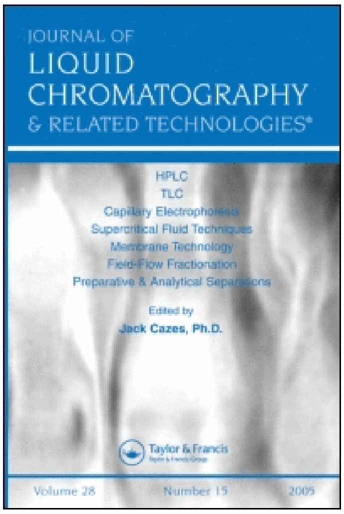

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Size Exclusion Chromatography of Poly(vinylpyrrolidone)

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To cite this Article Senak, L. , Wu, C. S. and Malawer, E. G.(1987) 'Size Exclusion Chromatography of Poly(vinylpyrrolidone)', Journal of Liquid Chromatography & Related Technologies, 10: 6, 1127 — 1150
To link to this Article: DOI: 10.1080/01483918708066758
URL: http://dx.doi.org/10.1080/01483918708066758

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(6), 1127-1150 (1987)

SIZE EXCLUSION CHROMATOGRAPHY OF POLY(VINYLPYRROLIDONE). II. ABSOLUTE MOLECULAR WEIGHT DISTRIBUTION BY SEC/LALLS AND SEC WITH UNIVERSAL CALIBRATION

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ABSTRACT

Poly(vinylpyrrolidone) and poly(ethylene oxide) separate by hydrodynamic volume on Toyo Soda TSK-PW columns in a mixed solvent mobile phase of 50:50 (v/v) $MeOH/H_2O$ containing 0.1M $LiNO_3$. From this separation a single universal calibration curve based on hydrodynamic volume $[\eta]M$ can be obtained. Accurate weight average molecular weights of PVP were obtained by both SEC/LALLS and universal calibration showing good agreement between the two methods. SEC/LALLS overestimates the number average molecular weight for broad distribution polymers due largely to the lack of sensitivity of the LALLS detector to the low molecular weight portion of the polymers, while the universal calibration method slightly underestimates the number average molecular weight as compared to osmometric values.

INTRODUCTION

A variety of SEC-related methods have been extensively used to produce polymer molecular weight distributions including narrow (direct) standard, polydisperse (broad) standard, and universal calibration as well as low angle laser light scattering (LALLS) detection. Neither narrow nor polydisperse standard calibration methods are considered to be viable absolute molecular weight methods for poly(vinylpyrrolidone)(PVP). The former is unsuitable because of the lack of commercially available monodisperse PVP standards while the latter depends upon time-consuming ancillary methods to determine (at least) two moments of the distribution and is subject to greater errors since the resulting calibration is derived from only two points.

The LALLS detector can be interfaced with an SEC system to obtain absolute molecular weight distributions (1). It has been applied successfully to aqueous polymers with relatively narrow molecular weight distributions whose polydispersities ($D = \bar{M}_w/\bar{M}_n$) are less than 2 (2-4). The SEC/LALLS technique typically overestimates the number average molecular weights of polymers (and thus under-estimates their polydispersities). Ouano and Kaye have ascribed this phenomenon to the fact that the molecular weight distribution calculation assumes monodisperse SEC slices while the resolution of commercial columns results in some band spreading (1). It is interesting to note that the effect of band spreading in SEC/LALLS on the apparent molecular weight distribution is the reverse of that in conventional SEC using narrow standard calibration. The application of SEC/LALLS to broad molecular weight distribution polymers, i.e., with polydispersities greater than 3 has received little attention (5).

The product of intrinsic viscosity and molecular weight, $[\eta]M$, which is proportional to the polymer hydrodynamic volume was demonstrated to be a universal calibration parameter for small polydispersity polymers of various geometries and chemical structures by Benoit and coworkers (6). Spatorico and Beyer discussed the application of universal calibration to hydrophilic and large polydispersity polymers (7). The problems caused by both heterogeneous and polydisperse polymers in the utilization of this technique (8) and the appropriateness of choosing the weight ($\bar{M}_w$), number ($\bar{M}_n$), or peak ($\bar{M}_p \sim (\bar{M}_w \cdot \bar{M}_n)^{\frac{1}{2}}$)average molecular weight in the expression $[\eta]M$ have been related (8,9).

The universality of $[\eta]M$ as a calibration parameter for aqueous SEC has been recently reviewed with emphasis on confounding nonsteric effects such as adsorption or electrostatic repulsion as well as significant polydispersity (10). Mori observed universal calibration behavior for PVP vis-a-vis poly(ethylene oxide)(PEO) standards in a nonaqueous mobile phase of 0.01M LiBr-DMF on a polystyrene gel support (11). Domard and Rinaudo studied PVP in aqueous 0.2M NH_4OAc on a cationically derivatized (with quaternary ammonium) silica support and noted a deviation from universal calibration behavior which was ascribed to residual adsorption (12). Belenkii et.al. also reported such a deviation for PVP in aqueous 0.3% NaCl on Sephadex which was interpreted in terms of selective macromolecular penetration of the walls of the Sephadex particles (13).

In a recent paper it was reported that the optimum size exclusion chromatographic (SEC) method for poly(vinylpyrrolidone) was found to be based upon a stationary phase of diol derivatized silica and mobile phase of 50:50 (v/v) $MeOH/H_2O$ containing 0.1M $LiNO_3$ (14). The large, irregular particles contained in that stationary phase do not lend themselves to a sufficiently high resolution separation to elucidate molecular weight distribution. To date, no vendor supplying a sufficiently derivatized 10 µm (or smaller) spherical packing material in the three pore sizes required, 4000, 500, and 60Å has been identified. These pore sizes were deemed necessary to insure the ability to differentiate over the widest dynamic range of molecular weights and, and if mixed according to their respective pore volumes, would result in a column set log-linear in molecular weight as a function of elution volume or time. Adequate derivatization is needed to insure that the chromatographic separation is controlled strictly by molecular size (entropic effects) rather than partially by adsorption (enthalpic effects).

The hydrophilic semi-rigid polymeric gel containing the chemical group $\leftarrow CH_2CHOHCH_2O \rightarrow$ and known as TSK-GEL type-PW (Toya Soda Co., Japan) was chosen as an alternative stationary phase. An aqueous SEC separation of PVP utilizing this medium has already been reported (15). The PW-gel is, however, inferior to the diol derivatized silica in mechanical stability and efficiency (theoretical plate count).

The first aim of the present work was to extend the previously reported chromatograhic method (14) to higher resolution by employing the aforementioned Toya Soda PW-gel support and, in conjunction with LALLS detection, produce absolute molecular weight distribution information for commercial PVP grades. The second aim was to use this data to construct a universal calibration plot and test the validity of the hydrodynamic volume parameter for PVP in an aqueous environment.

EXPERIMENTAL

The PVP samples investigated included commercial lots of molecular weight grades of K-90, K-60, K-30 and K-15 produced by GAF Chemicals Corporation, Wayne, NJ as well as fractions generated by classical solvent/nonsolvent precipitation using water/acetone. Each grade notation represents the nominal Fikentscher K-value which is related to the relative viscosity, η_{rel}, in aqueous solution and the concentration, c, (in g/dl) by (16):

$$\frac{\log \eta_{rel}}{c} = \frac{75K_o^2}{1 + 1.5K_oc} + K_o$$

and, $K = 1000\ K_o$

The exact K-values of these commercial lots were determined at 1 g/dl to be 89.6, 54.4, 30.4, and 18.6 respectively. A cross-linked PVP (Polyclar AT® from GAF Chemicals Corporation) was used to study preferential solvation. Seven Toya Soda and two Polysciences PEO standards were used in the universal calibration portion of this work whose $\bar{M}_w$'s ranged from 996,000 to 1400 amu with polydispersities ranging from 1.02 to 1.10.

The chromatograph employed in this study was a Waters Model GPC-1 with a module U6K injector (100 µl loop) and a column heater theromstatted at 25°C. The SEC column set used consisted of one column each of Toya Soda G6000PW, G5000PW, G3000PW and G2000PW grades as well as a guard column of TSK-GEL type G2000PW material, and was found to be log-linear over four decades (10^6 to 10^2 amu) representing the molecular range of all GAF commercial grades of PVP. The analytical columns were 30 cm long and had an i.d. of 7.5 mm. The efficiency of the column set was determined to be approximately 2,700 theoretical plates using n-methylpyrrolidone and the 5σ method. The mobile phase was identical to that reported earlier namely 50:50 (v/v) MeOH/H_2O

containing 0.1M $LiNO_3$ (14). The water and methanol used were Omnisolve HPLC grade obtained from EM Science (E. Merck) while the $LiNO_3$ was reagent grade obtained from Fisher Scientific.

The refractive index (RI) detector used was similar to the Waters Model R401 and employed attenuation settings of 4 for K-90, 8 for K-60 and K-30, and 16 for K-15. The LALLS detector was an LDC/Milton Roy (Chromatix) Model CMX-100 whose He-Ne laser operates at a wavelength of 632.8 nm. The LALLS incident power settings were 50 mv for K-90 and K-60 and 100 mv for K-30 and K-15. The laser differential refractometer, an LCD/Milton Roy (Chromatix) Model KMX-16, (used to determine dn/dc) operated at the same wavelength and was thermostatted at 25°C.

Intrinsic viscosities were determined at 25°C using a 0.64 mm i.d. Ubbelohde viscometer and a Schott Model AVS automated viscometer. A Wescan Model 232A vapor pressure osmometer (VPO) was used to determine $\bar{M}_n$'s of K-30 and K-15. The VPO was calibrated with benzil, thermostatted at 51°C and employed isopropanol as a solvent. A Wescan Model 230 membrane osmometer was used to determine $\bar{M}_n$'s of K-90 and K-60. It utilized an S&S Model B-20 membrane in aqueous 0.1M $LiNO_3$ at 40°C. A Mitsubishi Model KF-05 moisturemeter was employed to determine water levels by Karl Fischer titration. Gas chromatographic analyses were preformed on a Perkin-Elmer Model Sigma 1 GC containing a (80/100 mesh, 6 ft. x 2 mm i.d.) Porapak Q glass column and employing flame ionization detection.

The PVP sample solutions used in the SEC and SEC/LALLS experiments were prepared at concentrations of 0.2, 0.4, 0.85, and 1.5% w/w for PVP K-90, K-60, K-30, and K-15 respectively in the SEC mobile phase. These concentrations were chosen to maximize detector responses while avoiding concentration effects (e.g., viscous fingering). PEO standard solutions used for universal calibration were prepared at 0.1% w/v. All solutions were allowed to dissolve for ½ day on a slowly rotating wheel and were filtered through 0.45 µm Millipore HA filters prior to injection.

The data acquisition system consisted of a Digital Equipment Corporation MINC-11 computer and an LDC/Milton Roy (Chromatix) Model CMX-10 interface box. The Chromatix MOLWT2 and GPC2 programs were used to perform SEC/LALLS and SEC/universal calibration calculations respectively. The data collection window was 30 minutes and 256 timeslices were automatically recorded per chromatogram.

For the SEC/LALLS experiment, MOLWT2 calculates the instantaneous timeslices molecular weight, M_i, from the corresponding instantaneous concentration, c_i and the excess Rayleigh scattering factor, $\bar{R}_{\theta,i}$, according to a modified form of the Debye equation:

$$\frac{Kc}{\bar{R}_{\theta,i}} = \frac{1}{M_i} + 2A_{2,i}c_i$$

where, A_2 equals the second virial coefficient and the optical constant, K, is proportional to the squares of both the refractive index, n, and (dn/dc). $A_{2,i}$ is assumed to be constant throughout an individual sample's molecular weight distribution. For universal calibration, GPC2 calculates M_i according to

$$M_i = \left(\frac{[\eta_{s,i}]M_{s,i}}{K} \right)^{1/(a+1)}$$

where K and a are the Mark-Houwink constant for PVP in the SEC mobile phase and $[\eta_{s,i}]$ and $M_{s,i}$ are the instantaneous values of the PEO standards' intrinsic viscosities and molecular weights respectively. The latter are taken from a previously computed calibration curve for $[\eta_{s,i}]M_{s,i}$ versus $V_{e,i}$ (the elution volume) constructed from the individual PEO standards' $[\eta_s]$ and M_s values.

RESULTS AND DISCUSSION

A. Mobile Phase Studies

The mixed mobile phase consisting of a 50:50 (v/v) mixture of water and methanol with 0.1M $LiNO_3$ has been developed for a diol derivatized silica column system for PVP in the previous work (14). This mixed aqueous mobile phase was found to be satisfactory in the present work for a Toyo Soda TSK-PW column system with 100% polymer recovery determined by the method previously described (14). The omission of methanol from the mobile phase causes a significant sensitivity loss in light scattering measurement because the Rayleigh factor of the mobile phase is about twice the value of water alone.

No indication of preferential solvation of PVP by one of the mobile phase constituents was observed which, if present, would distort the molecular weight distribution. For example, the weight average molecular weights for a PVP K-90 sample were found to be virtually the same in the mixed mobile phase (1.43×10^6 amu) and in water with 0.1M $LiNO_3$ (1.57×10^6 amu) by static LALLS. In addition, the composition of the mixed mobile phase was compared to mixtures of 10% to 20% (w/w) crosslinked PVP (Polyclar AT®) in equilibrium with the mobile phase with respect to the water/methanol ratio by Karl Fischer titration and gas chromatography. (The hypothesis tested concerned the fact that if PVP were preferentially solvated by either component then its crosslinked analog would alter their ratio in the supernatant.) No compositional differences were found.

B. Intrinsic Viscosity

The measured intrinsic viscosities of the PEO standards and PVP samples in the mixed mobile phase at 25°C are compiled in Table 1. The Mark-Houwink constants, K and a, for PEO and PVP obtained under these conditions are given in Table 2. These constants are related to the intrinsic viscosity and the molecular weight of a polymer by the Mark-Houwink equation

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

or

$$\log [\eta] = a \log M + \log K$$

Thus K and a for both polymers were obtained from the slopes and intercepts of plots of log $[\eta]$ versus log M where M in this case is the experimentally determined weight average molecular weight, $\bar{M}_w$ (from Table 6).

The plot for all PVP samples is shown in Figure 1 where the straight line was constructed from linear regression data and the composite and individual correlation coefficients (r) are given in Table 2. The Mark-Houwink constants of the PVP commercial samples (2) were used in the subsequent universal calibration calculation of molecular weight distribution of PVP samples because they gave the best correlation with LALLS results. The K and a values were found to be nearly the same for commercial PVP samples and narrow fractions. This is probably due to the fact

TABLE 1

Intrinsic Viscosity Results

Sample	Intrinsic Viscosity, (dl/g)
PVP K-90	2.24
PVP K-60	0.739
PVP K-30	0.250
PVP K-15	0.0975
PVP Fraction 1	0.952
PVP Fraction 2	0.551
PVP Fraction 3	1.75
PVP Fraction 4	0.334
PEO, $\bar{M}_w$ = 996000	6.71
PEO, $\bar{M}_w$ = 594000	4.56
PEO, $\bar{M}_w$ = 252000	2.47
PEO, $\bar{M}_w$ = 145000	1.60
PEO, $\bar{M}_w$ = 86000	1.09
PEO, $\bar{M}_w$ = 39000	0.598
PEO, $\bar{M}_w$ = 18000	0.368
PEO, $\bar{M}_w$ = 9200	0.161
PEO, $\bar{M}_w$ = 1400	0.055

TABLE 2

Mark-Houwink Constants

Sample	K	a	r
PVP (all samples)	1.0×10^{-4}	0.70	0.9988
PVP (narrow fractions)	0.851×10^{-4}	0.72	0.9995
PVP (commercial samples)(1)	1.17×10^{-4}	0.69	0.9997
PVP (commercial samples)(2)	2.32×10^{-4}	0.65	0.9926
PEO	2.21×10^{-4}	0.75	0.9983

(Note: Set (1) is generated from this work and set (2) is taken from previous work.)

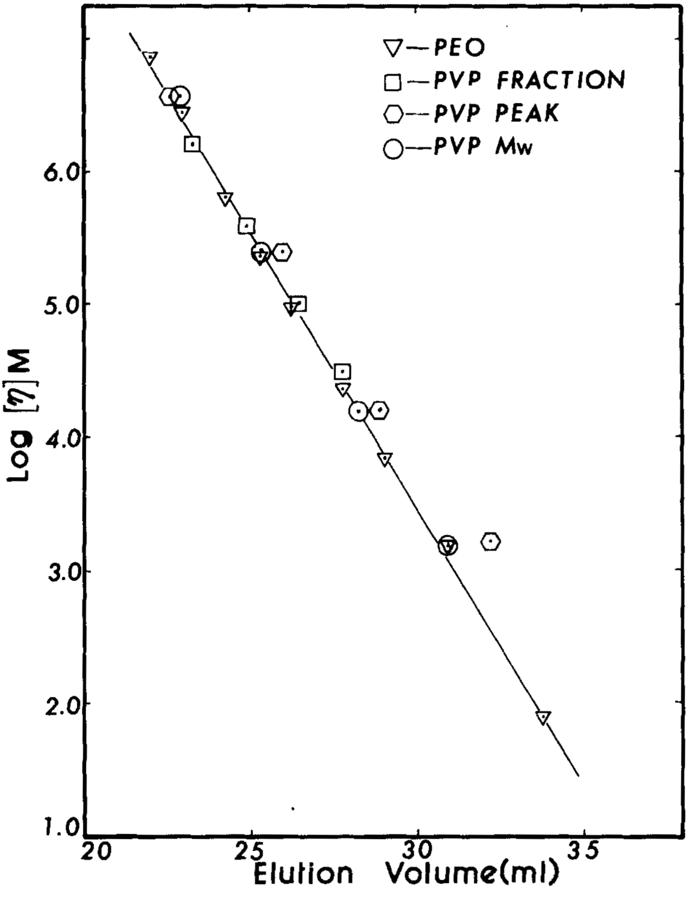

FIGURE 1. Mark-Houwink plot for commercial PVP grades and PVP narrow fractions in the mixed mobile phase at 25°C.

that the fractions are not monodisperse in molecular weight (as shown later in Table 8a).

C. Refractive Index Increments

The refractive index increments (dn/dc) of PVP in the mixed mobile phase at 25°C which are needed for the calculation of the Rayleigh optical constant (K) are listed in Table 3. No molecular weight dependence of the refractive index increment of PVP was observed.

D. Light Scattering Data

The weight average molecular weight and second virial coeffients of commercial PVP samples in the mixed mobile phase at 25°C as determined by static LALLS are given in Table 4. It can be shown from this data that the second virial coefficient of PVP

TABLE 3

Refractive Index Increments of PVP

Sample	$\frac{dn}{dc}$, $\frac{ml}{g}$
PVP K-90	0.173
PVP K-60	0.175
PVP K-30	0.174
PVP K-15	0.175

under these conditions decreases with increasing molecular weight according to the following relationship

$$A_2 = 0.01 \times M^{-0.23}$$

which is typical of linear polymers in good solvents (17).

The molecular weights of PVP obtained by static LALLS and SEC/LALLS have been found to be the same in this study. Therefore, only SEC/LALLS, a more convenient technique, was used to determine most of the PVP weight-average molecular weights reported in this paper. The equivalence of these two techniques in determining $\bar{M}_w$ is shown for three PVP samples in Table 5.

The molecular weight distributions of both commercial and narrow fraction PVP samples were analyzed by SEC/LALLS and the distribution moments and polydispersities summarized in Table 6.

TABLE 4

Static LALLS Results

	$\bar{M}_w$	Second Virial Coefficient,(mole ml/g^2)
PVP K-90*	1.43×10^6	$4.0 \pm 0.5 \times 10^{-4}$
PVP K-60*	3.3×10^5	$5.85 \pm 0.15 \times 10^{-4}$
PVP K-30*	4.6×10^4	$9.26 \pm 0.2 \times 10^{-4}$
PVP K-15*	1.40×10^4	1.12×10^{-3}

(Note: These samples are alternate lots to those reported on in Tables 1-3 and 6-8b)

TABLE 5

Comparison of Static LALLS and SEC/LALLS Results

Sample	$\bar{M}_w$ (Static LALLS)	$\bar{M}_w$ (SEC/LALLS)
PVP K-90*	1.20×10^6	1.18×10^6
PVP K-60*	3.33×10^5	3.44×10^5
PVP K-60*	2.89×10^5	2.85×10^5

(Note: These samples are alternate lots to those reported on in Tables 1-3 and 6-8b)

TABLE 6

Molecular Weights of PVP Samples by SEC/LALLS

Samples	K-values	$\bar{M}_w$	$\bar{M}_n$	D
K-90	89.6	1.52×10^6	6.38×10^5	2.38
K-60	54.4	3.37×10^5	1.57×10^5	2.14
K-30	30.4	6.24×10^4	3.10×10^4	2.01
K-15	18.6	1.68×10^4	1.10×10^4	1.53
Fraction 1		4.16×10^5	3.16×10^5	1.32
Fraction 2		1.82×10^5	1.67×10^5	1.09
Fraction 3		9.18×10^5	6.58×10^5	1.40
Fraction 4		9.29×10^4	7.75×10^4	1.20

The $\bar{M}_w$ values reported here are slightly higher than but in generally good agreement with those reported earlier by Bühler and Klodwig (18) and BASF AG (19).

The SEC/LALLS chromatogram for PVP K-90 (as depicted in Figure 2) did not exhibit any high molecular weight shoulder suggesting that no branched, high molecular weight component is present in PVP K-90. Branching normally decreases the second virial coefficient (17). Yet the second virial coefficient of PVP increases monotonically from K-15 to K-90 according to the aforementioned relationship. This further indicates the absence of branching in PVP K-90.

The number average molecular weights obtained by SEC/LALLS are much higher than those obtained by osmometry as shown in Table 7. The anomalously high number averages generated by

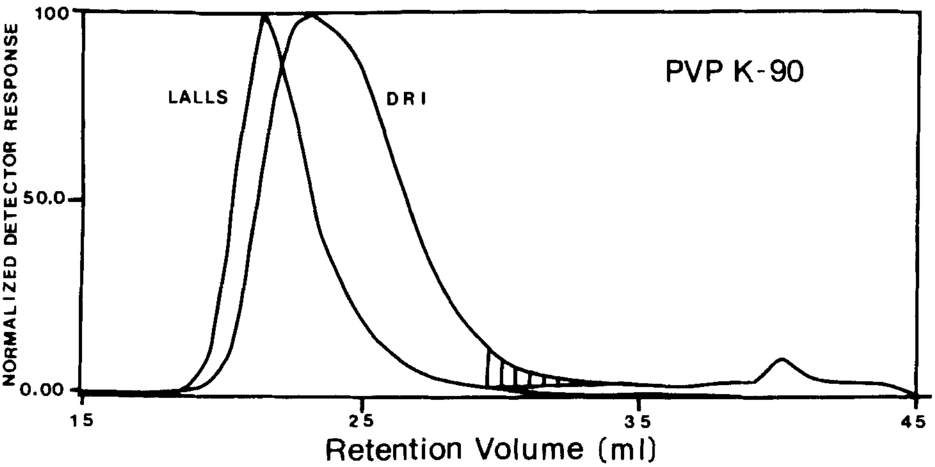

FIGURE 2. Comparison of LALLS and DRI detector outputs for PVP K-90 by SEC.

TABLE 7

Osmometry Results

Sample	Technique	$\bar{M}_n$
PVP K-90	Membrane Osmometry	374000
PVP K-60	Membrane Osmometry	67500
PVP K-30	Vapor Pressure Osmometry	8430
PVP K-15	Vapor Pressure Osmometry	5170

SEC/LALLS cause the corresponding polydispersities to be small. The discrepancy between $\bar{M}_n$ as obtained from SEC/LALLS versus osmometric methods is principally due to the lack of sensitivity of the LALLS detector toward the low molecular weight portion of broad distribution polymers where the concentration (RI) detector is still sensitive as depicted by the shaded area in Figure 2 for the case of PVP K-90. As discussed by Hamielec et.al., an electronic switching device and a technique for optimizing the sensitivity and signal to noise ratio of the LALLS detector throughout the SEC chromatogram is needed to improve the accuracy of $\bar{M}_n$ as obtained by SEC/LALLS (20). A secondary (lesser) cause of high number averages in SEC/LALLS is band broadening which was not treated in this work.

A log $\bar{M}_w$ versus retention volume calibration curve was generated from the results reported for the four narrow fraction PVP samples in Table 6. Fairly accurate molecular weights of PVP K-60 can be obtained from this direct standard calibration curve because the K-60 distribution lies within the molecular weight limits of that calibration curve. The weight average molecular weight of PVP K-60 based on this calibration curve is 3.32×10^5

amu which is the same as the SEC/LALLS result. The number average molecular weight is 4.81×10^4 which is much closer to the osmometry result than to the SEC/LALLS result. This indicates the overestimation of the number average molecular weight for broad distribution polymers by SEC/LALLS is due more to the insensitivity of LALLS to the low molecular weight portion of their distributions than to band broadening.

E. Universal Calibration

The universal calibration curve for PEO standards and commercial and narrow fraction PVP samples is shown in Figure 3. The straight line was constructed from the linear regression results of the PEO standards, the PVP fractions, and the commercial PVP samples weight average molecular weight retention volumes and exhibited a composite correlation coefficient of 0.9989. The narrow PVP fractions fall on the plot nicely. However, the commercial PVP samples which display broad molecular weight distributions are displaced from the plot if peak retention volumes are used. When the retention volumes corresponding to the weight average molecular weights (available from SEC/LALLS data) are employed, the commercial PVP samples also fall on the universal calibration plot.

The molecular weight averages and polydispersities of commercial and narrow fraction PVP samples based upon universal calibration are reported in Table 8a. The corresponding differential absolute molecular weight distributions of commercial PVP K-90, K-60, K-30, and K-15 are depicted in Figure 4. The agreement between universal calibration and SEC/LALLS with regard to $\bar{M}_w$ values is very good. Except for the case of PVP K-30, the number averages appear to be somewhat

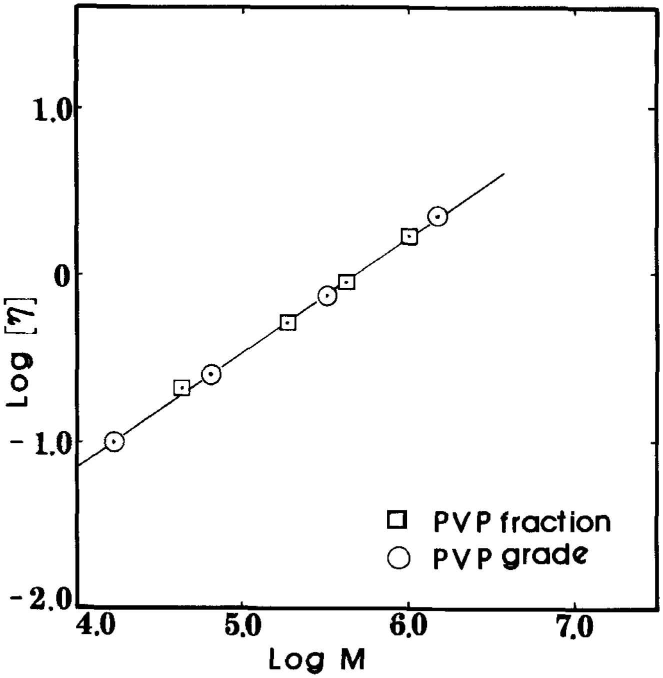

FIGURE 3. Universal calibration plot for PVP samples and PEO standards in the mixed mobile phase at 25°C using a Toya Soda TSK-GEL type PW column set (G6000PW, G5000PW, G3000PW, and G2000PW).

underestimated by universal calibration when compared to osmometry results. This may be due to SEC band broadening and to difficulty in calculating $\bar{M}_n$ due to uncertainties in the low molecular weight tails of the chromatograms (e.g., the effect of proximity to solvent peaks)(21). In addition, the vapor phase osmometric value of $\bar{M}_n$ can be readily affected by the presence of low molecular weight impurities in the sample. These potential errors may be large enough to prevent good agreement between the two methods.

TABLE 8A

Molecular Weights of PVP Samples by Universal Calibration
($a = 0.65$, $K = 2.32 \times 10^{-4}$)

Sample	$\bar{M}_w$	$\bar{M}_n$	D
K-90	1.24×10^6	2.06×10^5	6.02
K-60	3.40×10^5	5.23×10^4	6.51
K-30	6.19×10^4	1.28×10^4	4.84
K-15	1.12×10^4	4.18×10^3	2.68
Fraction 1	4.46×10^5	1.58×10^5	2.82
Fraction 2	1.84×10^5	6.88×10^4	2.67
Fraction 3	9.47×10^5	2.43×10^5	3.91
Fraction 4	8.99×10^4	3.07×10^4	2.92

The Mark-Houwink constants determined from different sets of commercial PVP samples in the mixed mobile phase were found in this laboratory to vary from 0.65 to 0.70 for a and 2.32×10^{-4} to 0.92×10^{-4} for K. Mark-Houwink constants are normally sensitive to polymer molecular weight. However, the PVP molecular weights calculated according to universal calibration were not observed to be sensitive to the Mark-Houwink constants used in the calculation. A higher value of K is accompanied with a lower value of a and all pairs of constants in the aforementioned range should give approximately the same molecular weight (21). For example, if the four commercial PVP samples' distributions were recomputed by an alternate, extreme set of constants ($a = 0.72$, $K = 0.851 \times 10^{-4}$) the molecular weights

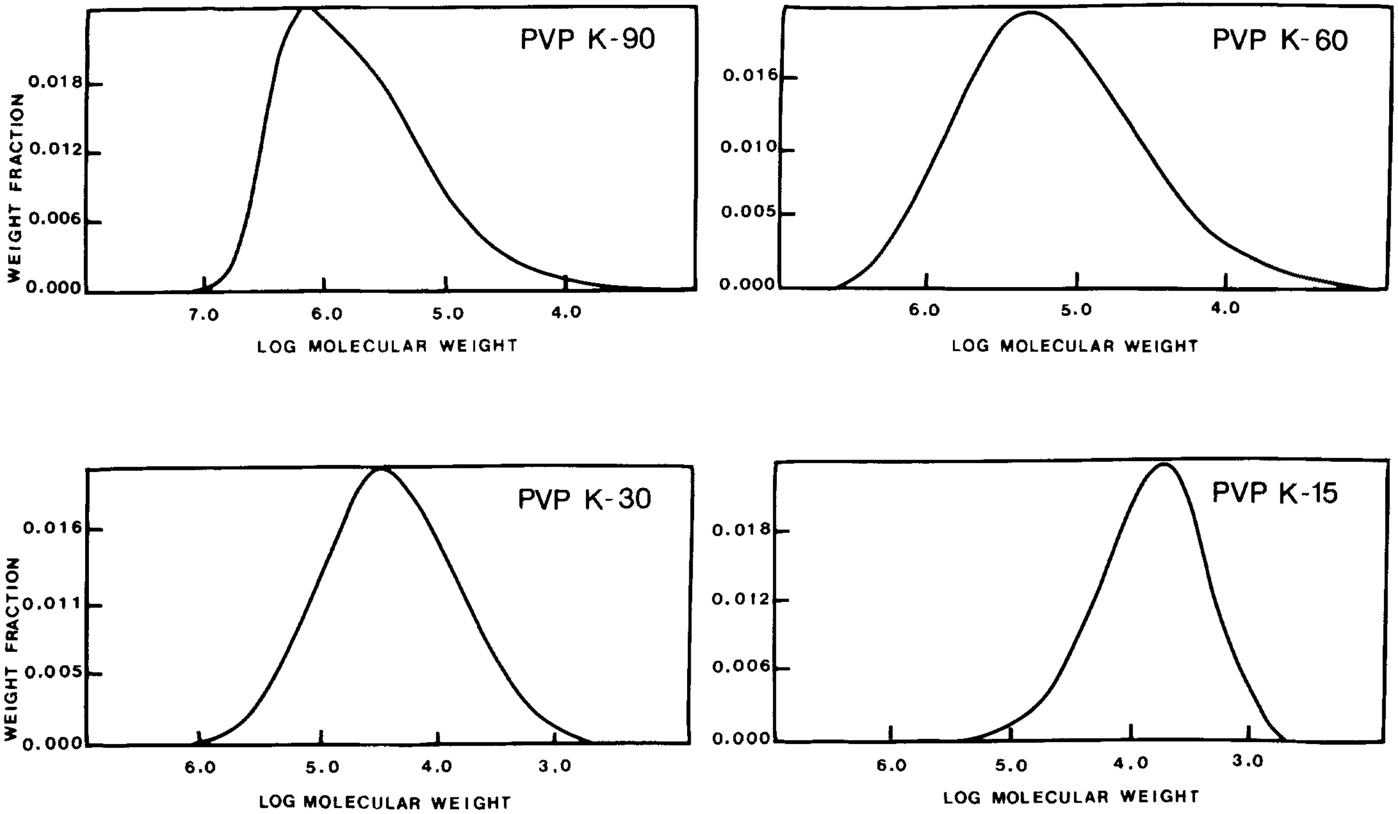

FIGURE 4. Absolute differential molecular weight distributions for PVP K-90, K-60, K-30, and K-15 grades based upon universal calibration.

TABLE 8b

Molecular Weights of PVP by Universal Calibration

(for $a = 0.72$, $K = 0.851 \times 10^{-4}$)

Sample	$\bar{M}_w$	$\bar{M}_n$
PVP K-90	1.22×10^6	2.36×10^5
PVP K-60	3.55×10^5	6.24×10^4
PVP K-30	6.94×10^4	1.60×10^4
PVP K-15	1.37×10^4	5.44×10^3

obtained as listed in Table 8b are very similar to those in Table 8a (as computed from $a = 0.65$ and $K = 2.32 \times 10^{-4}$). This suggests that for the purpose of calculating molecular weights by the universal calibration method the Mark-Houwink constants may be obtained from broad distribution polymers without fractionation.

CONCLUSIONS

In the mixed mobile phase of 50:50 (v/v) $MeOH/H_2O$ containing 0.1M $LiNO_3$, PVP and PEO were found to elute based on hydrodynamic volume on Toyo Soda TSK-PW columns. No preferential solvation of PVP by either MeOH or H_2O in the mobile phase was noticed. The refractive index increment of PVP in this mobile phase was found to be 0.174 ml/g and is independent of the molecular weight of PVP. The second virial coefficient of PVP in this mobile phase was found to decrease with increasing molecular weight according to the equation $A_2 = 0.01 \times M^{-0.23}$

An accurate weight average molecular weight for PVP can be obtained from SEC/LALLS, however, this method overestimates the number average molecular weight of PVP. This is due mainly to the lack of sensitivity of the LALLS detector to the low molecular weight portion of broad distribution polymers. No indication of a highly branched high molecular weight component was found in the PVP K-90 sample from the SEC/LALLS chromatogram or from the dependence of the second virial coefficient upon molecular weight. Universal calibration behavior (as reflected in a single plot based on hydrodynamic volume) was demonstrated for PVP and PEO. Accurate weight average molecular weights for PVP can be obtained from universal calibration. However, this method appears to underestimate the number average molecular weight due to band broadening and uncertainty in the low molecular weight tail of the chromatogram.

ACKNOWLEDGEMENT

The authors are grateful to GAF Chemicals Corporation for granting permission to publish this work and to W.J. Burlant and L. Blecher for their interest in and support of this research. The authors wish to thank the following colleagues in GAF's R&D Department for their help in this work: D.M. Chiou (GC), H.O. Locke (water contents), T.E. Smith (fractionation of PVP) and G.R. Siss (viscosity measurements). The authors also wish to thank the Chromatix (now LDC/Milton Roy) applications laboratory for helpful discussions.

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