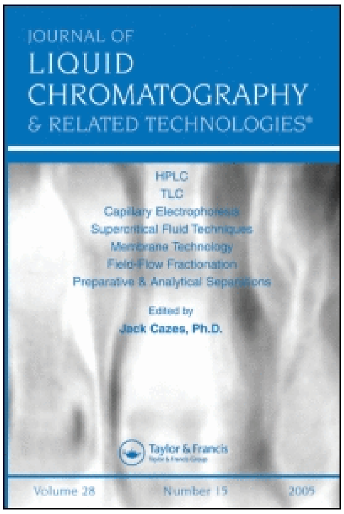

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Study On The Concentration Effect In Gel Permeation Chromatography. I. A New Model Theory For Concentration Dependence Of Hydrodynamic Volumes And Gpc Elution Volumes

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STUDY ON THE CONCENTRATION EFFECT IN GEL PERMEATION CHROMATOGRAPHY. I. A NEW MODEL THEORY FOR CONCENTRATION DEPENDENCE OF HYDRODYNAMIC VOLUMES AND GPC ELUTION VOLUMES

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ABSTRACT

A new model theory for concentration dependence of hydrodynamic volumes and GPC elution volumes was proposed. In this theoretical model both the reduction of hydrodynamic volumes and the viscosity phenomena in the interstitial volume are taken into account at the same time. The effective hydrodynamic volumes, V_{hs}, of a solvated macromolecule decrease with increasing reduced viscosity, (η_{sp}/c), and the GPC elution volumes,Ves, increase with increasing concentration, c, and intrinsic viscosity, $[\eta]$, respectively according to the following relations

$$V_{hs}=[\eta]\,M\,\beta_0\,\exp-\left\{\frac{\eta_{sp}/c}{[\eta]}\right\}$$

and

$$Ves=Veo+\frac{k_H[\eta]}{b}c-\frac{k'[\eta]^2}{b}c^2+\frac{k''[\eta]^3}{b}c^3+---$$

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This theory was used to predict the effects of polymer concentration on the hydrodynamic volumes of solvated macromolecules and peak elution volumes and to deduce the correlation between $(\frac{dV_{es}}{dc})_{c\to 0}$, the initial slope of concentration dependence of elution volumes, and the intrinsic viscosity, $[\eta]$, in GPC analysis. Some GPC observations with porous glass packings are in excellent agreement with these predictions.

INTRODUCTION

In previous papers(1-3) a number of methods for the evaluation of k and α parameters from the combination of GPC and $[\eta]$ or M measurements and for the construction of universal calibration equation with polydispersed samples have been presented.

It must be all performed in very low concentration of injected polymer solution. At higher concentration the effects of the shift of peak elution volumes(4), the axial spreading(5) and the chromatographic skewing(6) must be considered. These three effects are commenly designated as concentration effect which complicates the construction of universal calibration, the determination of polymer molecular weight and its distribution function by GPC analysis. In order to obtain the true universal calibration curve, the polymer molecular weight and its distribution function it is very important to study the concentration effect. It can be divided into three main parts: the shift of the peak elution volumes, the spreading function and the skewing effect.

As Rudin(7) pointed out that the effective concentration of the narrow distribution polymer in GPC separation process may be taken to be equal to the respective concentration of the solution which are injected into the columns. Since a monodispersed specimen would travel through the apparatus as a slug, without dilution, in the absence of spreading and skewing effects. Therefore in this study the first effect will be concerned only, that is, concentration dependence of hydrodynamic volumes and GPC elution volumes for narrow distribution polymers. The other two will be reported in furture.

Experimental results(7-8) show that the concentration effect is more pronounced for higher polymer molecular weight and higher concentration. This effect decreases as the thermodynamic quality of GPC solvents deteriorates and is practically non-existent in theta solvents.

Rudin(7) and Yamakawa(9) explained the concentration effect as a consequence of the reduction of the effective hydrodynamic volumes of solvated polymer coils with increasing concentration. Janca(10) considered the concentration effect as a result of the several participating processes, the predominate one of these processes consists in viscosity phenomena in the interstitial volume. In this paper a new model theory was proposed in which both the reduction of the hydrodynamic volumes and the viscosity phenomena in the interstitial volume were all taken into account.

THEORY

Model Theory of Yamakawa(9) and Rudin(7)

At present, two model theories were deduced by Yamakawa and Rudin independently. Both of them are founded on the same basis of the unswollen volume, v, of a polymer molecule. The hydrodynamic volume, V_{hc}, of a solvated polymer molecule is defined as

$$V_{hc} = V\alpha_s^3 = V\varepsilon \qquad (\alpha_s^3 = \varepsilon) \tag{1}$$

$$V = \frac{4\pi[\eta]_\theta M}{3\Phi'}$$

Where α_s^3 and ε are volume expansion coefficients. The perturbation theory of Yamakawa(9) predicts that α_s decreases with increasing concentration, c, according to

$$\alpha_s = \alpha_0 \exp\{-0.345 z\phi_2(\xi_0)[\eta]_\theta C\} \tag{2}$$

In the theory of Rudin ε and C are linearly related between the two limits, $\varepsilon = \varepsilon_0$, C=0 and $\varepsilon = 1$, C=C_x. This assumption leads to the equation (3) in which an expression for ε is a function of C.

$$\varepsilon = \frac{3\Phi'\Phi_x[\eta]}{[\eta]_\theta[3\Phi'\Phi_x + 4\pi N_0([\eta]-[\eta]_\theta)C]} \tag{3}$$

Substituting equation (2) and (3) into equation (1), then taking logarithm we have the following expressions:

Concentration Dependence of Hydrodynamic Volumes

$$V_{hy} = \frac{4\pi}{9.3\times10^{24}}[\eta]M\exp\{-1.035 z\phi_2(\xi_0)[\eta]_\theta C\} \tag{4}$$

$$V_{hR} = \frac{4\pi[\eta]M}{9.3\times10^{24} + 4\pi N_o([\eta]-[\eta]_\theta)c} \qquad (5)$$

Concentration Dependence of GPC Elution Volumes

$$V_{ey} = V_{eoy} + \frac{1.035}{b} z\Phi_2(\xi_o)[\eta]_\theta c \qquad (6)$$

and

$$V_{eR} = V_{eoR} + \frac{1}{b}\ln\left[1+0.8137([\eta]-[\eta]_\theta)c\right] \qquad (7)$$

In the above model theory there are quite a few of marked deficiencies: It shows a marked deviation from the experiments(7) (cf Figure 6b, in ref. 7b) at higher molecular weight and relatively higher concentration; It can not predict the experimental facts that $K_s = \frac{dV_{es}}{dc}$ is propertional to $[\eta]$(8) or A_2M(8) for linear polymers; There are a lot of parameters to be determined in their expression, And the viscosity phenomena in the interstitial volume is not taken into account. Therefore it is necessary to develop a more simple and more quantitative model theory in which both the reduction of hydrodynamic volumes and the viscosity phenomena in the interstitial volume should be all considered.

A New Model Theory

a) Concentration Dependence of Hydrodynamic volumes

In opposite to the model of Yamakawa and Rudin, Our model theory is started from the basis of the effective hydrodynamic volume, $V_{ho} = [\eta]M$, of a solvated polymer molecule at infinite dilution. The effective hydrodynamic volume, V_{hs}, of a solvated polymer molecule at a given concentration, c, is defined as

$$V_{hs} = V_{ho}\beta_c = [\eta]M\beta_c \qquad (8)$$

where β_c is volume contraction coefficient.

Recently Janca(10) found that the viscosity phenomena are connected with the change in concentration of solution and specific viscosity of an injected polymer solution. Therefore we follow the method of Yamakawa(9) and assume that β_c decreases with increasing concentration, c, and specific viscosity, η_{sp}, according to the relation

$$\beta_c = \beta_o \exp\left\{-\frac{\eta_{sp}/c}{[\eta]}\right\} \qquad (9)$$

where η_{sp} is specific viscosity, (η_{sp}/c) is reduced viscosity and $[\eta]$ is intrinsic viscosity. When the concentration of solution approaches to zero, $(\eta_{sp}/c)_{c\to 0}$ is equal to $[\eta]$, then (η_{sp} /c)/$[\eta]$ =1 and $1=\beta_0 e^{-1}$. Therefore β_0 =e, a constant.

The reduced viscosity increases with increasing concentration, c, according to the following equation(11)

$$(\eta_{sp}/c)=[\eta]+k_H[\eta]^2c+k'[\eta]^3c^2+k''[\eta]^4c^3 \tag{10}$$

At relatively low concentration equation (10) reduces to Huggins equation(12)

$$(\eta_{sp}/c)=[\eta]+k_H[\eta]^2c \tag{10'}$$

where k_H is Huggins coefficient which reflects polymer-solvent interaction. For flexible polymer molecules in good solvents k_H is often near 0.35, Some what higher values occur in poor solvents.

Substituting equation (10) into equation (9) yields

$$V_{hs}=[\eta]M\beta_0 \exp-\{1+k_H[\eta]c+k'[\eta]^2c^2+k''[\eta]^3c^3\} \tag{11}$$

At relatively low concentration equation (11) reduces to

$$V_{hs}=[\eta]M\beta_0 \exp-\{1+k_H[\eta]c\} \tag{11'}$$

Equation (11') is completely identical with equation (4), but it is more simple than equation (4) and contains only a Huggins coefficient to be determined.

b) Concentration Dependence of GPC Elution Volumes

Taking logarithm to equation (11) yields

$$\ln V_{hs}=a-bV_{es}=\ln([\eta]M)-k_H[\eta]c-k'[\eta]^2c^2-k''[\eta]^3c^3 \tag{12}$$

At relatively low concentration equation (12) reduces to

$$\ln V_{hs}=a-bV_{es}=\ln([\eta]M)-k_H[\eta]c \tag{12'}$$

where a and b are the constants of universal calibration equation, V_{es} is peak elution volume at a given concentration. Equation (12) and (12') can be rewritten in the form

$$V_{es} = V_{eos} + \frac{k_H[\eta]}{b}C + \frac{K'[\eta]^2}{b}C^2 + \frac{K''[\eta]^3}{b}C^3 \qquad (13)$$

and

$$V_{es} = V_{eos} + \frac{k_H}{b}[\eta]C \qquad (13')$$

where $V_{eos} = \frac{a - \ln([\eta]M)}{b}$. Equation (13') is completely identical with equation (6). But it is more simple than equation (6) and only contains a Huggins coefficient. It can predict that $k_s = (\frac{dV_{es}}{dc}) = k_H[\eta]/b$ where k_s is propertional to $[\eta]$.

c) Correlation between $(\frac{dV_{es}}{dc}) = k_s$ and $[\eta]$ or A_2M

The correlation between the concentration dependence of elution volume and the intrinsic viscosity, $[\eta]$, of injected polymer may be expressed by following equation

$$k_s = (\frac{dV_{es}}{dc}) = \frac{k_H[\eta]}{b} \qquad (14)$$

For good solvents the second virial coefficient A_2 is propertional to molecular weight according to the relation(13)

$$A_2 = k_{A_2}M^{-\nu} \qquad (15)$$

The low values of ν indicate a weak intramolecular excluded-volume effect, ν is approximately equal to the difference $1-\alpha$(8), α being the exponent of relation $[\eta]=KM^{\alpha}$, k_{A_2} is a constant. Substituting the above relation into equation (15) yields

$$A_2M = \frac{[\eta]}{K}k_{A_2}$$

Combining equation (14) and (15), we finally get the expression of $\frac{dV_{es}}{dC}$ as a function of A_2M

$$\frac{dV_{es}}{dC} = k_s = k_o' A_2 M \qquad (16)$$

where $k_o' = \frac{k_H K}{b K_{A_2}}$, for a given polymer-solvent-columns its value is determined by k_H, b and k constands, Equation (16) shows that $\frac{dV_{es}}{dC}$ increases with increasing A_2M.

At theta condition $A_2=0$, then equation (13') and (12') respectively reduce to

$$V_{e\theta} = \frac{a - \ln([\eta]_\theta M)}{b} \qquad (17)$$

$$V_{hs\theta} = [\eta]_\theta M \qquad (18)$$

It shows that the concentration effect is no-existent in theta conditions (or solvents), As similarity as in the measurement of light scattering or osmotic pressure of solution, the second virial coefficient can be determined from GPC concentration effect.

COMPARISON WITH EXPERIMENTS

Janca (11a) has presented data for concentration effects on the elution behavior of tetrahydrofuran solutions of polystyrene standards (Water Assoc.) with a very narrow molecular weight distribution on porous glass columns. All GPC measurements and molecular weight determinations have been described in more detail (11a), Experimental results are summarized in table 1.

Treatment of Data

The GPC data of Janca have been analyzed according to our model theory.

a) The Universal Calibration Curve

The experimental data of $[\eta]$, $\overline{M}w$, C and k_H in table 1 were used to calculate V_{hs} with equation (11').

TABLE 1

Molecular Parameters of PS Standards (THF) 25°C (10a)

sample	C (%)	Ves (counts)	[η] (dl/g)	$M_w \times 10^{-5}$	Veo (counts)	k_H
PS 1	0.80	18.2	4.665	26.1		0.362
	0.40	18.0				
	0.20	17.9				
	0.10	17.8				
	0.05	17.7				
	0.025	17.6				
	0.00				17.50	
PS 2	0.40	22.8	2.117	8.67		0.362
	0.20	22.3				
	0.10	21.8				
	0.05	21.7				
	0.025	21.6				
	0.00				17.50	
PS 4	0.80	25.8	1.423	4.98		0.362
	0.40	25.2				
	0.20	24.7				
	0.10	24.4				
	0.05	24.2				
	0.025	24.1				
	0.00				24.10	
PS 6	0.40	29.2	0.740	2.00		0.362
	0.20	28.9				
	0.10	28.9				
	0.05	28.9				
	0.025	28.9				
	0.00				28.85	

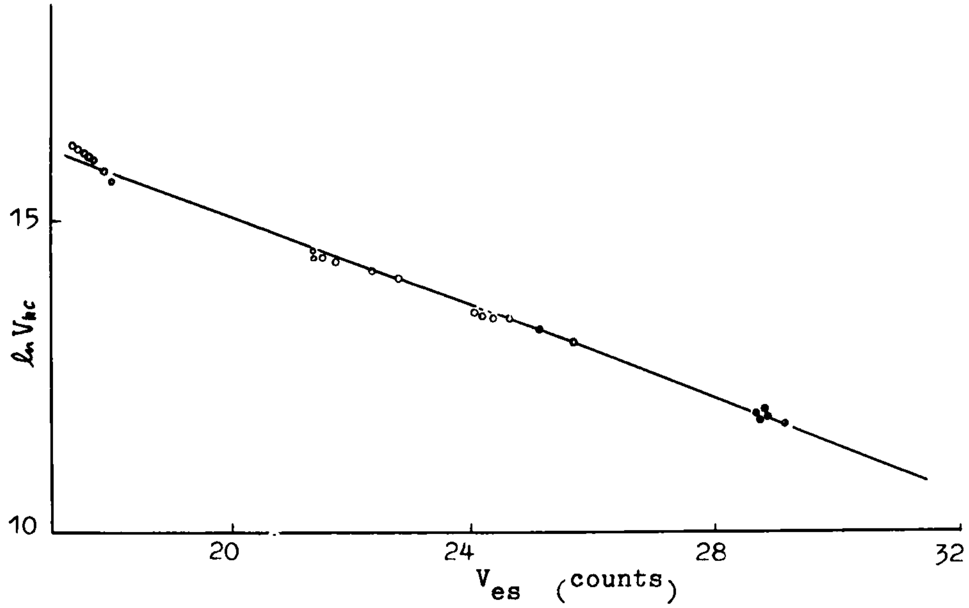

Figure 1. ln(hydrodynamic volume, V_{hc}) vs elution volume, V_{es}, for polystyrene standards in THF.

Then the universal calibration curve were constructed with equation (12') by polting $\ln V_{hs}$ vs V_{es}. This plot is given in Figure 1. Figure 1 shows that our model yields a common curve of ln(hydrodynamic volume) - elution volume for all concentrations and molecular weights of PS standards. and $\ln V_{hs}$ is a linear function of V_{es}.

This result also shows that the proposed model theory obviously fits the data very well. It seems reasonable to conclude that our model will account satisfactorily for the concentration effects in most GPC separations.

b) Concentration Dependence of GPC Elution Volumes

The experimental data of elution volumes, Ves, and concentration, C, for PS standards were used to plot Ves vs c with equation (13'). These plots are given in Figure 2. These results show that Ves is a linear function of C with slope Ks which was obtained by the

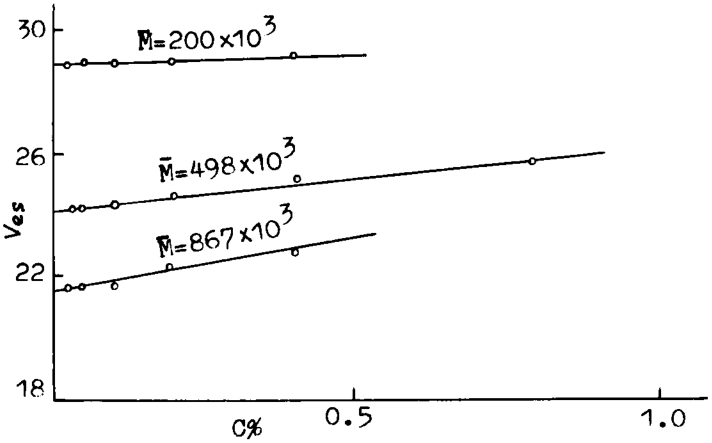

Figure 2. Plots of elution volumes, V_{es}, against concentration, C, for PS standards in THF.

least square method. For the PS standard with higher molecular weight ($Mw=2.61\times10^6$) and higher concentration the experimental data were used to plot $\ln(\frac{V_{es}-V_{eo}}{C})$ vs C with equation (18) and (18').

$$V_{es} - V_{eo} = \frac{k_H[\eta]}{b} C \left(1 + \frac{k'[\eta]}{k_H} C\right) \qquad (18)$$

$$\ln\left(\frac{V_{es}-V_{eo}}{C}\right) = \ln\left(\frac{k_H[\eta]}{b}\right) + \frac{k'[\eta]}{k_H} C + \cdots \qquad (18')$$

This plot is given in Figure 3. It shows that at lower concentration ($C \leq 0.4$) $\ln(\frac{V_{es}-V_{eo}}{C})$ is an approximately linear function of C with an intercept of ln $(\frac{k_H[\eta]}{b})$ which was obtained by least square method. Where is the initial slope, $(\frac{dV_{es}}{dC})_{C\to 0}$, for concentration dependence of elution volumes. It can be directly derived from equation (18).

c) Correlation Between k_s and $[\eta]$ or A_2M

The plot of k_s against intrinsic viscosity for four different PS standards is given in Figure 4. It shows that an approximately straight line passes throu-

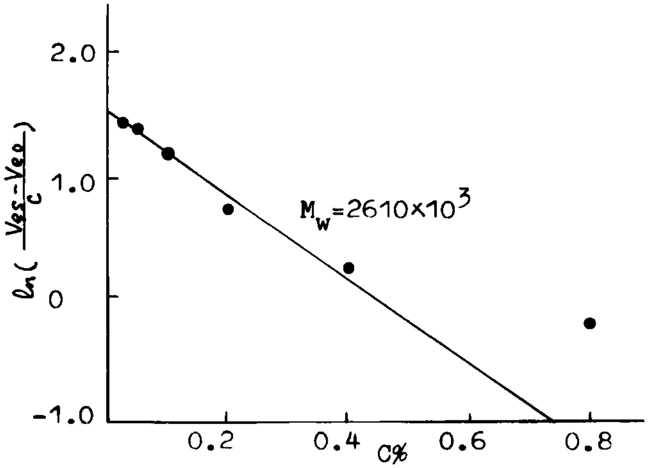

Figure 3. Plot of $\ln(\frac{V_{es}-V_{eo}}{c})$ against concentration, C, for PS standard in THF.

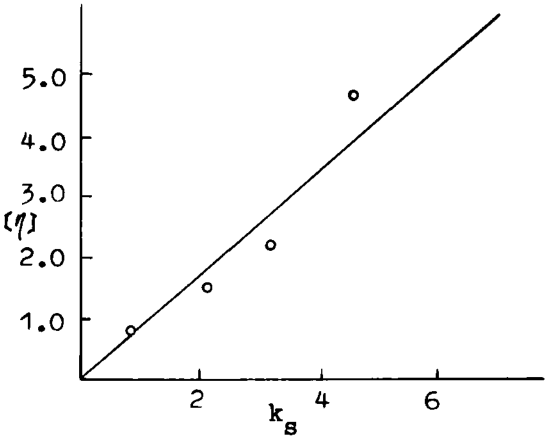

Figure 4. Plot of the slope k_s against intrinsic viscosity

gh the origin. This result is identical with Bleha's results(8). But it should be pointed out that in higher intrinsic viscosity the deviation from the linear dependence manifested in Figure 5a of ref.8 is due to that Bleha's values of k(slope of concentration dependence) for PS in THF is not the initial slope, $(\frac{dVes}{dc})_{c\to 0}=k_s$, of concentration dependence. For PS standard with higher molecular weight at the large range of concentration the concentration dependence of elution volumes is no longer linear function. Therefore equation (18) should be used to plot. The initial slope$(\frac{dVes}{dC})_{c\to 0}=k_s$ can be obtained from the intercept of $\ln(\frac{k_H[\eta]}{b})$ by ploting $\ln(\frac{Ves-Veo}{C})$ vs c. The value of $(\frac{dVes}{dC})_{c\to 0}=k_s$ obtained by that method is more large than the value of k. So that an approximately straight line passed through the origin can be yielded.

NOMENCLATURE

A	Second virial coefficient
a,b	Constants of universal calibration equation
C	Concentration of the injected polymer
Cx	Critical concentration of the injected polmer at which the volume has shrunk to its theta condition value
K	Mark-Houwink-Sakurada constants
k'	Second coefficient of the reduced viscosity equation
k"	Third coefficient of the reduced Viscosity equation
k_H	Huggins coefficient
k_{A_2}	A constant given by $K_{A_2}=\frac{M^{\nu}}{A_2^{-1}}$
k_s	$\frac{dVes}{dC}$
M	Molecular weight of polymer
$\bar{M}n$	Number average molecular weights of polymer
$\bar{M}w$	Weight average molecular weights of polymer
No	Avogadro's constant
V	Unswollen volume of polymer
Veo	Peak elution volume at infinite dilution
Veo_R	Peak elution volume of Rudin's model at infinite dilution
Ve_θ	Peak elution volume in theta condition
Veo_s	peak elution volume of Song's model at infinite dilution

V_{eoy}	peak elution volume of yamakawa's model at infinite dilution
V_{eR}	peak elution volume of Rudin's model at a given concentration
V_{es}	Peak elution volume of Song's model at a given concentration
V_{ey}	peak elution volume of yamakana's model at a given concentration
V_h	Effective hydrodynamic volume
V_{hc}	Effective hydrodynamic volume at a given concentration
V_{ho}	Effective hydrodynamic volume at infinite dilution
V_{hR}	Effective hydrodynamic volume of Rudin's model at a given concentration
V_{hs}	Effective hydrodynamic volume of Song's model at a given concentration
V_{hy}	Effective hydrodynamic volume of yamakawa's model at a given concentration
$V_{hs\theta}$	Effective hydrodynamic volume in theta condition
$\frac{dV_{es}}{dc}$	Rate of changing elution volume with the concentration
Z	The so-called interaction parameter
α	Mark-Houwink-sakurada constant
α_s	Linear expansion coefficient
α_0	The expansion factor at infinite dilution, $\alpha_0 \simeq ([\eta]/[\eta]_\theta)^{1/3}$
β_c	Volume contraction coefficient at a given concentration
β_0	Volume contraction coefficient at infinite dilution
ε	Volume expansion coefficient at a given concentration
ε_0	Volume expansion coefficient at infinite dilution
Φ'	Flory universal constant
Φ_x	Volume fraction of solvated polymer at concentration Cx
$f_2(\xi_0)$	$1-\{(1-\exp(-5.731\xi_0))/5.731\xi_0\}$
ξ_0	A parameter given by $\xi_0 = Z/\alpha_0^3$
η_{sp}	Specific viscosity of polymer solutions
$[\eta]$	Intrinsic viscosity
$[\eta]_\theta$	Intrinsic viscosity in theta conditions
ν	A parameter wich indicates intramolecular excluded-volume effect

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