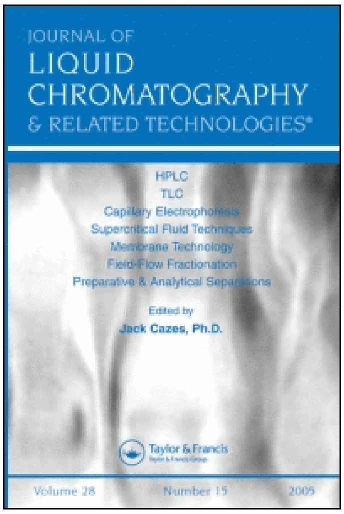

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A MARK-HOUWINK EQUATION FOR POLY(VINYL ALCOHOL) FROM SEC-VISCOMETRY

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ABSTRACT

A new Mark-Houwink equation for fully-hydrolyzed poly(vinyl alcohol) has been determined using aqueous size exclusion chromatography (SEC) with on-line, differential viscometry detection. The Mark-Houwink K and a constants have been measured at 35° C over a wide range of molecular weights in an aqueous solution of sodium nitrate, a commonly used mobile phase for SEC-molecular weight characterization of poly(vinyl alcohol). Absolute molecular weights determined using these Mark-Houwink values compare favorably among universal calibration, viscometry, and the Mark-Houwink (or intrinsic viscosity distribution) methods to those obtained from low-angle laser light scattering. The intrinsic viscosity distribution method is calibration independent and only requires a one time determination of the Mark-Houwink constants. This new method for characterizing molecular weight of an unknown poly(vinyl alcohol) is illustrated.

INTRODUCTION

The use of aqueous size exclusion chromatography (SEC) coupled with on-line viscometry detection has recently been utilized for characterizing with several types of water- soluble polymers (1-4). Other studies have included characterization of poly(vinyl alcohol), or PVA, the world's largest volume, synthetic water-soluble polymer (5,6). PVA is used in a wide range of applications such as adhesives, textile and paper sizing, emulsion polymerization, fibers, and as a precursor for poly(vinyl butyral). These end-use applications require accurate and economical means to characterize the molecular weight distribution (MWD) of PVA and provide a better understanding of product performance.

Differential viscometry detection, when used with SEC, is based on the concept of universal calibration. A requirement for molecular weight characterization with universal calibration in SEC is that the polymer hydrodynamic volume (the product of intrinsic viscosity, $[\eta]$, times molecular weight) determines the polymer separation rather than molecular weight alone (7). PVA has been shown to exhibit universal calibration behavior using commercial, Toyo Soda TSK-PW columns containing a hydrophilic polyether gel (6,8). The mobile phase commonly used for aqueous SEC of PVA is sodium nitrate of low ionic strength (0.05 or 0.10 Normal). Sodium nitrate provides a minimal salting-out effect on PVA compared to other salts such as those of the sulfate family: sodium, potassium, magnesium, etc. (9).

The relationship between molecular weight, M, and intrinsic viscosity, $[\eta]$, of a polymer is given by the widely used Mark- Houwink expression,

$$[\eta] = K(M)^a \qquad \{1\}$$

where K and a are the empirical Mark-Houwink constants for a particular polymer/solvent system. The importance of this equation is its relationship between molecular weight and volume per unit mass (intrinsic viscosity is usually reported in units of dL/g). Viscometry detection with aqueous SEC provides the means to measure on-line the intrinsic viscosity, absolute molecular weight, and Mark-Houwink constants of a polymer. However, values for K and a have not been established for fully-hydrolyzed PVA as a function of molecular weight under the conditions described above.

Recently, Yau introduced the concept of intrinsic viscosity distribution (IVD), which can be readily determined using SEC with an on-line viscometer (10,11). The IVD can be generated by taking the ratio of the viscosity and concentration detector response at every SEC elution time (an $[\eta]$-calibration curve). The MWD can then be determined directly by using the Mark-Houwink relationship with known values for K and a. The significance of this is that the MWD is calculated via a calibration-independent procedure and is highly insensitive to variations in SEC experimental conditions such as flow rate (11).

The objective of this work is two-fold. The first is to measure the Mark-Houwink constants of fully-hydrolyzed PVA as a function of molecular weight using on-line viscometry in 0.10 N sodium nitrate. The need for accurate values of the Mark-Houwink constants measured in 0.10 N $NaNO_3$, reflect the common use of this mobile phase for SEC characterization of PVA. The second objective is to use these values for examining the accuracy of the MWD obtained from universal calibration and IVD measurements and compare those values from viscometry and low-angle laser light scattering (LALLS).

BACKGROUND

Calculations of absolute molecular weights from SEC and intrinsic viscosity use one of three approaches: on-line specific viscometry, universal calibration, and the Mark- Houwink (or IVD) method. Since data will be presented using these methods, each is briefly reviewed.

On-Line Specific Viscometry:

An on-line SEC viscometer measures specific viscosity, η_{sp}, as a function of molecular weight. The intrinsic viscosity, $[\eta]$, is defined as,

$$[\eta] = (\eta_{sp}/c)_{c-->0} \quad \{2\}$$

where c is the concentration of the polymer solution as measured by the concentration detector such as a differential refractometer. The hydrodynamic volume of a polymer in a given solvent is expressed as,

$$HV = M[\eta] \quad \{3\}$$

where HV is the hydrodynamic volume. HV is the quantity used for universal calibration when measuring absolute molecular weights via SEC. Since a differential viscometry detector measures specific viscosity together with a concentration detector, a universal calibration curve (the product of $\log\{[\eta]*M\}$ versus elution volume) can be constructed using standards of known molecular weight. At any given elution volume,

$$[\eta]_1 M_1 = [\eta]_2 M_2 \quad \{4\}$$

where $[\eta_1]$ and M_1 are the intrinsic viscosity and molecular weight, respectively, of a polymer standard and $[\eta_2]$ and M_2 are the intrinsic viscosity and molecular weight, respectively, of the unknown polymer. For polymer standards, M_1 is known and $[\eta_1]$ and $[\eta_2]$ are measured on-line from specific viscosity. Thus, M_2 can be calculated for the unknown polymer across all elution volumes and an absolute molecular weight distribution determined. On-line specific viscometry does not require prior knowledge of the Mark-Houwink K and a values.

Universal Calibration:

The intrinsic viscosity of a polymer is related to its molecular weight by the Mark-Houwink equation {1}. The molecular weight of any polymer can be determined by SEC from Equations {1} and {4} using the relationship (12),

$$\log(M_2) = \{1/(1+a_2)\}\log(K1/K_2) + \{(1+a_1)/(1+a_2)\}\log(M_1) \qquad \{5\}$$

where the Mark-Houwink constants K_1 and a_1 are known for a polymer standard and K_2 and a_2 represent the Mark-Houwink constants of the unknown polymer. Using universal calibration, one needs to know the Mark-Houwink constants of the standards used for calibration and the Mark-Houwink constants of the polymer being measured. A concentration detector is usually used for universal calibration.

Mark-Houwink or IVD Method:

Equation {1} suggests that if the intrinsic viscosity and Mark-Houwink constants are known for a polymer, the molecular weight can be readily calculated. An IVD can be determined directly for an unknown polymer by using SEC-viscometry with a concentration-dependent detector such as a differential refractometer.

The output of the specific viscometry detector is the product of $[\eta]$ and sample concentration. By generating the curve of $[\eta]$ versus elution time (the ratio of the specific viscosity and the concentration detector response at all elution times) all the intrinsic viscosity data needed for an IVD are available (10). As with a molecular weight distribution, different intrinsic viscosity averages may be defined, such as weight-average intrinsic viscosity. From an IVD all molecular weight information can be calculated directly from,

$$[\eta_i] = K(M_i)^a \qquad \{6\}$$

where i refers to the intrinsic viscosity and molecular weight at the ith elution time increment and the Mark-Houwink K and a are known. The values for K and a can be determined from on-line SEC-viscometry measurements.

TABLE 1

Experimental Conditions

Columns:	TSK-PW, G1000, G2000, G3000, G4000, G5000, G6000, (each 30 cm x 7.5mm ID, Toyo Soda Manufacturing Company)
Mobile Phase:	0.10 N Sodium nitrate (Fisher Scientific Company, Pittsburgh, PA)
Flow Rate:	0.93 ml/min (measured)
Temperature:	35° C (for 150C, viscometer, and refractometer)
Injection Volume:	0.200 ml (samples and standards)

EXPERIMENTAL

Instrumentation:

Aqueous SEC was performed on a Waters 150C gel permeation chromatograph (Waters/ Millipore Corporation, Milford, MA). The 150C was coupled with a Viscotek Model 100 differential viscometer (Viscotek Corporation, Porter, TX) and a Waters Model 410 differential refractive index detector. The refractometer and viscometer were configured in a parallel arrangement to approximate a 50:50 split in flow rate through each detector. Other experimental conditions are summarized in Table 1. Aqueous SEC/LALLS conditions have been previously described (13).

Materials and Sample Preparation:

Six poly(ethylene glycol), or PEG, standards ranging from 975 to 17,500 molecular weight, and six poly(ethylene oxide), or PEO, standards ranging from 43,500 to 800,000 molecular weight were used to construct a universal calibration curve. The molecular weights and polydispersities of these standards have been previously summarized (14). PEG and PEO are both chemically identical with a repeat unit of $-(CH_2CH_2O)-$. The molecular weight products less than 20,000 are usually referred to as PEG and those greater than 20,000 as PEO. The concentrations of these standards ranged from approximately 0.40 mg/ml for the 800,000 PEO to 2.5 mg/ml for the 975 PEG. Low concentrations of high molecular weight PEO were used to avoid "viscous fingering" effects. The PEG and PEO standards were prepared in the mobile phase by gentle agitation at room temperature. All samples and standards were prefiltered through a 0.45 micron (25 mm diameter) Millex HV filter (Millipore Corporation, Bedford, MA).

Four fully-hydrolyzed, molecular weight grades of Airvol® PVA (98 mole percent, Air Products and Chemicals, Inc.) were used for these studies. These grades are referred to as super-high molecular weight (SHMW), high molecular weight (HMW), medium molecular weight (MMW), and low molecular weight (LMW). Sample concentrations were in the 1.0 to 2.0 mg/ml range.

Data Acquisition:

Data acquisition and analysis were performed using Viscotek's UNICAL Version 3.02 and 3.20 and GPCLS Version 3.0 software. For the column set used in these studies, data acquisition windows were set from 28 to 62 minutes per sample. An A/D gain setting of 2.0 and a differential pressure transducer sensitivity of 1.0 mV/Pa were used.

RESULTS AND DISCUSSION

Mark-Houwink Constants:

A universal calibration curve of $\log([\eta]*M)$ vs. elution volume (Figure 1) was constructed using a third order polynomial fit from SEC-viscometry data for PEG/PEO standards ranging from 975 to 800,000 molecular

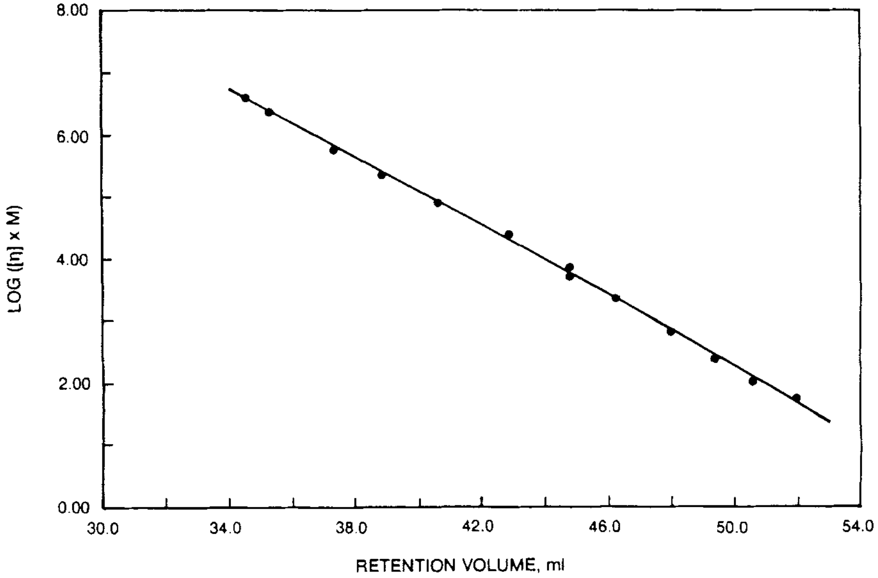

Figure 1

Universal calibration curve for PEO/PEG in 0.10 N $NaNO_3$ at 35° C.

weight. Using this calibration, along with the specific viscometry method, molecular weight and intrinsic viscosity data were computed for the four molecular weight grades of PVA. Specific viscosity and concentration chromatograms of these PVA polymers (Figures 2a, 2b) exhibit broad, unimodal molecular weight character. Molecular weight data are summarized in Table 2 and are the average of six to eight replicate determinations for each PVA type. M_w values range from 31,000 for low molecular weight PVA to about 250,000 for super high molecular weight PVA. PVA exhibits a molecular weight distribution and intrinsic viscosity consistent with 4% solution viscosity.

The Mark-Houwink constants, K and a, are determined from the intercept and slope of a plot of log[η] versus log(M) plot. As an example, the Mark-Houwink plot for the HMW grade of PVA is shown in Figure 3 and

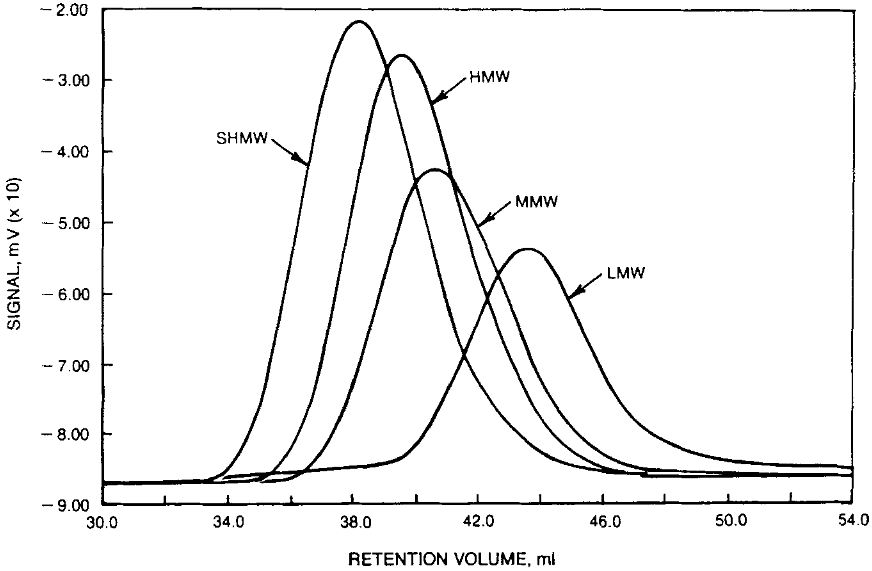

Figure 2a

Specific viscosity chromatograms for four molecular weight grades of PVA. SHMW = Super high molecular weight, HMW = High molecular weight, MMW = Medium molecular weight, LMW = Low molecular weight.

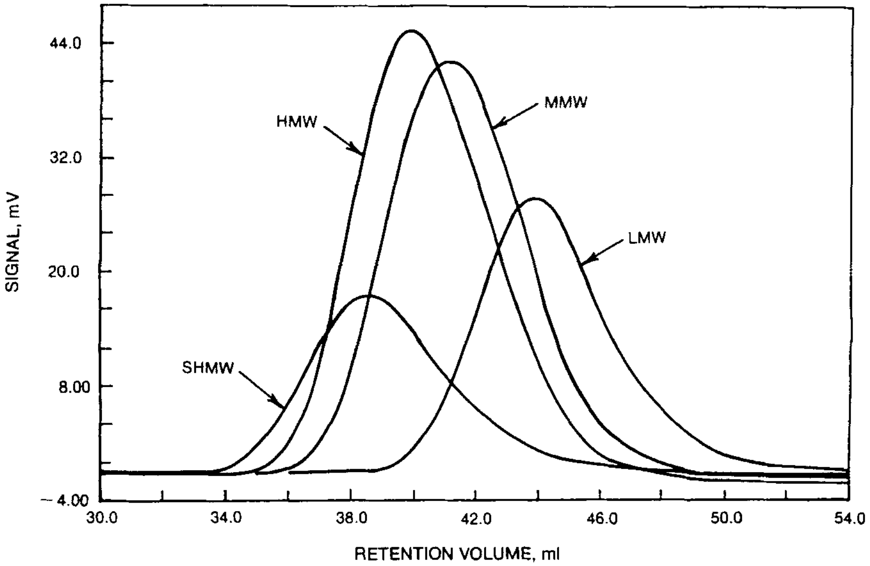

Figure 2b

Concentration chromatograms for four molecular weight grades of PVA. Same samples as given in Figure 2a.

TABLE 2

SEC-Viscometry Data for PVA

	SHMW	HMW	MMW	LMW
4% Viscosity cps, 20° C	234	60	30	6
M_w	249,000	143,000	98,400	31,600
M_n	91,600	63,900	44,900	13,400
M_w/M_n	2.7	2.2	2.2	2.4
$[\eta]$, dL /g	1.40	1.05	0.80	0.42

exhibits linear behavior over its respective molecular weight range. Note that the curve is plotted only over the major portion of the chromatogram. The extreme low and high molecular weight ends where there is poor signal-to-noise, were ignored and are shown by the extrapolated, broken lines.

Using the UNICAL software, the Mark-Houwink constants were calculated for each of the PVA grades. The K and a values from each of the multiple determinations (N = number of determinations) are summarized in Table 3 along with the mean and standard deviation. The values for K exhibit a higher degree of scatter (especially for SHMW and LMW) than those for a.

A one way analysis of variance run at the 0.05 level of significance, determined that there is no statistical difference among the four mean values for K and those for a, based on a small value of the f-statistic. The null hypothesis of equal averages could not be rejected. Thus, K

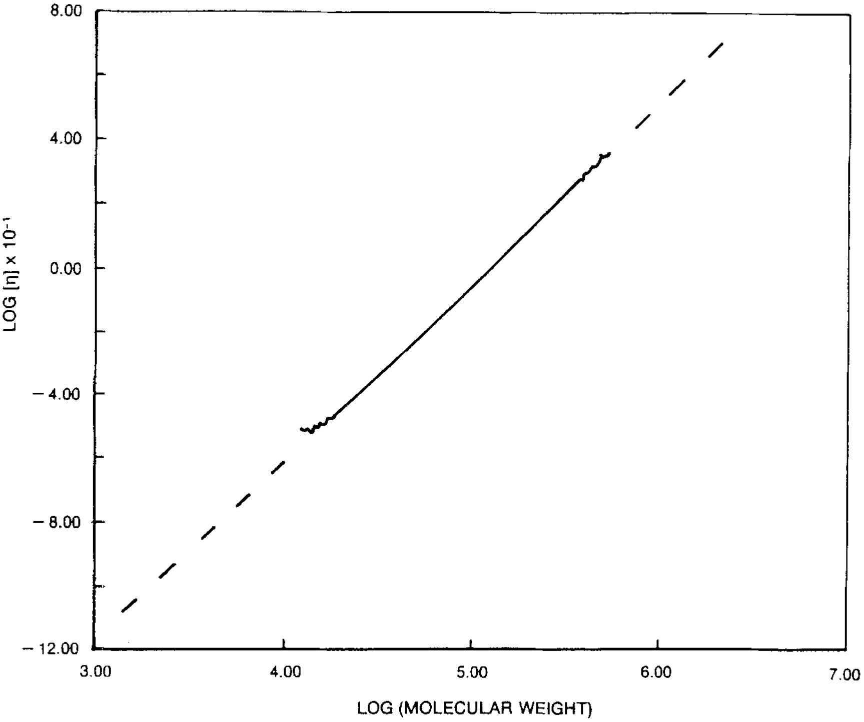

Figure 3

Mark-Houwink plot for high molecular weight grade of PVA.

and a can be considered constant over the range of molecular weight represented by these PVA grades (approximately 13,000 to 250,000, Table 2). Based on the total number of determinations (N = 27), the Mark-Houwink constants in 0.10 N $NaNO_3$ are $K = 1.332 \times 10^{-3}$ (std. dev. $= 0.251 \times 10^{-3}$) and $a = 0.566$ (std. dev. = 0.012). The Mark-Houwink equation becomes,

$$[\eta] = (1.332 \times 10^{-3})M^{0.566}$$

The value for a measured in 0.10 N sodium nitrate is in the 0.5 to 0.8 range expected for random-coiled polymers. Our value is slightly lower

TABLE 3

Experimental Mark-Houwink Constants for PVA

	SHMW	HMW	MMW	LMW
N	7	6	8	6
K, x 10^3	1.089	1.300	1.380	1.419
	1.774	1.429	1.274	1.026
	1.941	1.268	1.274	1.135
	0.993	1.245	1.449	1.178
	1.151	1.663	1.503	1.089
	1.114	1.230	1.183	1.837
	1.064		1.563	
			1.384	
Mean	1.304	1.356	1.376	1.281
Std. Dev., x 10^3	0.384	0.167	0.128	0.304
a	0.582	0.572	0.559	0.557
	0.542	0.562	0.568	0.585
	0.537	0.572	0.567	0.579
	0.590	0.574	0.556	0.576
	0.578	0.549	0.551	0.583
	0.580	0.575	0.572	0.533
	0.584		0.549	
			0.560	
Mean	0.570	0.567	0.560	0.569
Std. Dev.	0.022	0.010	0.008	0.020

TABLE 4

A Comparison of Mark-Houwink Constants for PVA

a	K, x 10^3	Reference
0.567	1.332	This work
0.61	0.690	14
0.62	0.887	15, 16
0.64	0.750	17

than those values reported in the literature and summarized in Table 4. This may be due to the fact that the previously reported values were taken from PVA determinations in water. The addition of sodium nitrate, although a weak salting-out species for PVA, contributes to a somewhat greater degree of chain compression and coil contraction of PVA in solution than pure water (9).

Molecular Weight / Intrinsic Viscosity Distributions:

To examine the accuracy of the experimentally determined Mark-Houwink constants, a PVA of unknown molecular weight was used as a test case. Molecular weights computed from the IVD and universal calibration methods were compared to the absolute methods, on-line viscometry and LALLS. Absolute molecular weights from SEC-LALLS and have been previously described (6,13).

Molecular weight results from the IVD, universal calibration, viscometry, and LALLS methods are summarized in Table 5. The IVD method uses our experimentally determined Mark-Houwink constants. The universal calibration method also uses these K and a values for the unknown PVA

TABLE 5

Molecular Weights of Unknown PVA using Calculated Mark-Houwink Constants

Method	M_w	M_n	M_w / M_n
Mark-Houwink (IVD)	71,500	30,300	2.4
Universal Calibration	72,900	33,500	2.2
Viscometry	70,200	33,500	2.1
LALLS*	75,100	43,100	2.2

* dn/dc for PVA = 0.150 (13)

sample and values of a = 0.68 and K = 4.44 x 10^{-4} for the PEO/PEG standards (18). The data from the IVD and universal calibration methods compare favorably with viscometry and LALLS, although there is slightly better agreement with on-line viscometry. The weight-average values are within 5% of those from viscometry and LALLS. The number-average molecular weight, especially for the IVD method, is considerably lower than LALLS. Some of this may at least reflect the decreased sensitivity of LALLS to low molecular weight polymer in the distribution.

The universal calibration and viscometry methods both utilize a calibration with PEG/PEO narrow molecular weight standards. The IVD method, however, is calibration-independent since the molecular weight is determined using Equation 6. The advantage of this procedure is that only a one-time determination of the Mark-Houwink constants is required.

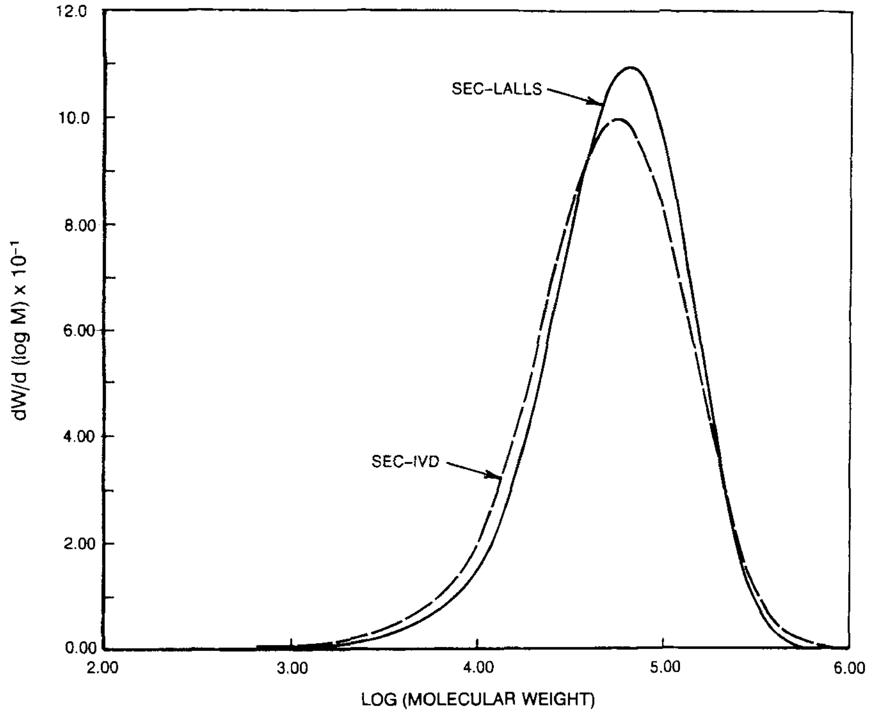

Figure 4

Overlay of IVD and LALLS weight-fraction distribution plots for unknown PVA.

Those values are subsequently used to calculate a molecular weight distribution via the IVD method. A comparison of the MWD from the IVD method and LALLS is shown in Figure 4 and illustrates the good agreement between the two techniques.

Using the IVD method, one does not need to necessarily maintain the integrity of a column calibration over time with the assumption that universal calibration is obeyed. The IVD method also has the advantage that changes in flow rate or elution time will not affect the desired

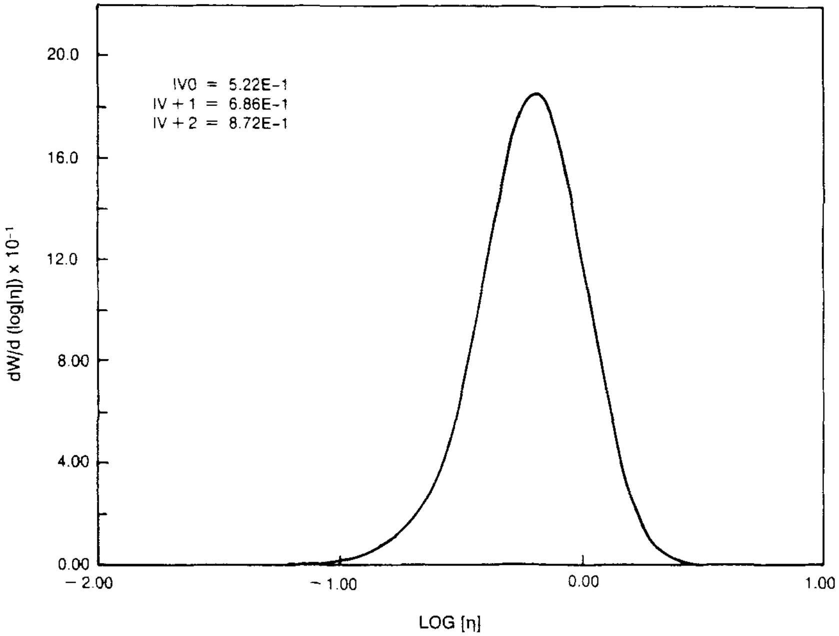

Figure 5

Intrinsic viscosity distribution of unknown PVA.

molecular weight analysis. As described by Yau, the IVD and corresponding intrinsic viscosity averages can be be calculated from the specific viscosity and concentration detector responses (Figure 5). The IV+1 value of 0.686 is very close to the [n] value for the sample from on-line viscometry.

The IVD method for calculation of molecular weights should prove very useful for PVA since accurate Mark-Houwink values have been determined over a wide molecular weight range. Since the IVD method is calibration-independent, quality control is a possible application. Applying this methodology to other types of PVA such as partially-hydrolyzed grades requires further investigation.

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