

Development of Huggins' and Kraemer's Equations for Polymer Solution Evaluations from the Generalized Viscosity Model for Suspensions

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ABSTRACT: This study found that the generalized viscosity model for suspensions recently published by this author could be successfully applied to polymer solutions to generate both Huggins' equation and Kraemer's equation. It was also found that the solute (particle) interaction coefficient, σ , as evaluated from the generalized viscosity model, characterizes the solubility of either a solute in a solution or a particle in a suspension. Suspensions would appear to be characterized as having a solute/particle interaction coefficient of $\sigma \geq 1$. Poor to intermediate solutions would be characterized as having a solute/particle interaction coefficient of $0 \leq \sigma < 1$. Good to excellent solutions would then be characterized as having solute/particle interaction coefficients of $\sigma < 0$. It was also found that a maximum in the reduced viscosity was predicted using the generalized viscosity model as applied to a Huggins-type plot for solutions. The experimental literature data of Hermans et al. confirmed that such a maximum can exist for a Huggins-type plot. Based on the available range of literature values of Kraemer's constant and other theoretical considerations from this study, the solute/particle interaction coefficient was found to have an apparent range from $-\lceil \eta \rceil \leq \sigma \leq \lceil \eta \rceil$, where $\lceil \eta \rceil$ is the Einstein-type intrinsic viscosity. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2319–2332, 1997

Key words: intrinsic viscosity; packing fraction; solutions; suspensions; particle (solute) interaction coefficient; relative viscosity; Kraemer's constant; Huggins' constant; generalized suspension viscosity equation; suspension viscosity

INTRODUCTION

The influence of concentration on the viscosity of polymer solutions continues to be of interest for such applications as coatings, paints, foods, oil recovery, and water treatment.¹ For many of these and other applications the evaluation of low concentration viscosities continues to be useful to evaluate the intrinsic viscosity, $[\eta]$, of both polymer solutions^{2,3} and polymer suspensions.⁴ However, the lack of an adequate formulation procedure to consistently predict viscosities at signifi-

cant concentrations for both solutions and suspensions continues to be an area of concern.^{4,5}

Recently, this author^{6–9} described the derivation of a new generalized equation that addresses the viscosity of suspensions. This new-generalized suspension equation has been shown to successfully predict the effects of particle/solvent interaction, particle size, particle size distribution, and packing fraction on suspension viscosity. Because this equation was found to work so successfully on suspensions, it was strongly suspected that the concentration/viscosity relationship for solutions could also be effectively predicted using this equation. The objective of this article, then, is to show how this new suspension equation can predict the

standard solution equations used to calculate intrinsic viscosity such as Huggins' equation and Kraemer's equation. Another objective was to elucidate some particularly interesting new characteristics of this generalized suspension equation that applies specifically to solutions.

Development of the Generalized Suspension Viscosity Equation for Solutions

In an earlier article⁶ this author introduced the following generalized equation to describe the viscosity–concentration relationship of suspensions.

$$\ln(\eta/\eta_o) = \left(\frac{[\eta]\varphi_n}{\sigma - 1} \right) \left\{ \left(\frac{\varphi_n - \varphi}{\varphi_n} \right)^{1-\sigma} - 1 \right\} \quad \text{for } \sigma \neq 1 \quad (1)$$

For the case where $\sigma = 1$, the resulting equation can be written as

$$\ln(\eta/\eta_o) = -[\eta]\varphi_n \ln\left(\frac{\varphi_n - \varphi}{\varphi_n} \right) \quad (2)$$

where η is the suspension viscosity, η_o is the viscosity of suspending medium, $[\eta]$ is the intrinsic viscosity, σ is the particle interaction coefficient, φ is the suspension particle volume concentration, and φ_n is the particle packing fraction.

This generalized equation has been found to include most of the primary suspension equations previously appearing in the literature, as reviewed by Rutgers.^{10,11} For example, by varying the particle interaction coefficient, σ , the Arrhenius equation^{12,13} results when $\sigma = 0$, the Kreiger-Dougherty equation¹⁴ results when $\sigma = 1$, and when $\sigma = 2$ the Mooney equation¹⁵ results. The equations resulting from these values of the particle interaction coefficient are summarized in Table I, where the "crowding factor," k , can also be defined as $k = 1/\varphi_n$. Fractional values for the particle interaction coefficient were also found⁶ to be useful and perfectly acceptable when optimizing the empirical fit of the literature data of Vand¹⁶ and Eiler.¹⁷

Further insight into the characteristics of the interaction parameter, σ , and the packing fraction, φ_n , can be obtained from the series expansion of the generalized suspension equation. A MacLaurin series expansion for eq. (1) gives

$$\begin{aligned} \eta = \eta_o & \left(1 + [\eta]\varphi + \left(\frac{[\eta]}{2} \right) \left\{ [\eta] + \left(\frac{\sigma}{\varphi_n} \right) \right\} \varphi^2 \right. \\ & + \left(\frac{[\eta]}{6} \right) \left\{ [\eta]^2 + 3 \left(\frac{\sigma}{\varphi_n} \right) [\eta] \right. \\ & \left. \left. + \left(\frac{\sigma}{\varphi_n} \right) \left(\frac{\sigma + 1}{\varphi_n} \right) \right\} \varphi^3 + \dots \right) \quad (3) \end{aligned}$$

For a suspension, when $[\eta] = 2.5$, it is apparent that the first two terms are the Einstein^{18,19} limiting terms for all possible values for the particle interaction coefficient, σ , and the packing fraction, φ_n . It has also been found that σ and φ_n always occur as a paired ratio for second-order and higher expansion terms. Because these two parameters are paired in second-order and higher terms, if $\sigma = 0.0$, then the packing fraction does not enter into the viscosity calculation. This observation is important because it suggests that when the solute (particle) interaction coefficient is zero that solute (particle) packing is not important and that solute (particles) molecules have a significantly reduced interference with each other. Further arguments that address the claim that particles have a significantly reduced interaction with each other when $\sigma = 0.0$ have been addressed previously.⁶

Another important observation is that if the solute (particle) interaction coefficient is $\sigma \geq 1$, then eq. (1) becomes undefined if $\varphi > \varphi_n$. For this case, it is also apparent that as the solute (particle) concentration, φ , approaches the packing fraction, φ_n , then the viscosity of the suspension or solution approaches infinity. Based on this argument, it would be expected that most well-defined suspensions would have a particle interaction coefficient with $\sigma \geq 1$.

If the particle interaction coefficient is $\sigma < 1$, then as the solute (particle) concentration, φ , approaches the packing fraction, φ_n , the viscosity of the suspension or solution described by eq. (1) approaches the following limit:

$$\ln(\eta/\eta_o) \rightarrow \left(\frac{[\eta]\varphi_n}{1 - \sigma} \right) \quad \text{for } \sigma < 1 \text{ and } \varphi \rightarrow \varphi_n \quad (4)$$

This finite limit for systems with $\sigma < 1$ would suggest that for this case the solute (particle) develops an improved miscibility in the solvent consistent with approaching more solution-like be-

Table I Generalized Suspension Viscosity Equation for Selected Values of the Particle Interaction Coefficient, σ

Particle Interaction Coefficient σ	Simplified Form of Generalized Equation	Previous Reference for Equation Derivation
-2	$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{3}\right)\{3k\varphi^2 - k^2\varphi^3 - 3\varphi\}$	
-1	$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{2}\right)\{k\varphi^2 - 2\varphi\}$	
0	$\ln(\eta/\eta_0) = [\eta]\varphi$	Arrhenius (1887, 1917)
.5	$\ln(\eta/\eta_0) = \left(\frac{2[\eta]}{k}\right)(1 - (1 - k\varphi)^5)$	
1	$\ln(\eta/\eta_0) = \left(\frac{-[\eta]}{k}\right)\ln(1 - k\varphi)$	Krieger-Dougherty (1959)
2	$\ln(\eta/\eta_0) = [\eta] \left\{ \frac{\varphi}{1 - k\varphi} \right\}$	Mooney (1951)
3	$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{2}\right)\left\{\frac{2\varphi - k\varphi^2}{(1 - k\varphi)^2}\right\}$	
4	$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{3}\right)\left\{\frac{3\varphi - 3k\varphi^2 + k^2\varphi^3}{(1 - k\varphi)^3}\right\}$	

havior. As a true solution system is approached, then the solute (or particle) would be expected to approach the solubilizing characteristics of the solvent. As the different distinguishing solubilizing characteristics between the solute (or particle) and the solvent continue to disappear, then the packing fraction for the solute (or particle) in the solvent would be expected to approach $\varphi_n = 1.0$.

As the solute (particle) interaction coefficient is reduced below $\sigma = 1$, then, the solute (particles) molecules and the solvent molecules would be expected to approach a significantly reduced interference with each other and to approach more desirable miscibility and potentially even solubility.

Huggins' and Kraemer's Equations for Solutions Developed from the Generalized Suspension Equation

Equation (1) can be converted from a suspension equation in terms of volume fraction, φ , to a solution viscosity equation using a solute concentration, c , in grams per cc of solution using an approach described by Huggins,²⁰ Elias,²¹ and Simha et al.²² with the following relationships:

$$\varphi = \frac{V_p}{V_p + V_s} = \frac{c}{\rho} \tag{5}$$

$$\rho = \frac{M}{NV_H} \tag{6}$$

where N is Avagadro's number (molecules/g mol), M is the solute molecular weight (g/g mol), ρ is the solute molecular density (g/cc of solute volume), c is the concentration (g/cc of solution volume), V_p is the volume of particle or solute (cc), V_H is the solute hydrodynamic volume per molecule (cc/molecule), V_s is the volume of solvent (cc).

Substituting into eq. (1) then gives

$$\begin{aligned} \ln(\eta/\eta_0) = & \left(\frac{[\eta]}{\sigma - 1}\right) \left(\frac{\rho}{\rho\varphi_n}\right)^{\rho\varphi_n} \left\{ \left(\frac{\rho\varphi_n - c}{\rho\varphi_n}\right)^{1-\sigma} - 1 \right\} \\ & \text{for } \sigma \neq 1 \tag{7} \end{aligned}$$

It will now be shown that eq. (7) can be expanded to develop both Kraemer's equation and Huggins' equation to describe solution behavior. It is interesting that eq. (7) has the same number of variables as eq. (1), with $\rho\varphi_n$ replacing φ_n and

$([\eta]/\rho)$ replacing $[\eta]$. Note, however, that the solute interaction coefficient, σ , has the same form in both equations.

Equation (7) can be expanded by developing a MacLaurin series for the right-hand side of this equation to give

$$\begin{aligned} \left(\frac{\ln(\eta/\eta_o)}{c}\right) = & \\ & \left(\frac{[\eta]}{\rho}\right) + \left(\frac{[\eta]}{\rho}\right)^2 \left\{ \left(\frac{1}{2}\right) \left(\frac{\rho}{[\eta]}\right) \left(\frac{\sigma}{\rho\varphi_n}\right) \right\} c \\ & + \left(\frac{1}{6}\right) \left(\frac{[\eta]}{\rho}\right) \left(\frac{\sigma}{\rho\varphi_n}\right) \left(\frac{\sigma+1}{\rho\varphi_n}\right) c^2 + \dots \quad (8) \end{aligned}$$

Equation (8) can then be reduced to the Kraemer²³ equation at low concentrations as

$$\begin{aligned} \left(\frac{\ln(\eta/\eta_o)}{c}\right) = & \\ & \left(\frac{[\eta]}{\rho}\right) + \left(\frac{[\eta]}{\rho}\right)^2 \left\{ \left(\frac{1}{2}\right) \left(\frac{\rho}{[\eta]}\right) \left(\frac{\sigma}{\rho\varphi_n}\right) \right\} c \\ & = \left(\frac{[\eta]}{\rho}\right) + \left(\frac{[\eta]}{\rho}\right)^2 \{K\} c \quad (9) \end{aligned}$$

The limit of eqs. (8) and (9) as $c \rightarrow 0$ give

$$\text{Limit}_{c \rightarrow 0} \left(\frac{\ln(\eta/\eta_o)}{c}\right) = \left(\frac{[\eta]}{\rho}\right) \quad (10)$$

Because eq. (3) was formed from an expansion of eq. (1) and because eq. (7) is simply another form of eq. (1), then eq. (7) can also be expanded using eq. (3) from a suspension equation in terms of volume fraction, φ , to a solution viscosity equation using a solute concentration, c , and the solute molecular density, ρ , along with the following relationship

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \quad (11)$$

where η_{sp} is the specific viscosity, to give

$$\begin{aligned} \left(\frac{\eta_{sp}}{c}\right) = & \\ & \left(\frac{[\eta]}{\rho}\right) + \left(\frac{[\eta]}{\rho}\right)^2 \left\{ \left(\frac{1}{2}\right) \right. \\ & + \left(\frac{1}{2}\right) \left(\frac{\rho}{[\eta]}\right) \left(\frac{\sigma}{\rho\varphi_n}\right) \left. \right\} c \\ & + \left(\frac{1}{6}\right) \left(\frac{[\eta]}{\rho}\right) \left\{ \left(\frac{[\eta]}{\rho}\right)^2 + 3 \left(\frac{\sigma}{\rho\varphi_n}\right) \left(\frac{[\eta]}{\rho}\right) \right. \\ & \left. + \left(\frac{\sigma}{\rho\varphi_n}\right) \left(\frac{\sigma+1}{\rho\varphi_n}\right) \right\} c^2 + \dots \quad (12) \end{aligned}$$

Equation (12) can then be reduced to the Huggins' equation²⁴ at low concentrations as

$$\begin{aligned} \left(\frac{\eta_{sp}}{c}\right) = \left(\frac{[\eta]}{\rho}\right) + \left(\frac{[\eta]}{\rho}\right)^2 \left\{ \left(\frac{1}{2}\right) + K \right\} c \\ = \left(\frac{[\eta]}{\rho}\right) + \left(\frac{[\eta]}{\rho}\right)^2 K' c \quad (13) \end{aligned}$$

The limits of eqs. (12) and (13) as $c \rightarrow 0$ give

$$\text{Limit}_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c}\right) = \left(\frac{[\eta]}{\rho}\right) \quad (14)$$

It is apparent that the constants from the Huggins' and Kraemer equations are related as

$$K' = \left(\frac{1}{2}\right) + K \quad (15)$$

Several authors^{21,25} have previously shown that this relationship must exist between Huggins' and Kraemer's constants. Some authors²⁶ have arbitrarily included a negative sign in front of Kraemer's constant; however, because Kraemer's²³ original article did not include such a negative sign, we will conveniently chose this original option. At this point it is useful to address the relative magnitude of these constants. Elias²¹ indicates that good solvents, by definition, have a Huggins' constant of less than 0.5 but typically range from 0.25–0.35. Flory²⁵ indicates that Huggins' constants for good solvents usually range from 0.35–0.4. Elias²¹ also indicates that intermediate, poorer solvents and theta solvents would

be expected to have Huggins' constants greater than 0.5. Specifically, Elias²¹ claims that theta solvents would be expected to have a Huggins' constant in the range of 0.5 to 0.7. Simha et al.²² also summarized data from the literature and indicate that the Huggins' constant can vary from approximately 0.33 to 0.77. The experimental Huggins' constants from the literature, then, appear to fall well within the range of $0 \leq K' \leq 1$. This range for the Huggins' constant would correspond to a range for Kraemer's constant of $-0.5 \leq K \leq 0.5$.

If a good solvent requires a Huggins' constant of less than 0.5, then a negative Kraemer's constant would appear to be required. The Kraemer constant derived from eq. (9) can be written as

$$K = \left(\frac{1}{2}\right)\left(\frac{\rho}{[\eta]}\right)\left(\frac{\sigma}{\rho\varphi_n}\right) = \left(\frac{1}{2}\right)\left(\frac{\sigma}{[\eta]\varphi_n}\right) \quad (16)$$

Equation (7) can, in most cases, be used to fit solution data over a large concentration range to give the solution intrinsic viscosity, $([\eta]/\rho)$, the solute/particle interaction coefficient, σ , and the packing fraction (assumed to be, $\varphi_n = 1$). In addition, if the same solution viscosity data at low concentration can be used to obtain Kraemer's constant, K , then eq. (16) can be used to obtain the Einstein-type intrinsic viscosity, $[\eta]$, as

$$[\eta] = \left(\frac{1}{2}\right)\left(\frac{\sigma}{K}\right) \quad (17)$$

which, in turn, can be used to estimate the solute molecular density, ρ , as

$$\rho = \frac{[\eta]}{\left(\frac{[\eta]}{\rho}\right)} \quad (18)$$

In addition, eq. (7) can be solved directly for the parameter, $\rho\varphi_n$, to allow the molecular density, ρ , to also be calculated as

$$\rho = \rho\varphi_n \quad (\text{If a solution is assumed @ } \varphi_n = 1) \quad (19)$$

The significance of the isolation of the molecular density, ρ , described by either eqs. (18) or (19) is that molecular density, ρ , would appear to be

an additional useful parameter that could be used to generate an independent measurement of solution molecular weight similar to that of the solution intrinsic viscosity, $([\eta]/\rho)$, which is currently used to make molecular weight measurements.

If Kraemer's constant must be negative to yield a Huggins' constant of less than 0.5 for good to excellent solute/solvent systems, then at least one of the constants in eq. (16) must be negative. Because the packing fraction range from $0 < \varphi_n \leq 1$ cannot be negative by definition, then either the solute (or particle) interaction coefficient, σ , must be negative or the Einstein intrinsic viscosity, $[\eta]$, must be negative. This author²⁷ has shown that the Einstein intrinsic viscosity, $[\eta]$, can be negative if the shear modulus of the solute (or particle) is much less than the shear modulus of the solvent (or matrix). However, because the intrinsic viscosity, $([\eta]/\rho)$, for most polymer solutions is predominantly positive and because the solute molecular density, ρ , cannot be negative, the obvious conclusion is that for polymer solutes or for particles the interaction coefficient, σ , must be negative to yield a Huggins' constant of less than 0.5.

Because we have already seen that eq. (1) can be modified to describe solutions as indicated by eq. (7), then likewise, eq. (1) can be conveniently used to describe solutions over the whole concentration range. With this assumption, then, the effect of the solute (or particle) interaction coefficient on solution viscosity is illustrated in Figure 1 using the general suspension viscosity equation described by eq. (1). In this figure the solute interaction coefficient ranges from -2 to $+2$ for a constant packing fraction of $\varphi_n = 1$, and the Einstein limiting intrinsic viscosity of $[\eta] = 2.5$. The data from Figure 1 has also been replotted in Figures 2 and 3 consistent with a Kraemer-type plot

$$\left(\frac{\ln(\eta/\eta_o)}{\varphi} \text{ vs. } \varphi\right)$$

(Fig. 2) and a Huggins-type plot

$$\left(\frac{\eta_{sp}}{\varphi} \text{ vs. } \varphi\right)$$

(Fig. 3). Note that negative solute (particle) interaction coefficients do give negative slopes on the Kraemer-type plot as expected. Also note that

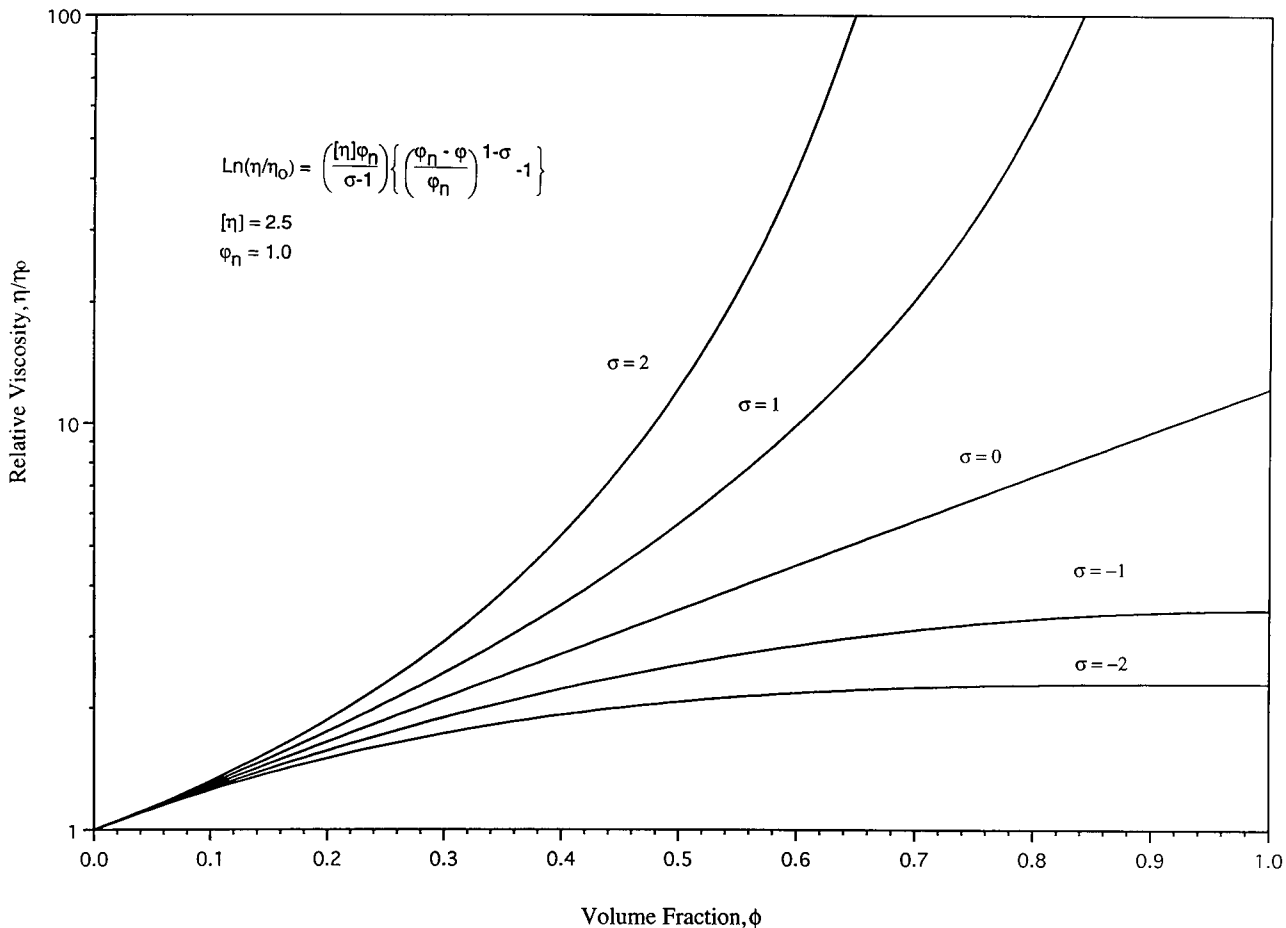


Figure 1 Generalized viscosity model for suspensions at different solute/particle interaction coefficients.

a solute interaction coefficient of $\sigma = 0$ gives a constant value of

$$\left(\frac{\ln(\eta/\eta_0)}{\varphi} \right)$$

for all concentrations. This result is manifested in Figure 1 simply as a constant slope of $\ln(\eta/\eta_0)$ versus φ for $\rho = 0$ at all concentrations. Again, a solute interaction coefficient of $\rho = 0$ has been shown⁶ to be consistent with a significantly reduced interaction between solute molecules because this condition has no dependence on the packing fraction. The significance of a negative solute interaction coefficient has not yet been fully elucidated.

Elucidation of the Maxima That Can Occur in Huggins-Type Plots for Solution and/or Suspension Data

When the solute interaction coefficient, σ , is negative, the slope of the Huggins' plot is normally

positive at low solute volume concentrations, ϕ ; however, at high-volume concentrations the slope can become negative for some solute/particle interaction coefficients, as indicated in Figure 3. This means that for some negative values of σ the Huggins' plot goes through a maximum. This mathematical maximum can be evaluated by rewriting eq. (1) in terms of specific viscosity, η_{sp} , to give

$$\left(\frac{\eta_{sp}}{\varphi} \right) = \frac{1}{\varphi} (e^{F(\varphi)} - 1) \quad (20)$$

where

$$F(\varphi) = \left(\frac{[\eta]\varphi_n}{\sigma - 1} \right) \left\{ \left(\frac{\varphi_n - \varphi}{\varphi_n} \right)^{1-\sigma} - 1 \right\}$$

for $\sigma \neq 1$ (20a)

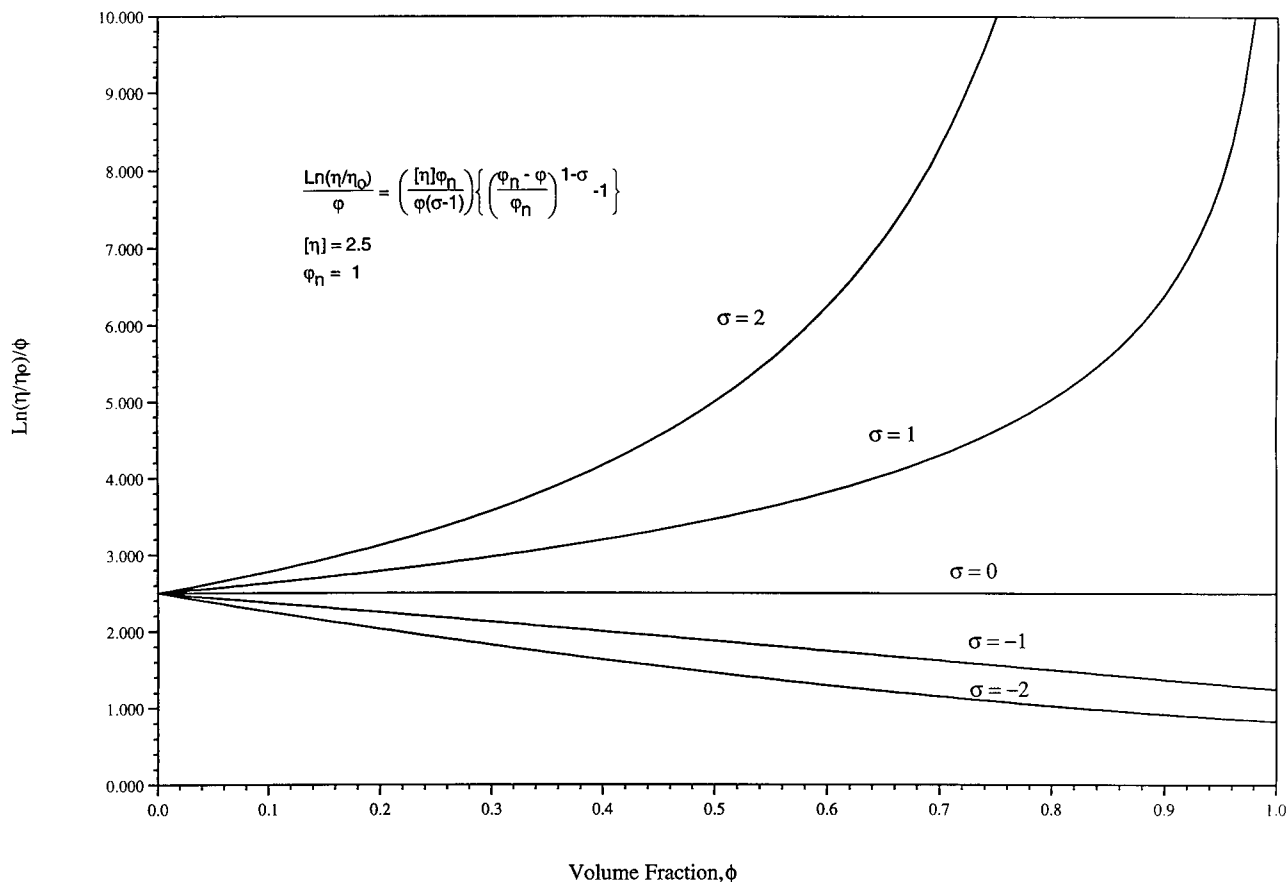


Figure 2 Generalized viscosity model at different particle interaction coefficients, σ , for $\text{Ln}(\eta/\eta_0)/\phi$ versus volume fraction, ϕ .

Now by setting the following derivative to zero

$$\frac{d\left(\frac{\eta_{sp}}{\phi}\right)}{d\phi} = 0 \quad (21)$$

the maximum for eq. (20) can then be shown to occur when

$$1 = \frac{\left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^\sigma}{\varphi[\eta]} \left(1 - \exp\left(\left(\frac{[\eta]\varphi_n}{\sigma - 1}\right) \times \left\{1 - \left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{1-\sigma}\right\}\right)\right) \quad (22)$$

Although the concentration $\varphi = 0$ always provides a correct solution to eq. (22), it is not always a maximum because this condition could also be

a minimum or an inflection point. Some additional evaluation process needs to be addressed to determine if the condition of $\varphi = 0$ is indeed a maximum. Other mathematical solutions to eq. (22) must be solved by trial and error. Maxima of the reduced viscosity, (η_{sp}/φ) , as described by eq. (20), are indeed indicated in the Huggins-type plots in Figure 3 at volume concentrations, φ , other than $\varphi = 0$.

A maximum in a Huggins-type plot has been found experimentally by Hermans and Paals²⁸ for the concentration dependence of the reduced viscosity, (η_{sp}/c) , of sodium pectinate in solutions of different NaCl concentrations (in mol/liter at 27°C) as indicated in Figure 4. Note in this figure that the maximum in the reduced viscosity moves to higher concentration, c , as both the intrinsic viscosity and the particle or solute interaction coefficient changes as a result of a different salt concentration in the solution.

This result is easier to visualize from the data generated for several generalized intrinsic viscos-

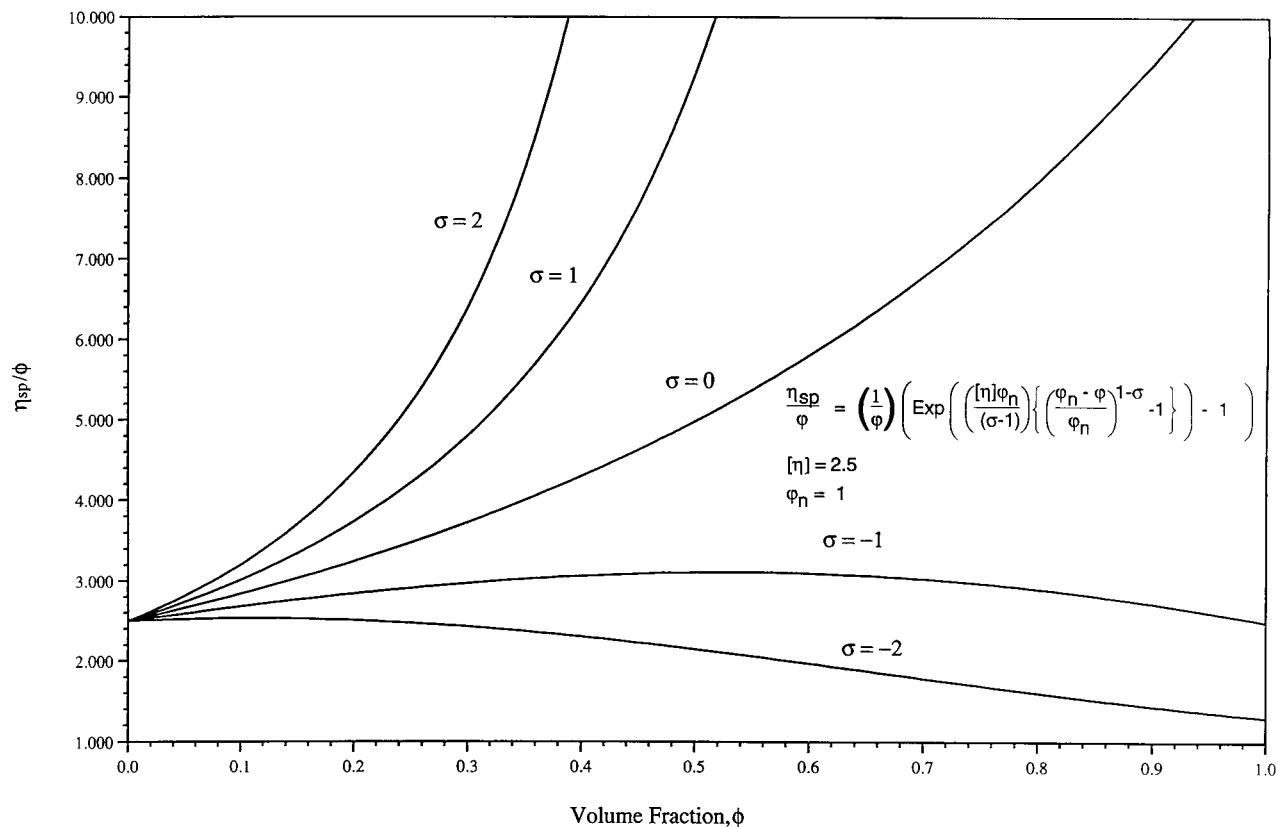


Figure 3 Generalized viscosity model at different particle interaction coefficients, σ , for η_{sp}/ϕ versus volume fraction, ϕ .

ity values and associated solute/particle interaction coefficients, as indicated in Figures 5 and 6. In Figure 5 each curve represents maxima in the reduced viscosities plotted against the concentration at which these maxima occur. Note in Figure 5 that for a constant Einstein intrinsic viscosity the maximum reduced viscosity increased with an increase in the volume concentration at which this maximum occurs. However, the data of Hermans et al.²⁸ in Figure 4 indicates a drop in the maximum reduced viscosity as the salt concentration is increased. In addition, there is also an apparent decrease in the intrinsic viscosity with an increase in salt concentration in the solvent.

The solute/particle interaction coefficients associated with the data in Figure 5 are summarized in Figure 6 as a function of the volume concentration at the maximum reduced viscosity. Note in Figure 6 that the solute/particle interaction coefficients associated with the data in Figure 5 increase with an increase in the volume concentration at the maximum reduced viscosity. The combined results of Figures 5 and 6 indicate that for the data of Hermans and Paals the shift to higher

volume concentrations for the maximum reduced viscosity as the salt concentration was increased is probably more sensitive to the reduction of the value of the intrinsic viscosity than to a shift in magnitude of the solute/particle interaction coefficient.

Based on the data of Hermans and Paals it is also apparent that a maximum obtained from a Huggins plot may make it difficult to obtain a linear plot of the data to obtain the intrinsic viscosity, $([\eta]/\rho)$, as the concentration approaches zero, $c \rightarrow 0$. On the other hand, it will be shown that a straight line as $c \rightarrow 0$ could potentially have been obtained for the data of Hermans and Paals²⁸ by simply plotting a Kraemer-type plot of

$$\left(\frac{\ln(\eta/\eta_0)}{c} \right)$$

versus c instead of the reduced viscosity. More importantly, the sign and relative magnitude of the solute interaction coefficient would have been

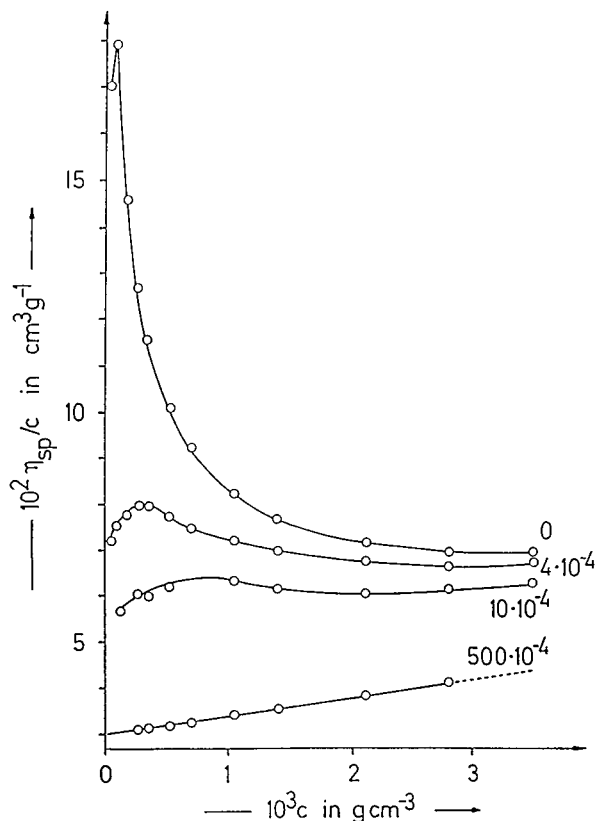


Figure 4 Concentration dependence of the reduced viscosity, η_{sp}/c , of sodium pectinate in solutions of different NaCl concentrations (in mol/L) at 27°C (data of J. J. Hermans and D. T. F. Paals; republished with permission of the authors).

obtained from a direct evaluation of Kraemer's constant.

Lower Limit of the Solute/Particle Interaction Coefficient for Good to Excellent Solvents as Described by an Apparent Lower Limit for Kraemer's Constant

The location of the extrema for a Kraemer plot of

$$\left(\frac{\ln(\eta/\eta_0)}{\varphi} \right)$$

versus φ as evaluated from eq. (1) can be shown to occur when

$$1 = \left(\frac{\varphi_n - \varphi}{\varphi_n} \right)^{-\sigma} \left(\frac{\varphi_n - \sigma\varphi}{\varphi_n} \right) \quad (23)$$

Note that the maxima or minima as calculated from eq. (23) are not a function of the intrinsic

viscosity, $[\eta]$. Although the concentration at $\varphi = 0$ always provides a correct solution to eq. (23), it is not always a maximum because this condition could also be a minimum or an inflection point. However, for a Kraemer plot of

$$\left(\frac{\ln(\eta/\eta_0)}{\varphi} \right)$$

versus φ , it can be shown that a concentration of $\varphi = 0$ always gives a minimum when $\sigma > 0$ and a maximum when $\sigma < 0$. Interestingly, it can also be shown that for a Kraemer-type plot there are no other minima or maxima between the concentrations of $\varphi = 0$ and $\varphi = \varphi_n$ other than at $\varphi = 0$.

At this point it is apparent that good solvents of polymer solutes are typically characterized by having a negative Kraemer's constant and an associated negative solute/particle interaction coefficient. It has been found, however, that there appears to be a limit of the definition of solubility for good to excellent solvents as described by Kraemer's constant. To illustrate this point, several Kraemer constants have been calculated in Figures 7 and 8 for the condition that yields a maximum in the reduced viscosity in a Huggins plot as described by eq. (22) and correlated with the volume concentration at that location. The results in Figures 7 and 8 have been calculated for all possible negative solute interaction coefficients that satisfy eq. (22) for three different values of the Einstein type intrinsic viscosity, $[\eta]$. Note that the calculated results in Figures 7 and 8 are the same calculated results utilized in Figures 5 and 6 as well. As indicated in Figure 7, Kraemer's constants for negative solute/particle interaction coefficients range from approximately 0 to -0.5 while the volume concentrations at the maximum reduced viscosity range from $\varphi = 1$ to $\varphi = 0$. This would correspond to a Huggins' constant range from 0.5 to 0. The results in Figure 8, calculated for two different packing fractions ($\varphi_n = 1$ and $\varphi_n = 0.75$) indicate that Kraemer's constant approaches zero as the volume concentration at the maximum reduced viscosity approaches the packing fraction $\varphi \rightarrow \varphi_n$. The results in Figures 7 and 8 also indicate that Kraemer's constant approaches a minimum value of $K \rightarrow -0.5$ as the concentration approaches zero. This result suggests that the absolute value of the solute interaction coefficient approaches the following maximum limit:

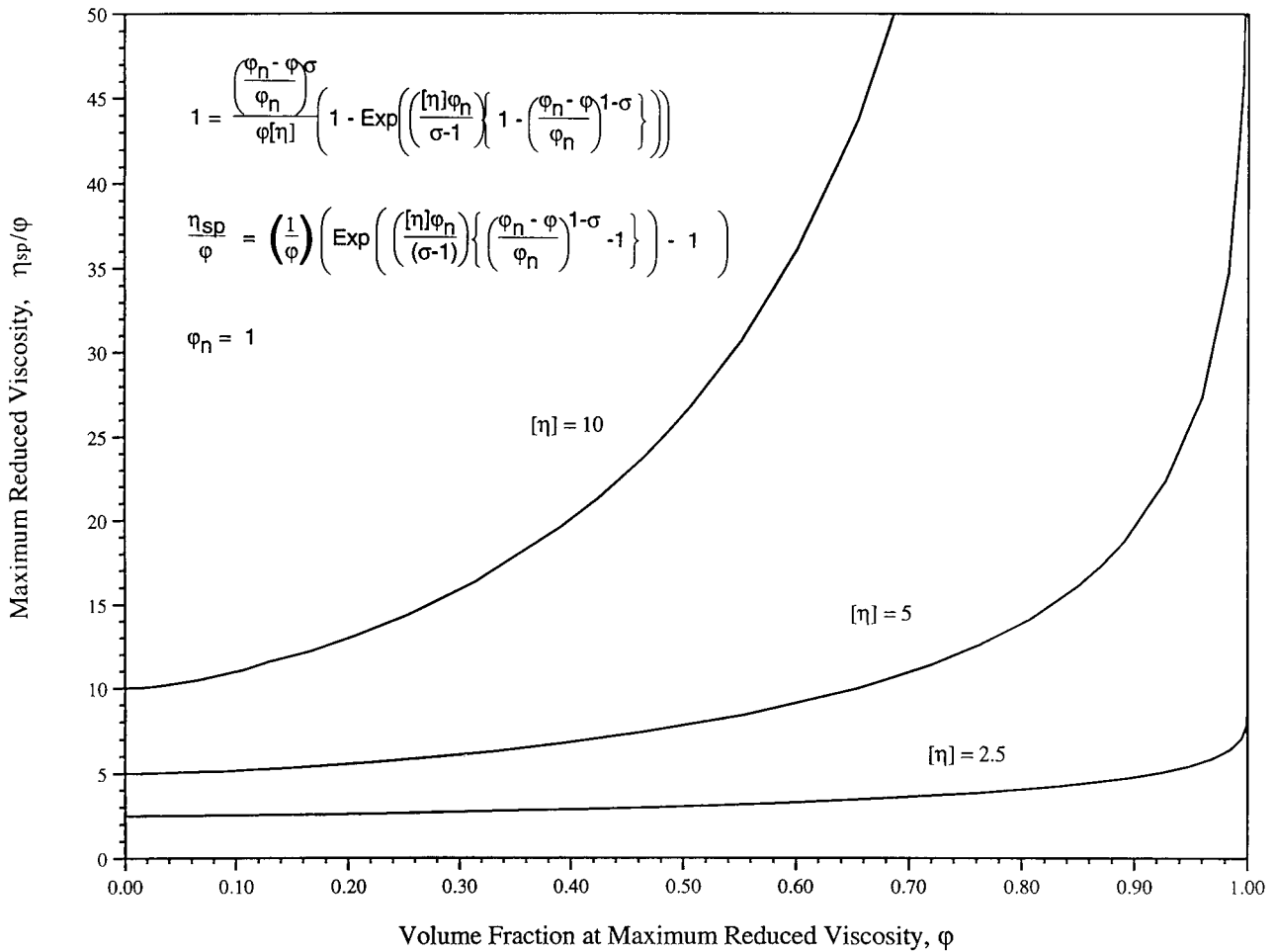


Figure 5 Maximum reduced viscosity versus volume fraction at maximum reduced viscosity for generalized viscosity equation.

$$|\sigma| \rightarrow \left(\frac{[\eta]}{\rho} \right) (\rho \varphi_n) = [\eta] \varphi_n \quad (24)$$

Because the maximum packing fraction has been found to approach $\varphi_n = 1$ when Kraemer's constant approaches $K \rightarrow -0.5$ as the volume concentrations approach $\varphi \rightarrow 0$ at the maximum reduced viscosity, then the lower limit for the solute/particle interaction coefficient, σ , for excellent solvents appears to approach the negative of the Einstein type intrinsic viscosity, $-[\eta]$.

Generalized Virial Coefficients for an Infinite Series with the Overlap Parameter as Derived from the Generalized Suspension Equation

It should also be noted that eqs. (8) and (12) can be written in the more general case as the following series:

$$\left(\frac{\ln(\eta/\eta_o)}{c} \right) = \left(\frac{[\eta]}{\rho} \right) + \left(\frac{[\eta]}{\rho} \right)^2 \{B_2\}c + \left(\frac{[\eta]}{\rho} \right)^3 \{B_3\}c^2 + \dots + \left(\frac{[\eta]}{\rho} \right)^n \{B_n\}c^{n-1} \quad (25)$$

and

$$\left(\frac{\eta_{sp}}{c} \right) = \left(\frac{[\eta]}{\rho} \right) + \left(\frac{[\eta]}{\rho} \right)^2 \{A_2\}c + \left(\frac{[\eta]}{\rho} \right)^3 \{A_3\}c^2 + \dots + \left(\frac{[\eta]}{\rho} \right)^n \{A_n\}c^{n-1} \quad (26)$$

It is also apparent that these constants are interrelated, because in general when $n \geq 2$

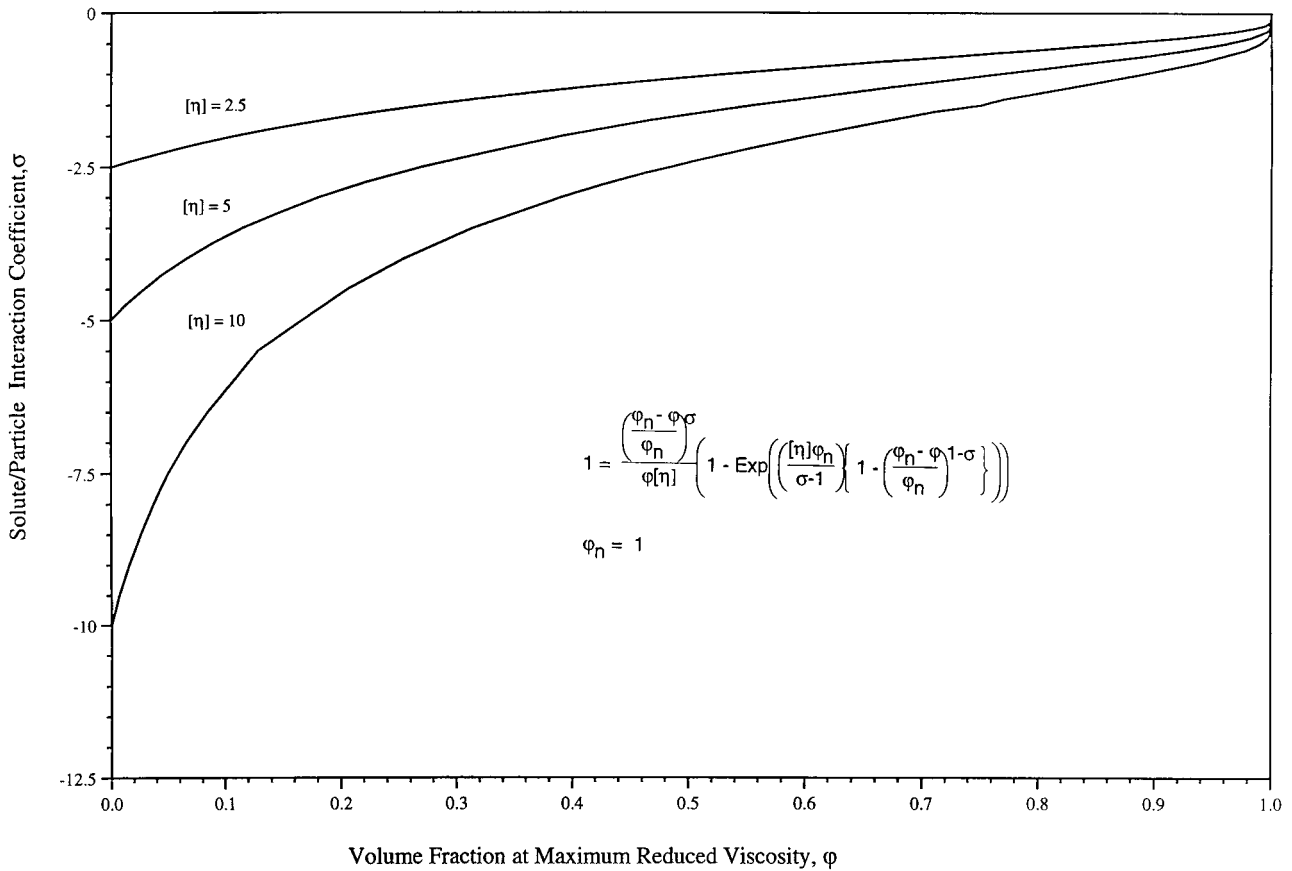


Figure 6 Solute/particle interaction coefficient versus volume fraction at maximum reduced viscosity for generalized viscosity equation.

$$A_n = \left(\frac{1}{n!}\right) + B_n + C_n \quad (27)$$

where if

$$F(\varphi) = \left(\frac{[\eta]\varphi_n}{\sigma - 1}\right) \left\{ \left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{1-\sigma} - 1 \right\} \quad (28)$$

and if $C_2 = 0$, then

$$B_n = \frac{F^n(0)}{n!(F^1(0))^n} \quad (29)$$

$$C_n = \frac{D_n(0)}{n!(F^1(0))^n} \quad (30)$$

where $D_n(0)$ is a function of a combination of derivatives of $F(\varphi)$ consistent with a McLaurin series evaluation to arrive at the extended form of eq. (12). For example, it can easily be shown that B_2 is the Kraemer constant K as described by eq.

(16). Two additional examples by comparison to eq. (12) would include:

$$B_3 = \frac{F^3(0)}{3!(F^1(0))^3} = \left(\frac{1}{6}\right) \left(\frac{\rho}{[\eta]}\right)^2 \left(\frac{\sigma}{\rho\varphi_n}\right) \left(\frac{\sigma + 1}{\rho\varphi_n}\right) = \left(\frac{1}{6}\right) \left(\frac{1}{[\eta]}\right)^2 \left(\frac{\sigma}{\varphi_n}\right) \left(\frac{\sigma + 1}{\varphi_n}\right) \quad (31)$$

$$C_3 = \left(\frac{1}{3!}\right) \left(\frac{3F^2(0)F^1(0)}{(F^1(0))^3}\right) = \left(\frac{1}{2}\right) \left(\frac{\sigma}{\rho\varphi_n}\right) \left(\frac{\rho}{[\eta]}\right) = \left(\frac{1}{2}\right) \left(\frac{\sigma}{\varphi_n}\right) \left(\frac{1}{[\eta]}\right) \quad (32)$$

Simha et al.²² have indicated that general considerations have suggested that the concentration dependence of “normal” colloid suspensions can be represented by a concentration power series as indicated for (η_{sp}/c) versus c by eq. (25). Simha

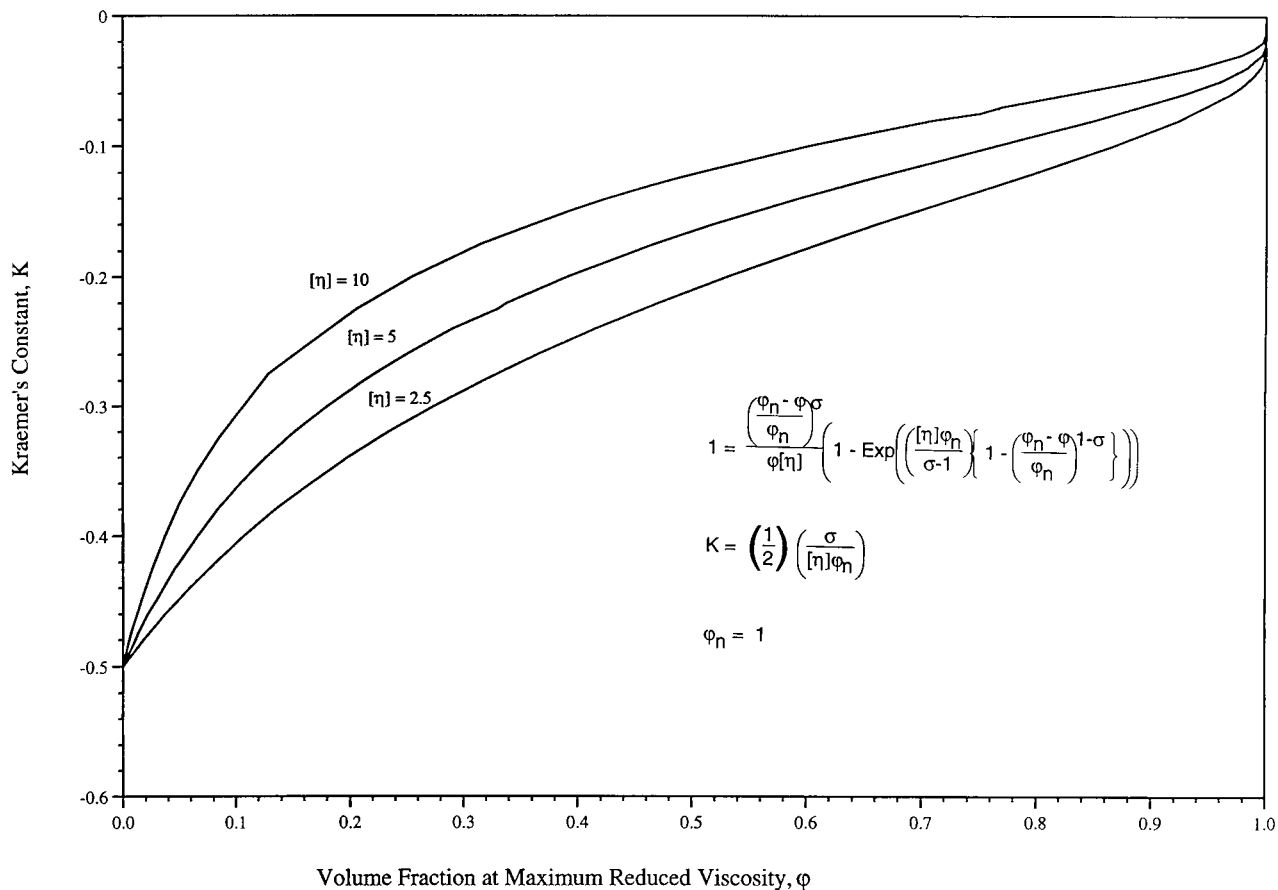


Figure 7 Kraemer's constant versus volume fraction at maximum reduced viscosity for generalized viscosity equation.

et al.²² have also pointed out that the virial constants in eq. (25) have been found to be functions of molecular weight heterogeneity, degree of branching, crosslinking, amounts of polar contamination in the polymer sample, and the sensitivity of the solute to the solvent as described by good and poor solvents.

The quantity sometimes referred to as the overlap parameter, $([\eta]/\rho)c = [\eta]\varphi$, is included in each term of both eqs. (25) and (26) to the same power as the number of the term in the series. This overlap parameter was first introduced using an empirical equation developed by Schulz and Blaschke²⁹ and extended by Huggins.²³ The overlap parameter, $([\eta]/\rho)c = [\eta]\varphi$, identified in conjunction with eq. (25) has been discussed in terms of several ranges by Simha et al.²² Below $\varphi = 0.25$ Maron et al.³⁰⁻³² found that latexes are mostly Newtonian with little shear sensitivity but they become very non-Newtonian and very sensitive to shear rate above a concentration of $\varphi = 0.4$. Simha³³ suggested that for concentrated solutions

the non-Newtonian flow in these systems is partly due to the destruction of aggregates that changes the rearrangement of suspended particles by shear. Simha et al.³⁴ also found that if (η_{sp}/c) is plotted against $([\eta]/\rho)c$ instead of c that the effects of molecular weight on viscosity are essentially eliminated for good solvents. Consequently, eqs. (25) and (26) would appear to be the ultimate forms preferred by the scientific community for solution viscosity applications. More importantly, the model presented in this study is consistent with these objectives.

CONCLUDING REMARKS

In earlier studies it has been shown that a change in magnitude of particle interaction coefficient in the generalized viscosity model for suspensions can yield the standard viscosity equations typically used to evaluate suspension viscosities. For example, by varying the particle interaction coef-

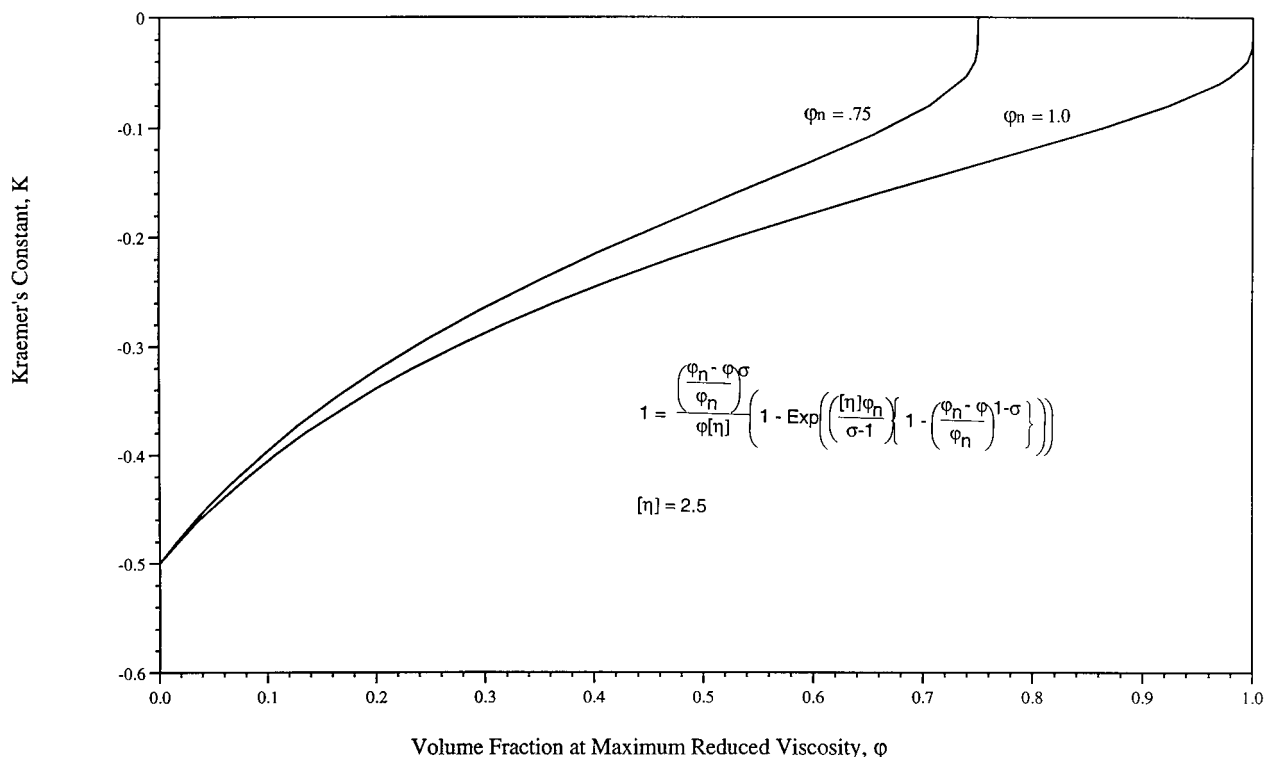


Figure 8 Kraemer's constant versus volume fraction at maximum reduced viscosity for generalized viscosity equation.

cient, σ , the Arrhenius equation results when $\sigma = 0$, the Krieger-Dougherty equation results when $\sigma = 1$, and when $\sigma = 2$ the Mooney equation results. Fractional values for the particle interaction coefficient have also been found to be useful and perfectly acceptable. As the interaction coefficient approaches zero solute (particles) molecules have been shown to approach a significantly reduced interference with each other and to effectively improve miscibility.

This study found that the generalized suspension equation can also be successfully applied to solutions. It predicts the Huggins' equation and the Kraemer's equation. It also predicts that the sign of Kraemer's constant is directly related to the sign of the particle interaction coefficient. It has also been found that for good solvents the solute (particle) interaction coefficient should normally be negative.

In general, then, it appears that the solute/particle interaction coefficient characterizes the solubility of a solute or particle in a solvent. Suspensions appear to be characterized as having a particle interaction coefficient of $\sigma \geq 1$. Poor to intermediate solutions are characterized as having a solute or particle interaction coefficients of

$0 \leq \sigma \leq 1$. Good to excellent solutions are then characterized as having solute or particle interaction coefficients of $\sigma < 0$.

Based on available literature values, this study found that the limits for Kraemer's constant appear to range from $-0.5 \leq K \leq 0.5$. With these limits and the definition of Kraemer's constant developed in this study, the solute/particle interaction coefficient was found to have a range from $-[\eta] \leq \sigma \leq [\eta]$, where $[\eta]$ is the Einstein type intrinsic viscosity.

It was also found that a maximum in the reduced viscosity was predicted using the generalized viscosity model as applied to a Huggins-type plot for solutions. The experimental literature data of Hermans et al.²⁸ confirmed that such a maximum can exist for a Huggins-type plot. This study also found that when the concentration at which the reduced viscosity maximum approaches $\varphi \rightarrow 0$ for solutions and suspensions, then Kraemer's constant approaches $K \rightarrow -0.5$ and the solute/particle interaction coefficient approaches $\sigma \rightarrow -[\eta]$.

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