPC instruments. KM_n^{a+1}, KM_w^{a+1}, and $[\eta]M_w$ were found to represent the hydrodynamic volume since these functions fell on the universal calibration plot for nearly nonodisperse polystyrene standards. The function $[\eta]M_n$ was displaced from the polystyrene universal calibration plot by factor which equaled M_w/M_n. The slopes and intercepts of the universal calibration plots were found to be completely consistent with the slopes and intercepts of the molecular weight calibration plots showing that the Mark-Houwink constants were correct. Intrinsic viscosity - molecular weight relations were presented for 12.0-12.6%N cellulose nitrate and for low molecular weight poly(oxypropylene), the latter relation being a correction of that of Sholtan and Lie (18).

INTRODUCTION

Since the introduction of the concept of universal gel permeation chromatography (GPC) calibration by Grubisic, Rempp, and Benoit (1) the nature of the hydrodynamic volume used in this calibration has been the subject of a number of papers (2-8). The expression for the hydrodynamic volume of the polymer molecules in the detector cell of the GPC apparatus at any one time was shown by A.E. Hamielec and A.C. Ouano (2) and Hamielec, Ouano, and Nebenzahl (3) to be $[\eta]M_n$ where $[\eta]$ is intrinsic viscosity and M_n is number average molecular weight. These workers employed what in effect were mixtures of polymers which had widely different shapes at the same molecular weight. Their results showed that the separation factor for this polymer mixture was also $[\eta]M_n$ across the whole chromatogram. On the other hand as shown by much experience there is no doubt that for a chromatogram the use of $[\eta]M_w$, where M_w is the weight average molecular weight, for hydrodynamic volume is ordinarily correct. This is because in most cases only one type of polymer of one size is present. However, on thinking about the subject it became apparent that our understanding of the averaging process in GPC statistics was incomplete. On looking at the matter in detail it was found, as will be shown below, that for a single kind of polymer the GPC separation factor averaged for a chromatogram should be KM^{a+1} at the elution volume corresponding to M, where M is molecular weight of any type average and K and a are the appropriate Mark-Houwink constants, rather than only $[\eta]M_w$ or KM_w^{a+1} at the peak elution volume. This conclusion was tested using GPC results on Cellulose Nitrate and Poly(oxypropylene) samples.

ARGUMENT

Several papers (2-8) have appeared concerning the nature of "the" hydrodynamic volume to use in the so-called universal calibration procedure for Gel Permeation Chromatography (GPC) devised by Grubisic, Rempp, and Benoit (1). Recent work by Hamielec and Ouano (2) has shown without any doubt that the calibration constant should be $[\eta]M_n$ where $[\eta]$ is the intrinsic viscosity and M_n is the number average molecular weight at any elution volume.

The universal calibration for GPC was based on Einstein's relation for the viscosity of a suspension of spheres (9):

$$[\eta] = \frac{kNVe}{M} \qquad \text{------------} \qquad 1$$

where $[\eta]$ = intrinsic viscosity

k = a constant

N = Avagadro's number

V_e = volume of a sphere equivalent to that of one solute molecule

M = molecular weight of solute

See Flory (10), p. 606. From Equation 1 the "hydrodynamic volume", NV_e is proportional to $[\eta]M$. $\text{Log}[\eta]M$ was found to be a linear function of elution volume for a number of polymers (1). $\frac{[\eta]M}{k}$ is an average of the size of all the solute molecules. Each molecule will have a molecular weight, M_i, and a characteristic intrinsic viscosity, $[\eta]_i$, so that:

$$[\eta]M = \frac{[\eta]_i M_i}{m} \qquad \text{----------} \qquad 2$$

where m is the number of molecules.

Following Hamielec and Ouano (2), if we define $[\eta]M$ as J, at any point on the elution volume curve J will be constant although M_w/M_n may vary. For that point let $[\eta] = \Sigma w_i[\eta]_i$ where w_i is the weight fraction of the ith species. That is, the intrinsic viscosity of the polymer is the weight, or better - viscosity, average of that of the fractions. But $J_i = [\eta]_i M_i$ and $[\eta]_i = J_i/M_i$. Therefore $[\eta] = \Sigma w_i J_i/M_i$. Hence $M = \frac{J}{[\eta]} = \frac{J}{\Sigma w_i\ J_i/M_i}$. But J is constant. Therefore $M = \frac{J}{J\Sigma w_i/M_i} = \frac{1}{\Sigma w_i M_i}$ which is the number average molecular weight., Hence M is M_n and J is $[\eta]M_n$.

In the general case as shown by Hamielec and Ouano (2) where the Mark-Houwink relation is not the same for all molecules, hydrodynamic volume varies with chromatographic elution volume in accordance with:

$$\text{Log } [\eta]M_n = \text{Log } A - bC \quad \text{- - - - - - - - - -} \quad 3$$

where A and b are constants and C is the elution volume, a relation which is linear or nearly so. If one is satisfied with molecular size, the average hydrodynamic volumes may be calculated statistically from h_i, the height of the elution curve at any point, and $J_i = [\eta]_i M_i$ read from the universal calibration curve determined for standard monodisperse samples.

$$J_n = \frac{\Sigma h_i}{\Sigma h_i/J_i} \quad \text{and } J_w = \frac{\Sigma h_i J_i}{\Sigma h_i} \quad \text{in volume per mol.}$$

However, Hamielec, Ouano, and Nebenzahl (3) have devised an approximation method to obtain M_n and M_w from h_i and J_i.

The statistical treatment of GPC results has always assumed that molecules of the same size in the detector cell have the same molecular weight. For most linear polymers the assumption is justified. If all the molecules are of the same size and obey the same Mark-Houwink relation, their molecular weights are the same.

$$[\eta]_1M_1 = [\eta]_2M_2$$
$$KM_1^aM_1 = KM_2^aM_2$$
$$M_1 = M_2$$

In such a case in the detector cell of the chromatograph and at any point on the elution volume axis, $M_n = M_w = M_v$. If for the whole sample the Mark-Houwink relation is the same for all the molecules, then size separation by GPC is proportional to molecular weight. Then if the same Mark-Houwink relation holds between different samples, comparison can be made between samples of various average molecular weights on the basis of elution volumes at these averages.

When a high molecular weight solute is polydisperse, we write the Mark-Houwink relation:

$$[\eta] = KM_v^a$$

where K and a = constants

M_v = viscosity average molecular weight

At a single elution volume if several species are present each obeying its own intrinsic viscosity - molecular weight relation, there will be a composite relation of the form KM_v^a. Thus $[\eta]M_n$ becomes $KM_v^aM_n$ which can be placed in terms of one molecular weight average only through the introduction of a dispersity term. If, however, at a single point on the elution volume curve all the molecules obey the same Mark-Houwink equation then they are all of the same molecular weight and the expresions M_v, M_w, and M_n have no meaning at that point and $[n]M_n$ becomes KM^{a+1}. If the same Mark-Houwink equation holds for all the polymer then KM^{a+1} becomes the size separation expression all along the elution volume curve. Separation is point by point along the chromatographic curve. If each point is associated with one molecular weight the type of average involved in separation does not enter the picture. When we then average a single curve, since various amounts of polymer are associated with different points, we will in general have various sizes and molecular weights each of which must at least approximately fit

$$\text{Log } KM^{a+1} = \text{Log } A - bC \qquad ---- \quad 4$$

$$\text{and} \quad \text{Log } M = \text{Log } \left(\frac{A}{K}\right)^{\frac{1}{a+1}} - \frac{b}{a+1} C \qquad ---- \quad 5$$

$$\text{Let} \quad \left(\frac{A}{K}\right)^{\frac{1}{a+1}} \equiv d \qquad ---- \quad 6$$

$$\text{and} \quad \frac{b}{a+1} \equiv e \qquad ---- \quad 7$$

$$\text{Then} \quad \text{Log } M = \text{Log } d - eC \qquad ---- \quad 8$$

If the molecular weight of the fractions is known one may then calculate M_w, M_v, M_n statistically for the whole polymer in the usual manner from the observed heights of the chromatogram and read off corresponding values of C_w, C_v, and C_n from a plot of Equation 8 so that one has:

$$\text{Log } M_{w,v,n} = \text{Log } d - eC_{w,v,n} \qquad ---- \quad 9$$

With a single polymer the three Equations 9 each connect two variables only and have the same intercept and slope and therefore form one curve for various samples of one kind of polymer. They must, since as the area of a chromatogram approaches zero, the three molecular weight averages approach each other.

If we substitute Equations 6 and 7 in Equation 9 and rearrange we obtain:

$$
\begin{aligned}
\text{Log } KM_n^{a+1} &= \text{Log } A - bC_n \quad \text{- - - - - - - - -} \quad 10 \\
\text{Log } KM_w^{a+1} &= \text{Log } A - bC_w \quad \text{- - - - - - - - -} \quad 11 \\
&\cong \text{Log } [\eta]M_w \quad \text{- - - - - - - - -} \quad 12 \\
\text{Log } KM_v^{a+1} &= \text{Log } A - bC_v \quad \text{- - - - - - - - -} \quad 13 \\
&= \text{Log } [\eta]M_v
\end{aligned}
$$

If Equation 10 is substracted from Equation 11:

$$
\text{Log } {}^{M_w}/_{M_n} = \frac{b(C_n - C_w)}{a+1} = e(C_n - C_w) \quad \text{- - -} \quad 14
$$

Here ${}^{M_w}/_{M_n}$ is the dispersity of the whole polymer.

EXPERIMENTAL

The ideas expressed above were tested using results obtained from eleven cellulose nitrate samples with nitrogen content varying from 12.0% to 13.1% and twelve poly(oxypropylene) mixtures of known dispersity varying from 1.03 to 1.53 (11). Two different instruments and three sets of columns were used.

a. Materials

Cellulose Nitrate was ideally suited for our purpose since it has a broad molecular weight distribution which varies greatly between samples. Eleven cellulose nitrate (N/C) samples were selected for characterization. The samples described in Table 1 were obtained from Hercules, Inc., Parlin, New Jersey and

TABLE 1

Cellulose Nitrate Samples

Hercules Lot	Type	Nitrogen Content, % (a)	Mol Wt. M_n Osm. (b)
3569	RS-0.5"	11.95	
4106	RS-5.4"	12.03	26133
1696	RS-15"	11.86	39985
4874	RS-33"	11.97	33515
4569	RS-60"	11.97	55908
4419	RS-125"	12.00	52428
7715	6"	12.60	39489
2234	10-15"	12.64	72200
7719	20"	12.61	52428
2238	36"	12.56	57700
9038	12"	13.13	57695

(a) Nitrogen was determined by the nitrometer method according to Mil. Std. 286B

(b) Osm - Membrane Osmometer

contained 30% ethanol. Viscosity grades of the samples varied from 0.5 to 125 seconds. Molecular weights were determined by the ArRo Laboratories, Joliet, Illinois in acetone solution using a Hewlett-Packard membrane osmometer. The membrane osmometer method employed would best be described as dynamic rather than static and low molecular weight impurities in the samples may not have diffused through the membrane. The cellulose nitrate solutions were allowed to stand two to three days to effect complete solution.

Polystyrene standards were obtaned from Waters Associates (12)and the Pressure Chemical Company (17).

Poly(oxypropylene) samples of nominal molecular weight 400, 1000, and 2000 were obtained from BASF-Wyandotte while 4000 molecular weight material was obtained from the Dow Chemical Co. Formulation and treatment of these materials are described in Reference 11.

The solvent for all measurements was tetrahydrofuran (THF).

b. Equipment

Two chromatographic instruments were used, a Waters Associates Model 200 and a modified Waters Associates 202/401 with a high pressure pump capable of reaching 2000 psi, equivalent to a Model 244. Cellulose nitrate was analyzed using both instruments. On the Waters 200 the columns employed were 2.5×10^4 AU (Cat. No. 39715), 1×10^5 AU (Cat. No. 39716), 3×10^5 AU (Cat. No. 39717), 1×10^6 AU (Cat. No. 39718), and 1×10^7 AU (Cat. No. 39719) designated column set B, while with the 202/401 the columns were 10^2, 10^3, 10^4, 10^5 and 10^6 AU pore size called column set C. Poly(oxypropylene) was run with the Waters 200 instrument using columns of 2.25×10^2, 1.4×10^3, 1.4×10^3 and 3.5×10^3 AU called column set II.

Column sets B and II were packed with Styragel while column set C was packed with Micro-Styragel of smaller particle size. In all cases a flow rate of 1.0 ml/minute was used at 25°C. The Waters 200 instrument was used at a sensitivity of four for the NC and a sensitivity of one for the Poly(oxypropylene).

c. Calibration with Polystyrene Standards

The GPC curves were analyzed by the successive approximation method described by Adams et al (13). The results for the column sets are shown in Tables 2, 3 and 4 and Figures 3, 4, and 5. The equations describing the polystyrene curves were:

Column set B, Waters 200: $\log M_n = 11.79 - 0.0317C$ - - 16

Column set C, Waters 202/401:
$\log M_n = 10.27 - 0.156C$ - - - - 17

Column set II, Waters 200:
$\log M_n = 7.91 - 0.0336C$ - - - - 18

where C is elution volume in ml at the number average molecular weight(M_n).

Polystyrene intrinsic viscosities were calculated from the equation of Spatorico and Coulter (8). These authors reviewed previous work and concluded that the intrinsic viscosity of polystyrene in THF at 25°C was best represented by

$$[\eta] = 1.11 \times 10^{-4} M_w^{0.725}, \text{ dl/g} \qquad \text{------} \quad 19.$$

The product of the weight average molecular weight of the standards and their calculated intrinsic viscosity at that

TABLE 2

Analysis of GPC Curves, Cellulose Nitrate and Standard Polystyrene
Waters200 Instrument and Column Set B

	Lot No.	M_n (GPC)	M_w (GPC)	M_w/M_n	C_n 5 ml	C_w 5 ml	C_n-C_w 5 ml	$[\eta]$ dl/g	$[\eta]M_w$ dl/mol	KM_n^{a+1} dl/mol	$[\eta]M_n$ dl/mol
Cellulose Nitrate	3569	22133	57900	2.62	45.0	42.4	2.6	0.851	49273	8610	18835
	4106	34163	177800	5.20	43.8	39.4	4.4	1.61	286258	18808	55000
	1696	44293	180904	4.08	43.1	39.3	3.8	1.87	338290	30016	82828
	4874	45707	234769	5.14	43.0	38.6	4.4	2.82	662048	31762	128893
	4569	54007	303073	5.61	42.5	32.9	4.6	3.12	945588	42890	168502
	4419	54000	298890	5.53	42.5	38.0	4.5	3.20	956448	42890	172822
	7715	72557	330200	4.55	41.8	37.7	4.1	3.51	1.16×10^6	72974	254675
	2234	66800	302700	4.53	42.0	37.9	4.1	4.40	1.33×10^6	62884	293920
	7719	76419	421200	5.51	41.6	37.0	4.6	4.10	1.73×10^6	80265	313646
	2238	57039	478900	8.40	42.4	36.7	5.7	4.81	2.3×10^6	47321	274358
	9038	59896	265300	4.43	42.3	38.3	4.1	3.84	1.02×10^6	51762	230000
Poly-styrene	4190038	773000	865760	1.12	37.1	37.0		2.24	1939302	1731520	
	4190037	392000	411600	1.05	39.2	39.1		1.31	539196	513520	
	41984	164000	173020	1.055	41.8	41.8		0.70	121114	114800	
	41995	96200	100048	1.04	43.0	42.9		0.47	47023	45214	
	21570	49000	50960	1.04	44.8	44.6		0.29	14778	14210	
	4190039	19086	19849	1.04	46.8	46.4		0.145	2878	2767	

* Measured Intrinsic Viscosity for Cellulose Nitrate, Calculated for Polystyrene
Cellulose Nitrate, 12.0-12.6%N: $K = 0.00013$, $a = 0.80$
Polystyrene: $K = 0.00011$, $a = 0.725$

TABLE 3

Analysis of GPC Curves, Cellulose Nitrate and Standard Polystyrene
Waters 202/401 Instrument and Column Set C

	Lot No.	M_n (GPC)	M_w (GPC)	M_w/M_n	C_n 1 ml	C_w 1 ml	C_n-C_w 1 ml	$[\eta]$* dl/g	$[\eta]$*M_w dl/mol	KM_n^{a+1} dl/mol
Cellulose Nitrate	3569	20686	43000	2.08	37.1	34.8	2.3	0.851	36593	7624
	4106	28877	86742	3.00	36.1	32.9	3.2	1.61	100637	13898
	1696	30803	98414	3.19	35.9	32.5	3.4	1.87	126312	15610
	4569	49320	133536	2.71	34.5	31.7	2.8	3.12	218786	36424
	9038	57962	178838	3.09	34.1	30.9	3.2	3.84	370144	48708
Poly-styrene	4190038	773000	842570	1.09	29.05	28.70	0.35	2.24	1.89×10^6	1.73×10^6
	41984	164010	177120	1.08	32.79	32.56	0.23	0.70	123984	114800
	41995	96200	101010	1.05	34.11	33.91	0.20	0.47	47475	45214
	4190039	19750	21330	1.08	38.48	38.40	0.08	0.149	3178	2943

* **Measured Intrinsic Viscosity for Cellulose Nitrate, Calculated for Polystyrene**
Cellulose Nitrate, 12.0-12.6%N: K = 0.00013, a = 0.80
Polystyrene: K = 0.00011, a = 0.725

TABLE 4

Analysis of GPC Curves, Poly(oxypropylene) and Standard Polystyrene
Waters 200 Instrument and Column Set II

	Lot No.	M_n (GPC)	M_w (GPC)	M_w/M_n	C_n 5 ml	C_w 5 ml	C_n-C_w 5 ml	$[n]*M_w$ dl/mol	KM_n^{a+1} dl/mol	$[n]M_n^*$ dl/mol
Polypropylene Oxide		500	527	1.05	29.80	29.65	0.15	15.0	13.7	14.2
	31	1030	1082	1.05	27.90	23.75	0.15	50.0	46.1	47.7
	21	1935	2012	1.04	26.05	25.95	0.10	142	133	137
		4000	4120	1.03	24.10	24.00	0.10	473	450	459
	22	1969	2185	1.11	26.02	25.70	0.32	163	137	147
	23	1902	2350	1.24	26.07	25.50	0.57	184	129	149
	24	2024	2598	1.28	25.95	25.30	0.65	218	143	170
	25	1991	2816	1.41	26.00	25.05	0.95	250	140	177
	26	1913	2922	1.53	26.10	24.95	1.15	266	130	174
	32	1099	1259	1.15	27.70	27.30	0.40	64.6	51.4	56.4
	33	1096	1350	1.23	27.70	27.10	0.60	72.6	51.2	59.0
	34	1122	1476	1.32	27.60	26.85	0.75	84.4	53.2	64.1
	35	1164	1621	1.39	27.50	26.55	0.95	98.7	56.6	70.9
	36	1198	1756	1.47	27.40	26.35	1.05	113	59.4	77.1
Polystyrene	12a	2027	2513	1.24	27.4	27.0	0.4	80.7	55.7	65.1
	11a	3659	4244	1.16	26.0	25.4	0.6	199	154	172
	8b	9966	11162	1.12	23.3	23.0	0.3	1056	868	943
	2a	18000	19800	1.10	21.8	21.6	0.2	2839	2408	2581

* Calculated Intrinsic Viscosity
Poly(oxypropylene): K = 0.00040, a = 0.68
Polystyrene: K = 0.00011, a = 0.725

TABLE 5

Analysis of GPC Calibration Curves in Terms of Linear Equations

Polymer	Waters GPC	Column* Set	Mark-Houwink Constants		Intercept Log d Fig. 3,4,5	Slope e ml^{-1} Fig. 3,4,5	Intercept Log Kd^{a+1}	Slope $e\,(a+1)$ ml^{-1}	Intercept Log A Fig. 6,7,8	Slope b ml^{-1} Fig. 6,7,8	Slope e ml^{-1} Fig. 9	Slope $e\,(a+1)$ ml^{-1}
			k dl/g x 10^4	a								
Cellulose Nitrate	200	B	1.3	0.80	11.83	0.0333	17.40	0.0599	17.20	0.0588	0.0325	0.0586
Cellulose Nitrate	202/401	C	1.3	0.80	9.99	0.154	14.10	0.277	14.05	0.275	0.154	0.277
Poly(pxypropylene)	200	II	4.0	0.68	7.42	0.0317	9.07	0.0533	9.49	0.0565	0.0332	0.0558
Polystyrene	200	B	1.1	0.725	11.79	0.0317	16.37	0.0548	17.20	0.0588		
Polystyrene	202/401	C	1.1	0.725	10.27	0.156	13.76	0.269	14.05	0.275		
Polystyrene	200	II	1.1	0.725	7.91	0.0336	9.69	0.0580	9.49	0.0565		

* Column Set B 2.5 x 10^4, 10^5, 3 x 10^5, 10^6, 10^7 A.U., Styragel packing

C 10^2, 10^3, 10^4, 10^5, 10^6 A.U., Micro-Styragel packing

II 2.25 x 10^2, 1.4 x 10^3, 1.4 x 10^3, 3.5 x 10^3, A.U., Styragel packing

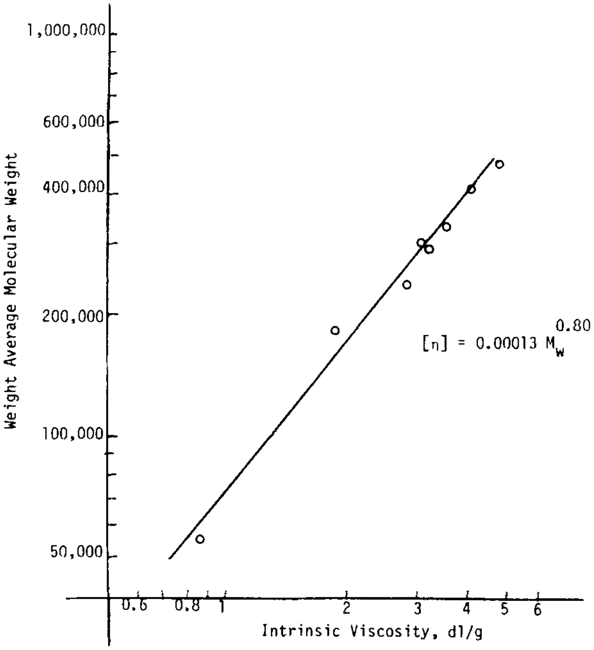

Figure 1: Mark-Houwink Relation for 12.0-12.6% N Cellulose Nitrate in THF at 25°C

molecular weight were plotted as the hydrodynamic volume against elution volume at peak height. The results are shown in Tables 2 , 3 , and 4 and as lines without points in Figures 6, 7, and 8.

d. Cellulose Nitrate and Poly(oxypropylene) Analysis

The GPC curves for cellulose nitrate and poly(oxypropylene) were analyzed using the method described above. In the case of cellulose nitrate the elution volumes at the peak heights were plotted against the number average molecular weight (Mn) that had

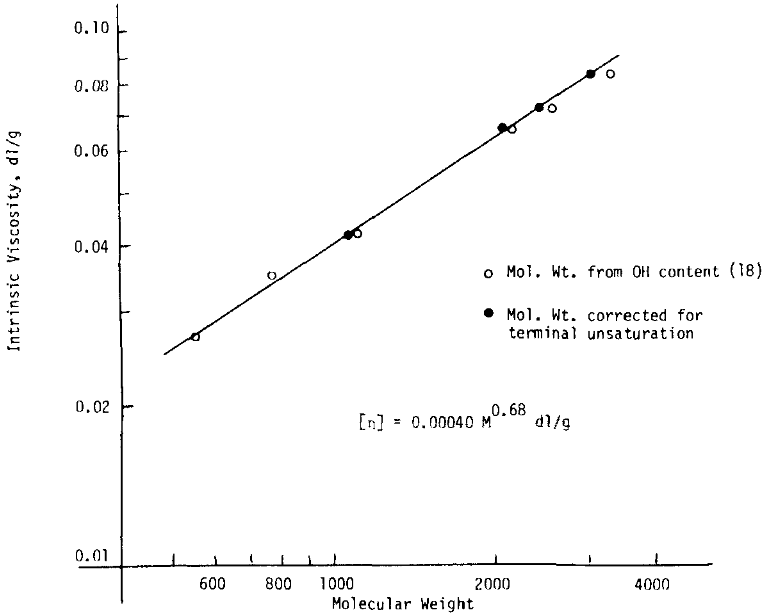

Figure 2: Intrinsic Viscosity - Molecular Weight Relation for Polypropylene Oxide of Narrow Molecular Weight Distribution in THF at 20°C

been determined independently by membrane osmometry. From the first approximate curve, the elution volumes at Mn were calculated. These elution volumes were in turn plotted against Mn (osmometer) forming a new calibration curve. The process was repeated and the final calibration curve approached by successive approximations. Elution volumes and molecular weights from fractionated N/C samples were also used to calculate calibration curves using data of Carignan and Turngren (14).

Results on cellulose nitrate using the Waters 200 and column set B are given in Table 2 and Figure 3 while those using the Waters 202/401 and column set C are shown in Table 3 and Figure 4. The scatter in the points is attributed mainly to the molecular weight procedure.

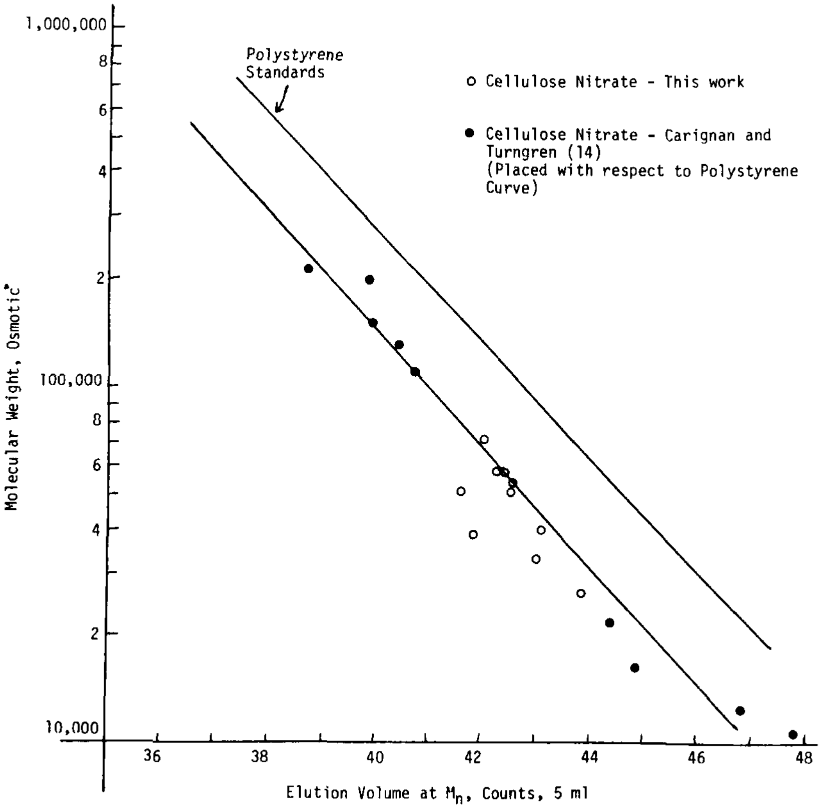

Figure 3: GPC Calibration Curve for Cellulose Nitrate Using Waters 200 Instrument and Column Set B

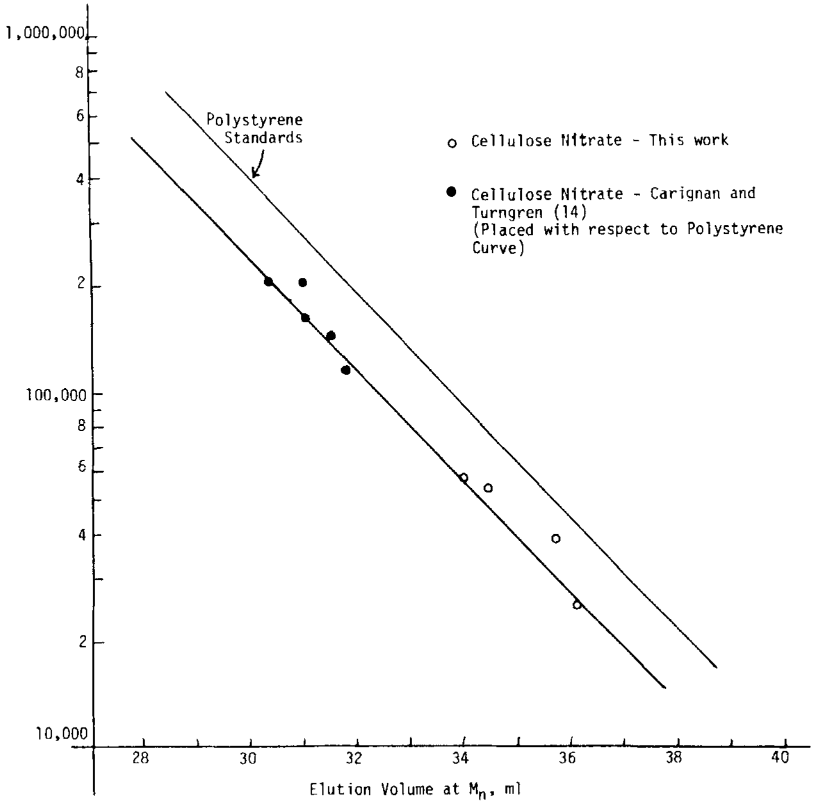

Figure 4: GPC Calibration Curve for Cellulose Nitrate with Waters 202/401 High Pressure Instrument and Column Set C

Results of Carignan and Turngren (14) were used to give a sufficient molecular weight range. Their data were placed with respect to the two polystyrene curves from their paper and this work. The cellulose nitrate calibration using column set B and the Waters 200 instrument was:

$$\text{Log } M_n = 11.83 - 0.0333C \text{ - - - - - - - - - - } 20.$$

With the high pressure Waters 202/401 and column set C the calibration was:

$$\text{Log } M_n = 9.99 - 0.154C \text{ - - - - - - - - - - } 21$$

where C is in milliliters.

Molecular weights calculated from this calibration curve (Eq. 21) for five cellulose nitrate lots are given in Table 3. As expected, the number average molecular weights are comparable with those obtained using the Waters 200 and column set B which was packed with Styragel as opposed to Micro-Styragel in column set C. However, in all cases the dispersity values, M_w/M_n, found with the Micro-Styragel in the high pressure instrument were lower than found with Styragel in the Waters 200. Since standard number average molecular weight values were used to calibrate each instrument, the two instruments must in principle yield the same number average molecular weights. The weight averages and dispersity may be different since different column sets were used. Columns of 10^7 AU pore size can be used with the low pressure Waters 200 instrument but can not be made for the 202/401. Hence exclusion results at high molecular weights with the latter instrument.

Results on Poly(oxypropylene) using the Waters 200 GPC and column set II are given in Table 4 and Figure 5. The line in Figure 5 obeyed the relation:

$$\text{Log } M_n = 7.42 - 0.031C \text{ - - - - - - - - - - } \quad 22$$

where C is in milliliters.

It must be noted that this relation is given incorrectly in the previous paper (11) which, however, does not invalidate the other data and conclusions reached therein.

Intrinsic viscosities [η] of cellulose nitrate were determined on the samples shown in Table 1 in tetrahydrofuran (THF) at

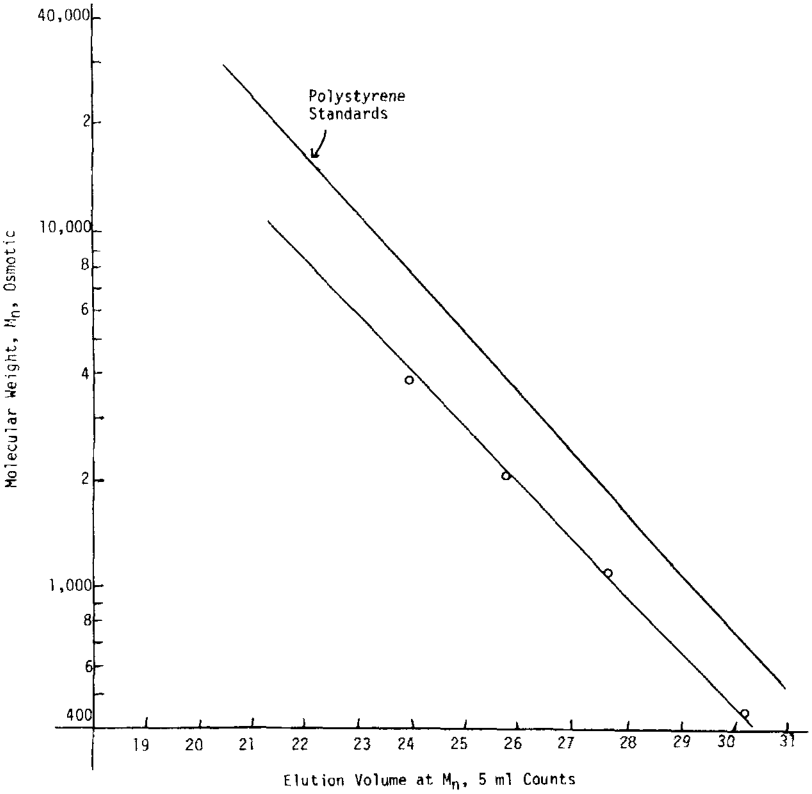

Figure 5: GPC Calibration Curve for Polypropylene Oxide Using Waters 200 Instrument and Column Set II

25°C with results given in Tables 2 and 3. A plot of the data in Figure 1 gave the relation:

$$[\eta] = 0.00013\ M_w^{0.80} \quad \text{- - - - - - - - - - - -} \quad 23.$$

This result compares with 0.00023 $M_w^{0.84}$ found by Timpa and Segal (15) for cellulose trinitrate in THF at 25°C. Concentration in both cases was in g/dl. If intrinsic viscosity in Figure 1 is corrected to give intrinsic viscosity of cellulose trinitrate using the method of Lindsley and Frank (16) one obtains

$$[\eta] = 0.00018\ M_w^{0.84} \quad \text{- - - - - - - - - - - -} \quad 24.$$

Intrinsic viscosities of the poly(oxypropylene) mixtures in THF were calculated from the equation

$$[\eta] = 0.00040\ M_w^{0.68},\ \text{dl/g at 20°C} \quad \text{- - - - -} \quad 25.$$

This relation is a modification of that of W. Scholtan and W.Y. Lie (18). These workers determined intrinsic viscosity as a function of molecular weight calculated from hydroxyl number. They did not correct for the presence of terminal unsaturation which becomes of some importance for poly(oxypropylene) above molecular weight 2000. Using results found previously (11) terminal unsaturation can be estimated as a function of molecular weight and used to correct equivalent weight from hydroxyl analyses. At molecular weight 1000 terminal unsaturation is 0.022 meq/g; at molecular weight 2000 it is 0.033 meq/g; and at molecular weight 4000 it is 0.074 meq/g. Figure 2 shows the results of Scholtan and Lie (18) after such a correction.

DISCUSSION

To summarize what was done as a result of work outlined in the previous section:

1. From known values of M_n and from elution volumes were determined calibration relations between Log M_n and elution volumes at M_n in the form of Equations 15, 17, 18, 20, 21, and 22 as shown in Figures 3, 4, and 5.

2. These calibration curves were used to calculate GPC values of M_n, M_w, ${}^{M_w}/M_n$, C_n, C_w, and (C_n-C_w) which are given in Tables 2 , 3 , and 4.

3. Using experimental values of intrinsic viscosity or known Mark-Houwink constants given in Equations 19 and 25 the functions $[\eta]M_w$, KM_n^{a+1}, and $[\eta]M_n$ were calculated and are shown in Tables 2, 3, and 4 .

4. The functions Log $[\eta]M_w$, Log KM_n^{a+1}, and Log $[\eta]M_n$ were plotted against elution volume as shown in Figures 6, 7, and 8 and the Logarithm of the dispersity, ${}^{M_w}/M_n$, was plotted against (C_n-C_w) as shown in Figure 9.

5. The slopes and intercepts of the linear curves in Figures 6, 7, 8 and 9 were calculated and tabulated in Table 5 together with those from Equations 15, 17, 18, 20, 21 and 22 taken from Figures 3, 4, and 5.

Since straight line calibration curves were used to relate Log M with elution volume, if Equations 10 and 11 hold, then plots of Log KM_n^{a+1} and Log KM_w^{a+1} versus elution volume must form straight

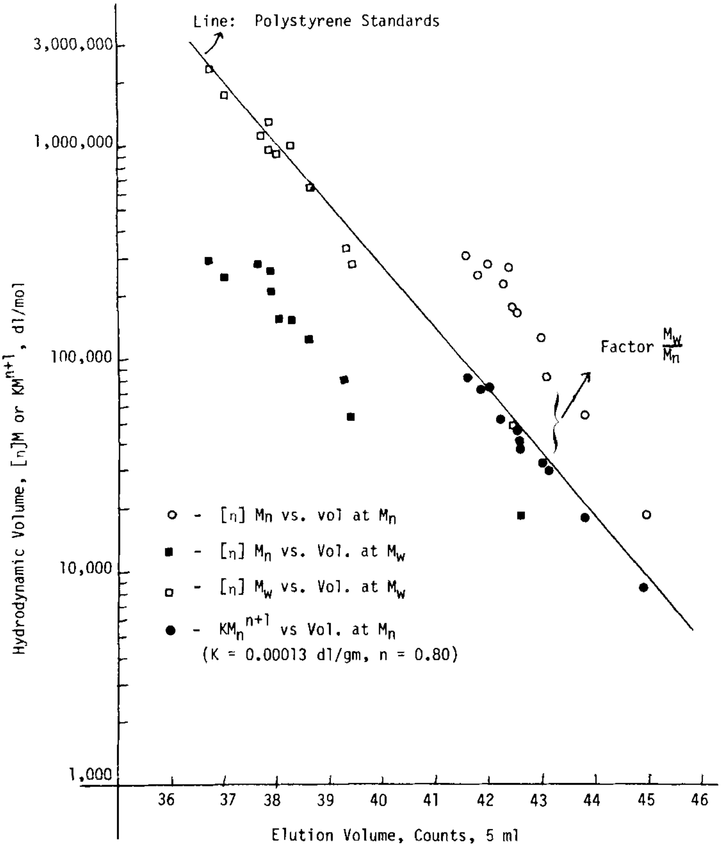

Figure 6 : Comparison of Number and Weight Average Molecular Weights for Universal GPC Calibration using Nitrocellulose Samples and Measured Intrinsic Viscosities.

lines. The line formed, however, will lie on that of the polystyrene standards only if the functions KM_n^{a+1} and KM_w^{a+1} represent true hydrodynamic volumes.

From the results we wish to see several things:

a. First, does Log $[\eta]M_n$ vary directly with elution volume for different samples and does the curve formed lie on the Log $[\eta]M$ versus

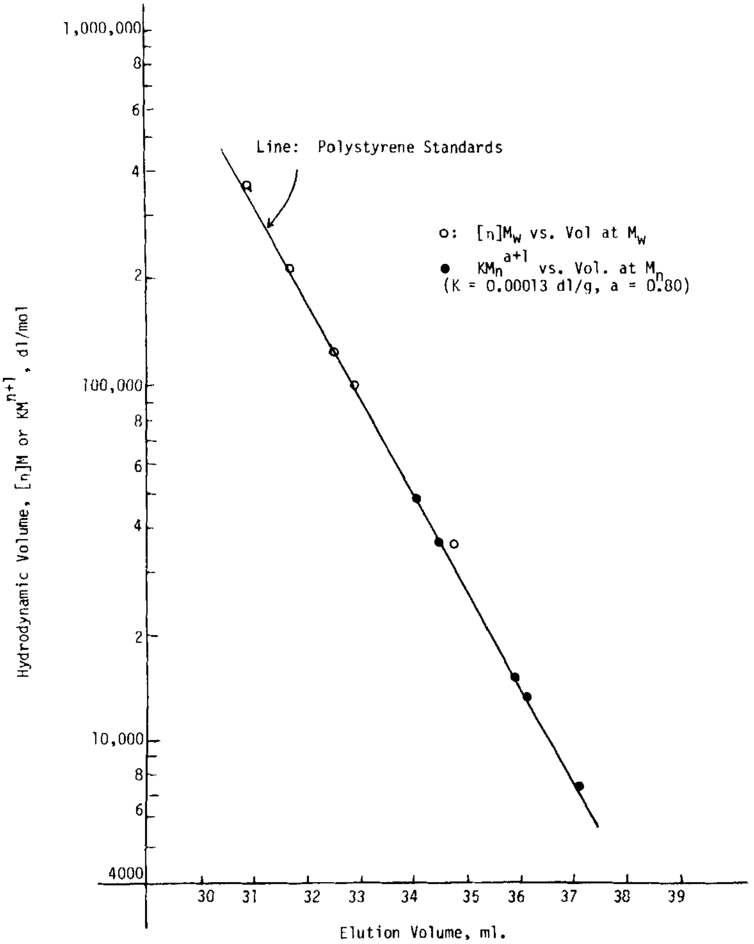

Figure 7: Low Resolution Universal GPC Plot for Cellulose Nitrate with the Waters 202/401 Instrument Using Measured Intrinsic Viscosities

elution volume curve for nearly monodisperse standard polystyrene samples? If it does not lie on the polystyrene curve, is the factor separating the two curves the dispersity M_w/M_n, in accordance with the factor between Equation 3 and Equations 10 and 11?

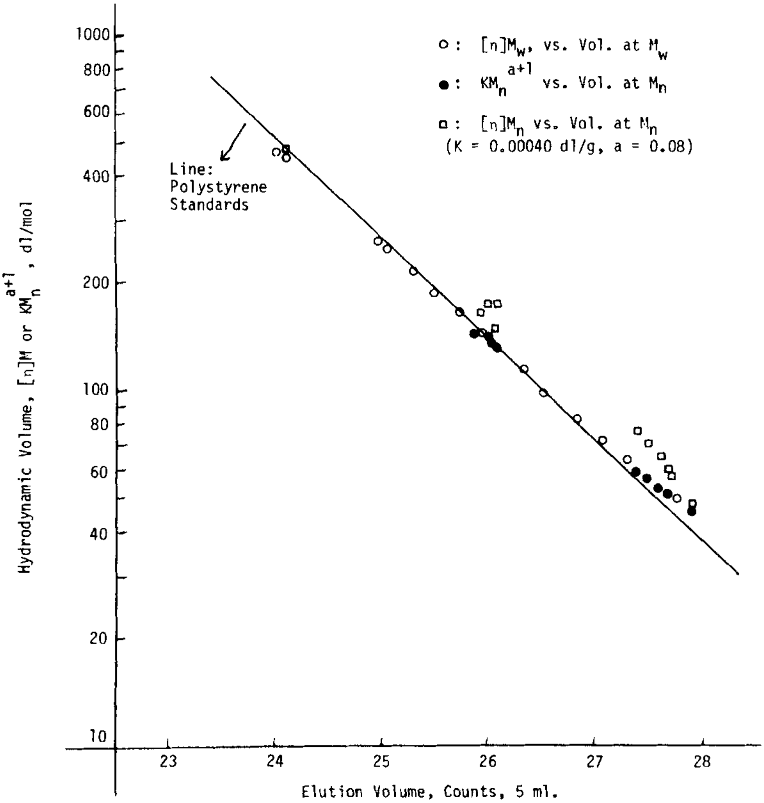

Figure 8: Comparison of Different Average Molecular Weights in Universal GPC Calibration Using Polypropylene Oxide Samples and Calculated Intrinsic Viscosities

An examination of Figures 6 and 8 shows that Log $[\eta]M_n$ plotted against either volume at M_n or M_w does not lie on the polystyrene universal plot. The factor between $[\eta]M_n$ for cellulose nitrate and $[\eta]M$ for polystyrene at the same elution volume is in fact equal to $^{M_w}/M_n$. In Figure 8 a clear progression is shown between $[\eta]M_n$ for poly(oxypropylene) and the polystyrene curve as the dispersity increases from 1.03 to 1.53.

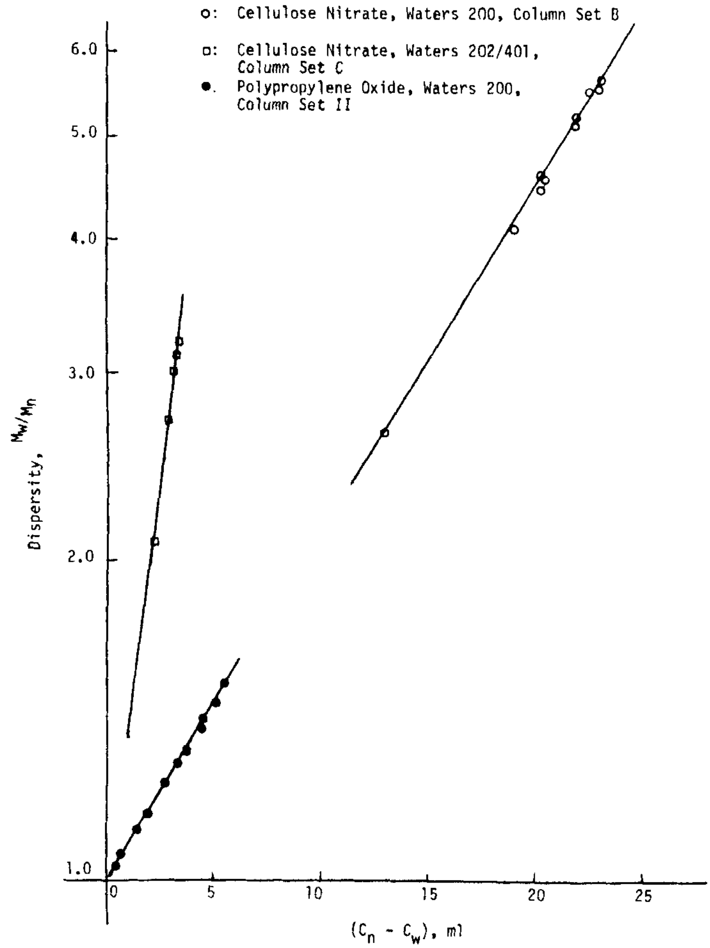

Figure 9: Relation Between GPC Dispersity and Elution Volume Separation, C_n-C_w.

b. Secondly, do Log KM_n^{a+1} and Log $[\eta]M_w$ (or Log KM_w^{a+1}) versus M_n and M_w respectively fall on the polystyrene curve in accordance with Equations 10, 11, and 12? Figures 6, 7, and 8 show that these equations are certainly obeyed within the limits of error.

c. Thirdly, is the dispersity related to the difference between elution volume at M_n and M_w in accordance with Equation 14 and does the constant in Equation 14 have the same value as e in Equation 9? The logarithm of the dispersity is plotted against (C_n-C_w) in ml in Figure 9. Linear relations result whose slope is given in the next to the last column of Table 5. In the three cases the slopes are essentially the same as found from Equation 9 in Figures 3, 4, and 5. As above, the excellence of the fit of the points to the lines is because linear calibration curves were employed and not because of the quality of the experimental techniques.

d. Fourth, do the relations between the constant in Equation 9 and Equations 10 and 11 satisfy Equations 6 and 7? The intercept, Log d, and slope, e, from Equation 9 taken from Figures 3, 4, and 5 are given in Table 5 for the various systems. In accordance with Equations 6 and 7 these were converted to Log Kd^{a+1} and e(a+1) to give values of Log A and b. These values are compared in Table 5 with Log a and b from Equations 10, 11, and 12 determined from Figures 6, 7, and 8. Close agreement is found.

The numbers in Table 5 may be used to compare the column sets used with cellulose nitrate in the Water's 200 and 202/401 instruments. The resolution of the systems is $-\frac{dc}{dJ} = \frac{1}{2.3026bJ}$ where J is the hydrodynamic volume. That is, the higher the molecular weight the poorer the resolution. For the 200 instrument $-\frac{dc}{dJ} = \frac{7.39}{J}$ and for the 202/401 $-\frac{dc}{dJ} = \frac{1.58}{J}$. These values for the particular column sets employed would be higher for the 202/401 if a higher porosity column could have been used.

CONCLUSION

When the molecules in the detector all obey the same Mark-Houwink relation, Equations 10, 11, and 13 constitute a "Universal GPC Calibration" in term of KM^{a+1} of any molecular weight average, of $[\eta]M_v$, or approximately of $[\eta]M_w$. None of these expressions, however, is $[\eta]M_n$ which indeed has no meaning other then $[\eta]M$ when only one species is present. When the dispersity of the whole sample is large, use of KM_n^{a+1} doubles the number of points available for determination of the calibration curve because the points placed by KM_n^{a+1} will be at the low molecular weight end of the universal curve and those from KM_w^{a+1} will be at the upper. In theory one such sample might suffice for a determination of the curve. The factor between Equations 10, 11, and 13 and Equation 3 is the dispersity of the sample. As the dispersity approaches 1.0 a point placed by Equation 3 will approach the curve formed by Equations 10, 11 or 13.

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