COMMUNICATIONS TO THE EDITOR

Calculation of Curves Relating Non-Newtonian Viscosity to Stress

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In connection with my recent article (*1*) the questions have arisen how the curves of Figure 3 were calculated, and if a simple series expansion exists for them. The purpose of this communication is to discuss these questions.

The curves relate the reduced apparent capillary viscosity to the shear stress at the wall, $\tau_w = PR/2L$, for various values of two parameters $\bar{\eta}_\infty$ and σ, through the integral [Equation (9) of the article]:

$$1/\bar{\eta}_a = \int_0^R \frac{4\,r^3\,dr}{R^4\,[\bar{\eta}_\infty + (1-\bar{\eta}_\infty)e^{-\sigma Pr/2L}]} \qquad (1)$$

This could not be integrated directly, nor could a single expansion be found, valid for the entire ranges of $\bar{\eta}_\infty$ and $\sigma\tau_w$. Instead, three expansions had to be used, covering different but overlapping parts of the ranges.

When the stress is small, and $\bar{\eta}_\infty$ is not very small, the integrand can be expanded in a Taylor series about $r = R$ and integrated term by term, giving

$$\bar{\eta}_w/\bar{\eta}_a = 1 - \frac{(1-\bar{\eta}_\infty)\sigma\tau_w e^{-\sigma\tau_w}}{5\,\bar{\eta}_w} + \frac{(1-\bar{\eta}_\infty)\,\sigma^2\,\tau_w^{\,2}\,e^{-\sigma\tau_w}\,[(1-\bar{\eta}_\infty)e^{-\sigma\tau_w} - \bar{\eta}_\infty]}{30\,\bar{\eta}_w^{\,2}} \qquad (2)$$

where $\bar{\eta}_w = \bar{\eta}_\infty + (1-\bar{\eta}_\infty)e^{-\sigma\tau_w}$.

This expansion diverges at large stress when $\bar{\eta}_\infty < ½$. In practice it becomes unwieldly when more than the terms explicit in (2) must be evaluated, and that is when the term in the first power of stress exceeds 0.3.

If $\bar{\eta}_\infty$ were so small that it could be neglected, (1) would be directly integrable:

$$\bar{\eta}_a = \frac{e^{-\sigma\tau_w}}{K(\sigma\tau_w)} \qquad (3)$$

where

$$K(\sigma\tau_w) = \frac{4\,e^{-\sigma\tau_w}}{R^4}\int_0^R r^3\,e^{\sigma\,Pr/2L}\,dr \qquad (4)$$

This is the curve for $H = \infty$ in Figure 3.

If $\bar{\eta}_\infty$ is small enough, the form of (3) can be used as the basis of an expansion. Equation (1) is written in the form

$$1/\bar{\eta}_a = \int_0^R \frac{4r^3e^{\sigma\,Pr/2L}}{R^4(1-\bar{\eta}_\infty)}\cdot\frac{dr}{1+\dfrac{\bar{\eta}_\infty e^{\sigma Pr/2L}}{(1-\bar{\eta}_\infty)}} \qquad (5)$$

and the second factor expanded in a binomial series. Term-by-term integration gives

$$(1-\bar{\eta}_\infty)/\bar{\eta}_a = e^{\sigma\tau_w}K(\sigma\tau_w) - \frac{\bar{\eta}_\infty}{1-\bar{\eta}_\infty}\,e^{2\sigma\tau_w}K(2\sigma\tau_w) + \frac{\bar{\eta}_\infty^{\,2}}{(1-\bar{\eta}_\infty)^2}\,e^{3\sigma\tau_w}K(3\sigma\tau_w)\quad\ldots\ldots \qquad (6)$$

which may be evaluated with the aid of a graph for *K*. This expansion converges so long as $\bar{\eta}_\infty < (1-\bar{\eta}_\infty)e^{-\sigma\tau_w}$, that is if the stress is not too large. However, the series begins to oscillate widely as the convergence limit is approached, and its use is best confined to the small stress region for small values of $\bar{\eta}_\infty$.

To handle the case where stress is large, the integrand in (1) was replaced by a closely approximating function which is integrable in closed form:

$$1/\bar{\eta}_a = \int_0^R \frac{4\,r^3\,dr}{R^4\,\bar{\eta}_\infty}\cdot\psi(x) \qquad (7)$$

$\psi(x)$ is the cumulative probability integral function

$$\psi(x) = \int_{-\infty}^{x}\phi(\xi)\,d\xi = \int_{-\infty}^{x}\frac{1}{\sqrt{2\pi}}\,e^{-\xi^2/2}\,d\xi \qquad (8)$$

The relation between *x* and *r* is

$$x = \frac{\sqrt{2\pi}}{4}\,\frac{\sigma Pr}{2L} - H \qquad (9)$$

where

$$H = \frac{\sqrt{2\pi}}{4}\ln[(1-\bar{\eta}_\infty)/\bar{\eta}_\infty] \qquad (10)$$

On substituting (9) and (10) into (7) and integrating, one obtains

$$\left(\frac{\sqrt{2\pi}\,\sigma\tau_w}{4}\right)^4 \frac{\bar{\eta}_\infty}{\bar{\eta}_a} = G\left\{\frac{\sqrt{2\pi}}{4}\sigma\tau_w - H\right\} - G\{-H\} \tag{11}$$

in which

$$G\{x\} = [(x+H)^4 - (H^4 + 6H^2 + 3)]\psi(x) + [x^3 + 4Hx^2 + (6H^2+3)x + (4H^3 + 8H)]\phi(x) \tag{12}$$

Equation (11) is mainly useful in the high stress region for any value of $\bar{\eta}_\infty$.

Because (11) is by far the most difficult of the approximations, the curves were calculated only for integral and half-integral values of H. H turns out to be an aid to interpolation with Figure 3, because as H increases the curves become equally spaced at high stress:

$$H \xrightarrow[\bar{\eta}_\infty \to 0]{} -\frac{\sqrt{2\pi}}{4}\ln \bar{\eta}_\infty$$

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NOTATION

L = length of capillary tube
P = pressure difference between ends of capillary tube
R = radius of capillary tube
r = distance from axis of capillary
$\bar{\eta}_a$ = apparent capillary viscosity (Poiseuille), divided by viscosity at zero shear stress
$\bar{\eta}_\infty$ = above at infinite stress
σ = parameter
τ_w = shear stress at capillary wall
G, H, K, x, $\bar{\eta}_w$, and Φ and ψ = functions defined in text

LITERATURE CITED

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Virial Coefficients, Kihara and Lennard-Jones Parameters for Methyl Borate

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Information related to the behavior of methyl borate molecules is valuable because this compound is a starting material for many important reactions in the field of boron chemistry.

The present study determined second and third virial coefficients for methyl borate. Kihara and Lennard-Jones parameters were then determined from the second virial coefficient-temperature data.

Virial coefficients were derived from the data of Griskey, Gorgas, and Canjar (*1*) by fitting the relation

$$v(Z-1) = B + c/v \tag{1}$$

with the least-squares technique. The range of average deviations (in cubic centimeters per gram mole) obtained in fitting the experimental data to Equation (1) were 0.00 to 8.93.

No direct check of the virial coefficient data was possible, since no literature values existed. Indirect comparisons were, however, possible with published correlations for hydrocarbons.

Figure 1 compares the reduced second virial coefficients of the present work with correlations for hydrocarbons derived by McGlasahan and Potter (*2*). The value of V_c used to reduce the methyl borate data was that given by Hansen and Hughes (*3*). As can be seen, the behavior of the methyl borate data is similar to that of the hydrocarbons.

Reduced third virial coefficients for methyl borate are compared with a generalized hydrocarbon correlation de-