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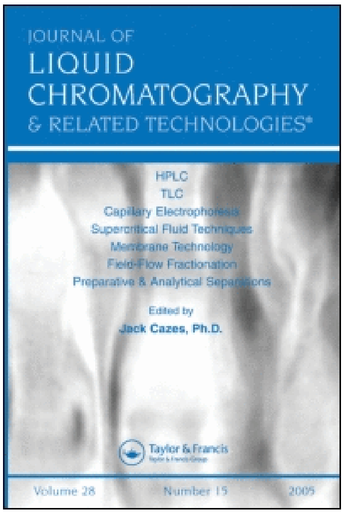

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Study on the Concentration Effects in Gel Permeation Chromatography. Ii. a Model Theory of Concentration Effects for Polydispersed Polymers

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STUDY ON THE CONCENTRATION EFFECTS IN GEL PERMEATION CHROMATOGRAPHY.

II. A MODEL THEORY OF CONCENTRATION EFFECTS FOR POLYDISPERSED POLYMERS

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ABSTRACT

In this paper a model theory of concentration effects for polydispersed polymers was presented. It is based these facts and assumptions that the total concentration effects are considered as the summation of the individual concentration effect, that each effects have also been explained as the consequence of both the reduction of hydrodynamic volumes and the viscosity phenomena of each species , and the entanglements between the macromolecules are negligeable. The relationships between the concentration of injected solutions with the hydrodynamic volumes,the elution volumes and the polydispersed index of hydrodynamic volumes were derived from this model theory. It can predict quantitatively the effects of concentration on the shift of peak elution volumes, the axial spreading and the skewing effects for polydispersed polymers.

INTRODUCTION

The effects of sample concentration on gel permeation chromatography (GPC) elution volumes and hydrodynamic volumes for polymers with narrow molecular weight distribution are well established (1-5). Peak elution volumes tend to increase with increasing concentration in the feed to the GPC columns. The concentration effect is more pronounced for higher the molecular weight of the polymer and higher concentration. The seversity of concentration related-effects in the elution volumes and hydrodynamic volumes also depends on solvent goodness, and in the solvents GPC elution volumes are essentially independent of concentration.

The concentration effects of polymer with narrow molecular weight distribution in the GPC solvents have been characterized by a simple model theory (6) which accounts quantitatively for such effects in terms of polymer molecular weight, viscosity and concentration. This model theory can be extended directly to serve as universal calibration method which takes account of the concentration effects of narrow molecular weight distribution standards. In this application, the effective concentrations of the narrow distribution polymers in GPC separation process are taken to be equal to the respective concentration of the solutions which are injected into the columns, since a monodispersed specimen would travel through the apparatus as a slug in the absence of spreading and skewing. The calibration curve derived in this manner reduced to that of Grubic, Rempp, and Benoit when the concentration effects are not significant.

For a specimen with broad distribution and higher concentration the effects of concentration on the shift of peak elution volumes, the axial spreading and the skewing must be considered at the same time. As given by Blasdon (7) the higher concentration of whole polymers in good solvents can cause distortion of chromatograms and show a marked tailing. Therefore in this article we attempt to develop a new model theory for broad distribution polymers which can predict the shift of peak elution volumes, the axial spreading and skewing of the polymeric chromatograms. This model theory is based on the facts and assumptions that the total concentration effects are considered as the summation of each individual concentration effect, the each individual concentration effect has also been explained as the consequence of both the reduction of the effective hydrodynamic volumes and the viscosity phenomena of each species, and that when the product of the concentration and the intrinsic viscosity, $[\eta]C$, is below one, the entanglement effect between the macromolecules is negligeable.

THEORY

1. Characteristics of Chromatograms by Hydrodynamic Volumes

According to Tung(8) the chromatogram of the polymers is the convolution of two distributions. One is the distribution C(v) of the polymers as a function of elution volumes v, C(v)dv is the amount of polymers with an elution volume between v and v + dv, and $G(v-v_e)$ is the axial dispersion function of instrument. It represents the shape of the chromatogram for a monodispersed sample with elution volume v_e and normalization at unity of the area between the curve and the elution volume axis.

This chromatogram, then, has the following equation:

$$F(v_e) = \int_0^\infty C(v)\, G(v-v_e)\, dv \tag{1}$$

where $F(v_e)$ is the response of a detector sensitive to the concentration and $\int_0^\infty F(v_e)dv_e$ is the total amount of polymer injected.

The first hypothesis we shall make is to asuume that $G(v-v_e)$ is Gaussian distribution and has the following equation;

$$G(v-v_e) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left\{-\frac{(v-v_e)^2}{2\sigma^2}\right\} \tag{2}$$

where σ is the axial dispersion parameter. This assumption is not limiting the generality of our solution, since in practice with an apparatus in good working conditions, the curve obtained for a narrow dispersed polymers has always this shape.

Another approximation is related to the calibration curve. It is better to use the universal calibration and the hydrodynamic volumes V_h to characterize the set of columns. In this case, one will write

$$v-v_e = A \ln (V_h/V_{he}) \qquad (3)$$

If we use these relations $V_{ho} = [\eta]\cdot M$ and $[\eta] = K \cdot M^{\alpha}$, it is possible to change the variable v to the quantities V_h, the concentration of polymers with elution volumes $C(v)dv$ is transformed to the $C(V_h)dV_h$, thus we have

$$F(V_h) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} C(V_h)\exp\left\{(A^2/2\sigma^2)\ln(V_h/V_{he})\right\}dV_h \qquad (4)$$

The quantity under the integral is the contribution of polymer with the hydrodynamic volumes between V_h and $V_h + dV_h$. The $C(V_h)$ represents the true or theoretical chromatogram of the sample. The $F(V_h)$ is the observed or experimental chromatogram which has broaden by the chromatographic column disporsion process. For narrow dispersed polymers the function of $F(V_h)$ usually has the Wesslau type of distribution.

a). Concentration Dependence of Hydrodynamic Volumes

According to our model theory the effective hydrodynamic volumes, V_{hc}, of a solvented polymer molecule with monodisperse at a given concentration, C, is defined as follows:

$$V_{hc} = V_{ho}\beta = \beta_o \exp -\left\{\frac{\eta_{sp}/C}{[\eta]}\right\} \cdot V_{ho} \qquad (5)$$

where β is the volume contraction coefficient. It decreases with increasing concentration, C, the specific viscosity, η_{sp}, and the intrinsic viscosity, $[\eta]$.

For polydispersed polymer there are j kinds of molecules with different effective hydrodynamic volumes, V_{hcj}. At a given concentration the weight average effective hydredynamic volumes which has been corrected the axial dispersion may be calculated by the following equation:

$$\langle V_{hc} \rangle_w = \sum_{j=1}^{\infty} W_j V_{hcj} \qquad (6)$$

where V_{hcj} is the effective hydrodynamic volume of the solvented molecules for the jth kind; W_j is the weight fraction of molecules for jth kind.

Substituting the equation of (5) into the equation of (6) yields

$$\langle V_{hc} \rangle_w = \sum_{j=1}^{\infty} \beta_o \left[\exp\left\{-\frac{\eta_{spj}/C_j}{[\eta]_j}\right\}\right]\left[V_{hoj}\right] \qquad (6')$$

where β_o = e, a constant. For each monodispersed polymer the $\frac{\eta_{spj}/C_j}{[\eta]_j}$ may be expressed by the relation(9)

$$\frac{\eta_{spj}/C_j}{[\eta]_j} = 1 + K_H [\eta]_j C_j + K' [\eta]_j^2 C_j^2 \qquad (7)$$

Therefore the equation of (6') may be written as follows:

$$\langle V_{hc} \rangle_w = \sum_{j=1}^{\infty} V_{hoj} W_j \exp - \left\{ K_H [\eta]_j C_j + K' [\eta]_j^2 C_j^2 \right\} \quad (8)$$

In the equation of (8) the summation is with respect to the j of W_j, C_j, and $[\eta]_j$. But the average values to be calculated is the weight average of hydrodynamic volumes, therefore it is necessary to change the $C_j [\eta]_j$ to the hydrodynamic volumes, V_{hcj}, by the relation

$$C_j [\eta]_j = [\eta]_j C_j M_j / M_j = V_{hcj} C_{jM}$$

where $C_{jM} = C_j / M_j$, it represents the mole concentration of molecules for jth kind. Substituting this relation into the equation of (8) yields

$$\langle V_{hc} \rangle_w = \sum_{j=1}^{\infty} V_{hoj} W_j \exp - \left\{ K_H V_{hoj} C_{jM} + K' (V_{hoj} C_{jM})^2 \right\} \quad (9)$$

when the mole concentration is expressed by the weight mole fraction, the equation of (9) may be rewritten as follows:

$$\langle V_{hc} \rangle_w = \sum_{j=1}^{\infty} V_{hoj} W_j \exp - \left\{ K_H V_{hoj} W_j C_M + K' (V_{hoj} W_j)^2 (C_M)^2 \right\} \quad (10)$$

Taking the average we have

$$\langle V_{hc} \rangle_w = \langle V_{ho} \rangle_w \exp - \left\{ K_H \langle V_{ho} \rangle_w C_M + K' \langle V_{ho} \rangle_w^2 C_M^2 \right\} \quad (10')$$

where K_H is the Huggins coefficient which reflects the polymer-solvents interaction; K' is a constant; C_M is the mole concentration for the whole polymer molecules; $\langle V_{ho} \rangle_w$ is the weight average hydrodynamic volumes at infinitive dilution, it is independent on the concentration, but it is only determined by the molecular weight, it's distribution of the sample and the polymer-solvents systems. At relatively low concentration the equation of (10') reduces to

$$\langle V_{hc}\rangle_w = \langle V_{ho}\rangle_w \exp -\left\{K_H \langle V_{ho}\rangle_w C_M\right\} \tag{11}$$

It is usually assumed$^{(11)}$ that the distribution of the studied polymers obeys the logarithmic normal function. Then the $\langle V_{ho}\rangle_w$ may be expressed by the relation$^{(12)}$

$$\langle V_{ho}\rangle_w = [\bar{\eta}]\bar{M}_w Q_{1w} \tag{12}$$

where Q_{1w} represents a corrected factor for molecular weight distribution obtained by the method of weight average of hydrodynamic volumes, it is the function of polydispersity index and polymer-solvents systems. Substituting this relation into equations of (10') and (11) yields

$$\langle V_{hc}\rangle_w = [\bar{\eta}]\bar{M}_w Q_{1w} \exp -\left\{K_H [\bar{\eta}] Q_{1w} C + K'[\bar{\eta}]^2 Q_{1w}^2 C^2\right\} \tag{13}$$

and

$$\langle V_{hc}\rangle_w = [\bar{\eta}]\bar{M}_w Q_{1w} \exp -\left\{K_H [\bar{\eta}] Q_{1w}\, C\right\} \tag{14}$$

where C is the weight concentration for the whole polymers.

b). Concentration Dependence of GPC Elution Volumes

It is known that the average effective hydrodynamic volumes of polydispersed polymers is not unique function of the elution volumes of peak. For establishing this relation between them we have proposed a corrected method(13). In which a corrected factor Q_{2w} was derived. it is shown that Q_{2w} is the function of the polydispersity index of molecular weight distribution, the intrinsic viscosity, the concentration and the polymer-solvents systems. It's analytical form is given in elsewhere(13). Introducing the above corrected factor into the equations of (13) and (14), the effective hydrodynamic volumes of peak, $\hat{V}_{hcp}$, may be written in this form

$$\hat{V}_{hcp} = [\bar{\eta}]\bar{M}_w (Q_{1w}/Q_{2w}) \exp -\left\{K_H[\bar{\eta}]Q_{1w}C + K'[\bar{\eta}]^2 Q_{1w}^2 C^2\right\} \quad (15)$$

and

$$\hat{V}_{hcp} = [\bar{\eta}]\bar{M}_w (Q_{1w}/Q_{2w}) \exp -\left\{K_H[\bar{\eta}]Q_{1w}C\right\} \quad (16)$$

where $\hat{V}_{hcp}$ is the effective hydrodynamic volumes of peak at a given concentration. Taking the logarithm of equations of (15) and (16) yields

$$\ln\hat{V}_{hcp} = a - bv_{es} = \ln[\bar{\eta}]\bar{M}_w + \ln(Q_{1w}/Q_{2w}) - K_H[\bar{\eta}]Q_{1w}C - K'[\bar{\eta}]^2 Q_{1w}^2 C^2 \quad (17)$$

and

$$\ln\hat{V}_{hcp} = a - bv_{es} = \ln[\bar{\eta}]\bar{M}_w + \ln(Q_{1w}/Q_{2w}) - K_H[\bar{\eta}]Q_{1w}C \quad (18)$$

where a and b are the constants of universal calibration equation, v_{es} is the elution volumes of peak at a given concentration. The equations of (17) and (18) may be rewritten in this form

$$v_{es}= v_{eos}+(K_H/b)\,[\bar{\eta}]\,Q_{1n}C+ K'Q_{1n}^2\,C^2\,[\bar{\eta}]^2/b \qquad (19)$$

and

$$v_{es}= v_{eos}+ K_H[\bar{\eta}]Q_{1n}\,C/b \qquad (20)$$

where $v_{eos}=[a-\ln([\eta]\,\bar{M}_w)-\ln(Q_{1w}/Q)]/b$, Q_{1n} is a corrected factor for molecular weight distribution obtained by the method of number average hydrodynamic volumes, it is also only the function of polydispersity index and polymer-solvents systems, but it differs from the Q_{1w}. Q is a corrected factor for polydispersity index of hydrodynamic volumes at the infinitive dilution.

When the polydispersity index of molecular weight distribution is equal to one ($Q_{1w} = 1$, $Q_{1n} = 1$, $Q = 1$ and $Q_{2w} = 1$). then the equations of (16) and (20) respectively reduce to $V_{hc}= [\bar{\eta}]M\ \exp-\{K_H[\bar{\eta}]\,C\}$ and $v_{es}= [a-\ln[\bar{\eta}]\,M]/b+(K_H/b)[\bar{\eta}]\,C$. They are identical with the other results(6).

c). Correlation between $(dv_{es}/dC) = K_s$ and $[\eta]$ or A_2M

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

$$K_s = dv_{es}/dC = (K_H[\eta]Q_{1n})/b \qquad (21)$$

For polydispersed polymer in good solvents the second virial coefficient A_2 is proportional to the molecular weight according to the relation$^{(14)}$

$$A_2 = K_{A2}\,\bar{M}_w^{-\nu}\left(\frac{\bar{M}_w}{\bar{M}_n}\right)^{-(\nu+3/2)} = K_{A2}\,\bar{M}_w^{-\nu}Q_{A2} \qquad (22)$$

The low values of ν indicates a week intermolecular excluded-volume effect, ν is approximately equal to the difference $(1-\alpha)^{(3)}$, α being the exponent of relation $[\eta] = K\,M^{\alpha}$. K_{A2} is a constant. Q_{A2} is a corrected factor for polydispersity. Substituting the above relation into the equation of (22) yields

$$\bar{M}_w A_2 = [([\eta] \quad)/K]K_{A2}Q_{A2}$$

Combining the equations of (21) and (22), we finally get the expression of dv_{es}/dC as a function of A_2M

$$(dv_{es}/dC) = K_s = K''A_2\bar{M}_w\,\frac{Q_{1n}}{Q_{A2}} \qquad (23)$$

where $K'' = K_H\,.K/bK_{A2}$. For a given polymer-solvent-columns it's value is determined by K_H, b, K, and K_{A2}. They are all constants. Equation of (23) shows that (dv_{es}/dC) increases with increasing $A_2\bar{M}_w\,\frac{Q_{1n}}{Q_{A2}}$.

At thea condition $A_2 = 0$, then the equations of (16) and (20) respectively reduce to

$$\hat{V}_{hc\theta} = [\bar{\eta}]\bar{M}_w(Q_{1w}/Q_{2w}) \qquad (24)$$

and

$$v_{es\theta} = [a - \ln([\bar{\eta}]_\theta\bar{M}_wQ_{1w}) + \ln Q]/b \qquad (25)$$

The equations of (24) and (25) show that the concentration effect is non-existent. When the polydispersity index of molecular weight distribution is equal to one ($Q_{1w}=1$, $Q_{2w}=1$ and $Q=1$), then the equations of (24) and (25) respectively reduce to the $V_{hc\theta}=[\eta]_\theta M$ and $v_{eso}=[a-\ln([\eta]_\theta M)]/b$. They are identical with the other results$^{(6)}$.

2. Concentration Dependence of Polydispersity Index for Hydrodynamic Volumes

a. The Average Hydrodynamic Volumes of True Polymer

According to the definition the weight and number average hydrodynamic volumes of the original polymer at a given concentration and infinitive dilution which has been corrected the axial dispersion are given by the following equation:

For infinitive dilution

$$\langle V_{how}\rangle_c = \int_0^\infty C(V_{ho})V_{ho}\,dV_{ho} \tag{26}$$

and

$$\langle V_{hon}\rangle_c = 1/\left[\int_0^\infty \left\{C(V_{ho})/V_{ho}\right\} dV_{ho}\right] \tag{27}$$

For a given concentration

$$\langle V_{hcw}\rangle_c = \int_0^\infty C(V_{hc})V_{hc}\,dV_{hc} \tag{28}$$

and

$$\langle V_{hcn}\rangle_c = 1/\left[\int_0^\infty \left\{C(V_{hc})/V_{hc}\right\} dV_{hc}\right] \tag{29}$$

Where $V_{hc} = V_{ho}\ \exp -\{K_H V_{ho} \cdot C_M\}$.

If the polymers has a Wesslau type distribution function and it obeys the Mark-Houwink relation $[\eta] = K\bar{M}^{\alpha}$, then the distribution function $C(V_h)$ has the following form:

$$C(V_h) = C'(\ln V_h) = \frac{1}{\sqrt{2\pi}}\frac{1}{r^*}\exp-\left\{\frac{1}{2r^*}\ln^2\left(\frac{V_h}{V_{ho}}\right)\right\} \qquad (30)$$

where $r^* = \sigma/A$. Then the equations of (26), (27), (28) and (29) may be rewritten in the following form:

For infinitive dilution

$$\langle V_{how}\rangle_c = V_{hoe}\exp\{r^*/2\} \qquad (26')$$

and

$$\langle V_{hon}\rangle_c = V_{hoe}\exp-\{r^*/2\} \qquad (27')$$

For a relatively lower concentration

$$\langle V_{hcw}\rangle_c = V_{hoe}\exp\{r^*/2\}\ \exp-\{K_H[\bar{\eta}]CQ_{1w}\} \qquad (28')$$

and

$$\langle V_{hcn}\rangle_c = V_{hoe}\exp-\{r^*/2\}\ \exp-\{K_H[\bar{\eta}]CQ_{1n}\} \qquad (29')$$

where V_{hoe} is the hydrodynamic volumes of peak.

b). The Polydispersity Index of Hydrodynamic Volumes for True Polymer

The polydispersity index of hydrodynamic volumes which has been corrected axial dispersion at a given concentration and infinitive dilution can be obtained from the definition and they are given as follows:

For infinitive dilution

$$D_o = \langle V_{how}\rangle_c / \langle V_{hon}\rangle_c = \exp(r^*) \qquad (31)$$

For a given concentration

$$D_c = \langle V_{hcw}\rangle_c / \langle V_{hcn}\rangle_c = D_o \exp\{K_H[\bar{\eta}]C(Q_{1n} - Q_{1w})\} \qquad (32)$$

In the equation of (32) Q_{1n} is always smaller than the Q_{1w}. Thus the $\exp\{K_H[\bar{\eta}]C(Q_{1n} - Q_{1w})\}$ is always less than one. This result shows that the polydispersity index of hydrodynamic volumes at a given concentration is narrowed. The degree of narrowing is not only determined by the concentration, but also by the polydispersity index of molecular weight distribution. It decreases with increasing the concentration, C, the polydispersity index, (M_w/M_n), the polymer-solvent system, (α), and the intrinsic viscosity, $[\eta]$.

In contrast to the hydrodynamic volumes, the width of the chromatogram for the elution volumes is broaden by the concentration effects through the relation $\Delta V_{hD} = a\exp(-b\Delta v_{eD})$. Where ΔV_{hD} represents the decrement of the width of chromatogram for hydrodynamic volumes due to the concentration effects; Δv_{eD} represents the increment of the width of chromatogram for elution volumes due to the concentration effects. The above relation demonstrates that the increment of width of chromatogram for elution volumes increases with decreasing the width of the chromatogram for hydrodynamic volumes. It is easy to show that when the sample has a monodispersity index $(Q_{1w} = Q_{1n})$

then the D_c is equal to the D_o, so that the axial spreading due to the concentration effects has no longer existent.

3. Dependence of Concentration on the Skewing Effect

a). The Average Hydrodynamic Volumes of Uncorrected Axial Dispersion

The response of hydrodynamic volumes for a general detector at a given concentration is given by the equation of (4). Under the integral sign, we have the product of two functions; one is sharped, its shape being governed by the efficiency of the column set through the parameter r^* and the concentration effects through the $K_H[\bar{\eta}]\, C\, Q_1$ quantity; the other one is used to characterize the polydispersity of the original samples. If the polymer distribution function $C(V_h)$ is considered as a function of $\ln V_h$, then at a given concentration the weight and number average hydrodynamic volumes of uncorrected axial dispersion may be calculated by the Marais's$^{(15)}$ method of integration with the equation of (4). These results are given as follows:

$$\langle V_{hcw}\rangle_{uc} = V_{hoe} \exp-\{K_H[\bar{\eta}]CQ_{1w}\}\exp\{r^*/2\}\cdot$$

$$\left[1 + r^{*2}\frac{C'}{C} + r^{*4}\left(\frac{C''}{2C} + \frac{1}{2}\,\frac{C''}{C} - \frac{1}{2}\,\frac{C'C''}{C^2}\right)\right] \quad (33)$$

and

$$\langle V_{hcn}\rangle_{uc} = V_{hoe}\exp-\{K_H[\bar{\eta}]CQ_{1n}\}\exp\{-r*/2\}$$

$$\left[1 + r*^2\,\frac{C'}{C} + r*^4\left(\frac{-C''}{2C} + \frac{1}{2}\,\frac{C'''}{C} + \frac{C'^2}{C^2} - \frac{C'C''}{2C^2}\right)\right] \tag{34}$$

At a given concentration the polydispersity index of hydrodynamic volumes of uncorrected axial dispersion is given as follows:

$$D_{uc} = \langle V_{hcw}\rangle_{uc} / \langle V_{hcn}\rangle_{uc}$$

$$= \mathrm{Exp}\{K_H[\bar{\eta}]C(Q_{1n} - Q_{1w})\}\exp\{r*\}\left[1 + r*^4\left(\frac{C''}{C} - \frac{C'^2}{C^2}\right)\right] \tag{35}$$

In the equation of (35) the Q_{1n} is always smaller than the Q_{1w}. Then the $\exp\{K_H[\bar{\eta}]C(Q_{1n} - Q_{1w})\}$ is always less than one, so that the polydispersity index of hydrodynamic volumes at a given concentration is always narrowed. Where C, C', C", and C" are the Newton's expansion coefficients; $\langle V_{hcw}\rangle_{uc}$ and $\langle V_{hcn}\rangle_{uc}$ are the weight and number average hydrodynamic volumes of uncorrected axial dispersion at a given concentration.

b). Dependence of Concentration on The Skewing Effects

At a given concentration the ratios of the average hydrodynamic volumes of corrected and uncorrected axial dispersion can be obtained from the equations of (28'), (29'), (33) and (34). They are given as follows:

$$\langle V_{hcw}\rangle_c/\langle V_{hcw}\rangle_{uc} = 1/\left[1 + r*^2\,\frac{C'}{C} + r*^4\left(\frac{C''}{2C} + \frac{C'''}{2C} - \frac{C'C''}{2C^2}\right)\right]$$

$$= \frac{1}{A_w} \qquad (36)$$

and

$$\langle V_{hcn}\rangle_c/\langle V_{hcn}\rangle_{uc} = 1/\left[1 + r*^2\,\frac{C'}{C} + r*^4\left(-\frac{C''}{2C} + \frac{C'''}{2C}\right.\right.$$

$$\left.\left.+ \frac{C'^2}{C^2} - \frac{C'C''}{2C^2}\right)\right] = \frac{1}{A_n} \qquad (37)$$

Owing to the presence of skewing effects the equations of (36) and (37) are no longer on an equality with both side. Therefore the skewing effects can be characterized by Balke's(16) method. We have

$$SK = \langle V_{hcw}\rangle_c/\langle V_{hcw}\rangle_{uc} + \langle V_{hcn}\rangle_c/\langle V_{hcn}\rangle_{uc}$$

$$- (1/A_w + 1/A_n) \qquad (38)$$

It is usual to assume that

$$\langle V_{hcw}\rangle_c/\langle V_{hcw}\rangle_{uc} = B_1/A_w$$

$$\langle V_{hcn}\rangle_c/\langle V_{hcn}\rangle_{uc} = B_1/A_n \qquad (39)$$

Substituting the equation of (39) into the equation of (38) yields

$$B_1 = 1 + (SK/2)\left[1 + r*^2\,\frac{C''}{C} + r*^4\left(\frac{C'^2}{C^2} - \frac{1}{2}\,\frac{C'C''}{C^2}\right)\right] \qquad (40)$$

Then substituting the value of B_1 into the equation of (39), we have

$$\langle V_{hcw}\rangle_c(r*, SK) = \langle V_{hcw}\rangle_{uc}\left[1 + \frac{SK}{2}\left(1 + r*^2\,\frac{C''}{C}\right.\right.$$

$$\left.\left.+ r*^4\,\frac{C'^2}{C^2} - \frac{r*^4}{2}\,\frac{C'C''}{C^2}\right)\right]\frac{1}{A_w} \qquad (41)$$

and

$$\langle V_{hcn}\rangle_c(r^*,SK) = \langle V_{hcn}\rangle_{uc}\left[1 + \frac{SK}{2}\left(1 + r^{*2}\frac{C''}{C} + r^{*4}\frac{C'^2}{C^2} - \frac{r^{*4}}{2}\frac{C'C''}{C^2}\right)\right]\frac{1}{A_n}$$

Where $\langle V_{hcw}\rangle_c(r^*,SK)$ and $\langle V_{hcn}\rangle_c(r^*,SK)$ represent the weight and number average hydrodynamic volumes having been corrected axial spreading and skewing effects at a given concentration.

The verification of this theory by experiments will be reported in the next paper.

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