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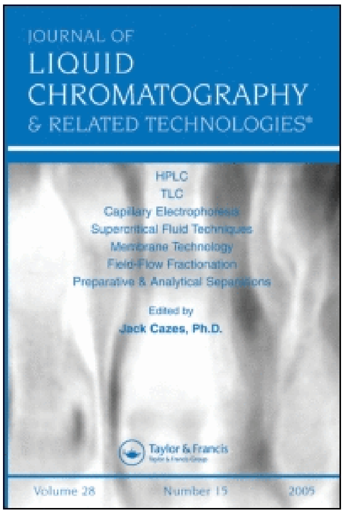

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G. Samay[a]
[a] Research Institute for the Plastics Industry, Budapest, Hungary

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SUPPLEMENT TO THE METHOD OF WEISS-COHN-GINSBERG IN GEL-PERMEATION CHROMATOGRAPHY

G. Samay
Research Institute for the Plastics Industry
H-1950 Budapest, Hungary

ABSTRACT

Methods are proposed to transform GPC chromatograms into molecular mass distributions /MMD/ using the universal calibration and the intrinsic viscosity of the material measured at GPC circumstances, and in conditions, for which KMHS-constants are known. The results of the calculation are the MMD and the interrelation between the Kuhn-Mark-Houwink-Sakurada constans, K and a for GPC circumstances. It is also shown, that as a simplification a-values available for any condition can be used for the calculation using the experimentally measured intrinsic viscosities in GPC circumstances and within circumstances, for wich KMHS-constants are known.

INTRODUCTION

Recently Deniz and Güven (1) have published a calculation which makes possible to determine the Kuhn-Mark-Houwink-Sakurada /KMHS/ constants for any conditions using the chromatograms of gel-permeation

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chromatographic measurements /GPC/ together with the Benoit's universal calibration curve (2) and the intrinsic viscosities measured at circumstances pertinent to the GPC conditions and also for other conditions of interest. Using the algebraic rearrangements of the fundamental equations, as proposed by Weiss and Cohn-Ginsberg (3), the unperturbed dimensions of the dissolved molecules were determined and compared to literature data and data measured by different extrapolation methods.
The most common problem in the routine work with GPC is however, that the KMHS constants for the polymers to be tested and adequate for the GPC conditions are often not available. From a practical point of view, therefore, it is much more important to determine the KMHS-constants for the polymer system in the GPC conditions using literature data. A reversal of Deniz-Güven's procedure might give a solution to this problem. The present work is aimed to illustrate this possibility.

THEORETICAL

The Benoit and Grubisic-Gallot's universal calibration gives the molecular-size parameter /J_i/ for each point of the separation range as the product of M_i, the molecular mass, and the intrinsic viscosity $[\eta]_i$:

$$J_i = M_i[\eta]_i$$

Having a GPC chromatogram, thus we have a set of weight fractions w_i, pertinent to J_i. The molecular-mass-distribution function /MMD/ and also the parameters of the MMD can be computed using the KMHS-constants. For the intrinsic viscosity it holds:

$$[\eta] = K^{\frac{1}{a+1}} \sum_i w_i J_i^{\frac{a}{a+1}} \qquad 1$$

By using the algorithm of Deniz and Güven we arrive at equation which gives an expression for the intrinsic viscosity of the tested polymer at any conditions different from that of the GPC ones:

$$[\eta] = K\, K_o^{\frac{-a}{a_o+1}} \sum_i w_i J_i^{\frac{a}{a_o+1}} \qquad 2$$

where the subscript o denotes the conditions pertinent to the GPC measurements.

$[\eta]_o$ can also be expressed replacing a by a_o in Eq 1:

$$[\eta]_o = K^{\frac{1}{a_o+1}} \sum_i w_i J_i^{\frac{a_o}{a_o+1}} \qquad 3$$

Since $[\eta]$ can easily be measured for any solvent, having measured the intrinsic viscosities for the GPC-circumstances and for the circumstances for which KMHS data are available in the literature, the required constants can be computed. For the calculation the following ways can be proposed:

From eq. 3, K_0 can be computed for any a_0 value:

$$K_0 = \left[\frac{[\eta]_0}{\sum_i w_i \; J_i^{\frac{a_0}{a_0+1}}} \right]^{a_0+1} \qquad 3a$$

By a systematic variation of a_0 a set of K_0 can be obtained, and thus $[\eta]$'s can be computed using Eq. 2. Having reached a value for $[\eta]$ close enough to the measured one the K_0 and a_0 constants can be accepted as an optimal approximation.

Another possibility is to express K_0 as a function of a_0 via Eq. 2:

$$K_0 = \left[\frac{[\eta]}{K \sum_i w_i \; J_i^{\frac{a}{a_0+1}}} \right]^{-\frac{a_0+1}{a}} \qquad 2a$$

and calculate $[\eta]_0$ on the basis of Eq. 3, untill a good enough agreement between the calculated and measured values of $[\eta]$ is reached.

For practical work some further simplications can be used. It has been shown by several authors (4) that a certain relation exists between the K and a values measured at different conditions. Moreover, literature data for KMHS-constants, although measured in the same conditions are rather discordant (5). It was also shown (5), that the transformation of w(V) into w(M) is not very sensitive to changes of the KMHS-constants, provided the constants obey the above-mentioned interrelation. Therefore, for practical use - as a rough approximation - one can take a_0=a. In this case K_0 can be expressed simply by:

$$K_o = K \frac{[\eta]_o}{[\eta]} \qquad 4$$

EXPERIMENTAL

The materials used here were homo and copolymers of styrene and n-alkyl methactrylates having relatively narrow molecular-mass distribution. The experimental conditions for the GPC runs were given elsewhere (6) along with the calibration procedures. Knowing the KMHS-constants for the GPC-conditions for the samples to be tested (6) the moments of the MMD could be calculated. The correction for zone-spreading was made by the simple Pierce-Armonas method (7).

The chromatograms were used to calculate the MMD of the samples, using universal calibration and independently measured KMHS-constants. Having the MMD's of the samples, intrinsic viscosities could be computed for any pair of KMHS-constants using Eq. 1. The intrinsic-viscosity values for the polymers pertinent to some KMHS-constants available in the literature (8) /see Appendix/ were calculated in this way. The KMHS-constants according to Eq. 4 were also calculated using the intrinsic viscosities obtained by the above mentioned calculation. Using this latter KMHS-constants MMD's were also computed. The main results of these computations are collected in Table 1.

CALCULUS

Programs in BASIC were written for the two possible procedures described in the theoretical part.

Using systematically varied values for a_o, K_o's were computed by Eq. 3a, and $[\eta]$'s were obtained using these KMHS-constans in Eq. 2.
An objective-function, /OF/ was defined, as

$$OF = \frac{[\eta]_{exp} - [\eta]_{calc}}{[\eta]_{exp}} \cdot 100$$

/subscripts "exp" and "calc" refer to experimental, and calculated values, respectively/, and the minimum value of this objective-function, OF_{min}, was accepted as best estimation for K_o and a_o. This method is referred as "Iteration I", later in the text.

In method "Iteration II" K_o's were computed for different a_o using Eq. 2a, and $[\eta]_o$'s were calculated for these constants with the help of Eq. 3. The objective function was defined in this case as

$$OF = \frac{[\eta]_{o,exp} - [\eta]_{o,calc}}{[\eta]_{o,exp}} \cdot 100$$

Values for a_o were changed in the region of 0,50-0,85 with an increment of 0,01 in both cases. The results of these calculations are shown in Tables 1 and 2.

DISCUSSION

A comparison of the data of the same row in Table 1 shows, that the two iterative procedures and the use of the estimated values of K and a on the basis of Eq. 4 give similar values. It means,

TABLE 1

The characteristics of the MMD's computed by different ways: M_m - mass-average molecular mass, P - degree of polydispersity /M_m/M_n = P/, OF_m -minimum value of the objective function.

Material	Independent KMHS's		Estimated KMHS's		Iteration I			Iteration II		
	$M_m \cdot 10^{-3}$	P	$M_m \cdot 10^{-3}$	P	$M_m \cdot 10^{-3}$	P	OF_m	$M_m \cdot 10^{-3}$	P	OF_m
poly-/Buthyl-methacrylate/	531	1.57	473	1.58	514	1.60	1.8	529	1.60	2.8
poly-/ethyl-methacrylate/	555	1.54	553	1.51	546	1.84	1.8	568	1.84	3.9
bimodal poly/ethyl-methacrylate/	478	2.25	429	2.19	429	2.90	0.2	493	2.90	0.2
Styrene-ethyl-methacrylate	92	1.74	91	1.60	97	1.70	4.2	92	1.70	6
Styrene-octyl-methacrylate	336	1.50	335	1.49	344	1.58	1.1	338	1.58	1.6
Styrene-buthyl-methacrylate	450	1.47	450	1.49	458	1.76	0.01	457	1.74	0.01

that using either the iterative process or the estimation, we arrive at a good agreement with the data obtained using independently measured KMHS-constants. The only advantage of the iteration might be the excess information, namely the KMHS-constants. The KMHS-constants obtained by different ways are shown in Table 2. These KMHS constants, however, are remarkably differing from the experimentally measured ones. The reason for this good agreement in MMD's is in the error-structure of the calculations. As far as the intrinsic viscosity-data were computed on the basis of the chromatograms, these values were free of experimental error. The only source of the deviation between the input and calculated data was the error of the integrations, therefore the convergency of the data should depend purely on the correctness of the integration method. In Fig. 1 the dependence of the objective-function on "a" is shown for two materials. In the case of "A" the minimum is in the range of the calculation, in the case of "B" the minimum is out of this range.

The curvature is very flat, and the difference in the objective-function is less than 0.1 % within the whole range. Similar behavior of the objective-function was obtained in each case and this also proves the well-known fact, that any pair of KMHS-constants obeying a certain interrelation gives reliable results in GPC calculations. Thus it is much more important in GPC-practice to know this interrelation rather than the KMHS-constants themselves. The excess information of the iterative method is therefore this interrelation, which can be easily obtained as a result of the computation. If this relation is unknown, KMHS-constants given by Eq. 4 can be reliably used for a rapid, but rough estimation.

TABLE 2

The KMHS constants for GPC conditions as measured by independent way using narrow, characterized fractions, estimated using Eq. 4, and calculated by the two possible interative processes.

Material	Independent		Estimated		Iteration I.		Iteration II.	
	$K_o \cdot 10^2$	a_o	$K_o \cdot 10^2$	a_o	$K_o \cdot 10^2$	a_o	$K_o \cdot 10^2$	a_o
Poly-/Buthyl-methacrylate/	0.503	0.758	3.14	0.62	0.152	0.85	0.144	0.85
Poly-/ethyl-methacrylate/	1.549	0.68	1.06	0.71	17.1	0.5	16.1	0.5
bimodal /ethyl-methacrylate/	1.549	0.68	1.03	0.71	17.0	0.5	16.9	0.5
Styrene /ethyl-methacrylate/	10.5	0.56	2.18	0.70	2.33	0.70	2.11	0.70
Styrene-octyl-methacrylate	2.39	0.64	9.22	0.71	1.03	0.71	1.00	0.71
Styrene-buthyl-methacrylate	0.37	0.80	0.547	0.77	3.45	0.63	4.48	0.61

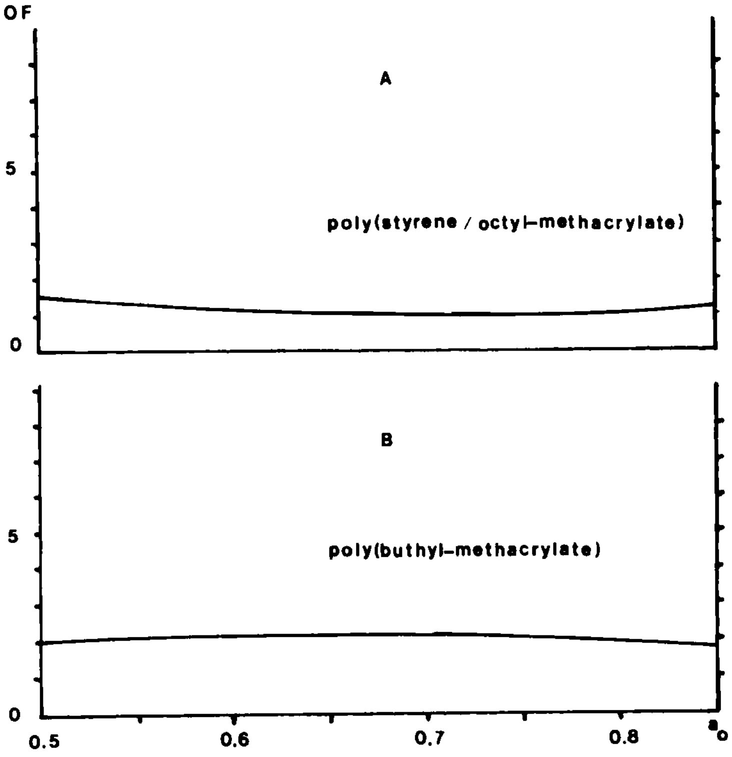

FIGURE 1

The dependence of the objective function on the KMHS exponent in two cases:

A/ the minimum is in the range of interest

B/ the minimum is out of the range of interest

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APPENDIX

The KMHS constants for non-GPC conditions were taken from the "Polymer Handbook" (8) as follows:

P(buthyl methacrylate): $[\eta]^{25^\circ C}_{Acetone} = 1.84 \cdot 10^{-2} \cdot M^{0.62}$

P(ethyl methacrylate): $[\eta]^{35^{\circ}C}_{ethylacetate} = 8.6\cdot10^{-3}\,M^{0.71}$

co(styrene-ethylmetacrylate):

$$[\eta]^{25^{\circ}C}_{butanone} = 1.2\cdot10^{-2}\cdot M^{0.70}$$

co(styrene-octylmethacrylate):

$$[\eta]^{25^{\circ}C}_{butanone} = 7.8\cdot10^{-3}\cdot M^{0.71}$$

co(styrene-buthylmethacrylate):

$$[\eta]^{25^{\circ}C}_{butanone} = 4.9\cdot10^{-3}\cdot M^{0.77}$$