In this equation X_n is the fractional area occupied by the nth flow unit on the shear surface, $\alpha_n = (\lambda\lambda_2\lambda_3)_n/2kT$ and $\beta_n = 1/[(\lambda/\lambda_1)2k']_n$, where k is Boltzmann's constant, T the temperature, and the summation is the extension to all the flow units present. Here $\lambda_2\lambda_3$ is the cross-sectional area of a certain flow unit, λ the distance a unit moves between equilibrium positions, λ_1 the distance between planes of flow units of a certain kind, and k' the rate constant for passage of the unit over a potential energy barrier.

The experimental data of greases are explained in terms of Newtonian and non-Newtonian flow units, e.g.,

$$f = X_1\beta_1/\alpha_1\dot{s} + X_2/\alpha_2 \sinh^{-1}\beta_2\dot{s}. \quad (27)$$

The subscripts 1 and 2 refer to the Newtonian and non-Newtonian units, respectively. If it is assumed that $X_1\beta_1/\alpha_1 \ll X_2\beta_2/\alpha_2$ (the inequality is due to the fact that $\beta_1/\alpha_1 <<< \beta_2/\alpha_2$ while $X_1 \gg X_2$) then (6) becomes

$$f = X_2/\alpha_2 \sinh^{-1}\beta_2\dot{s}. \quad (28)$$

Pressure increases and decreases effect an equilibrium transition between Newtonian and non-Newtonian flow. Thus when $X_1 \gg X_2$,

$$X_2 \cong \exp(-\Delta F/RT)$$

and from (1)

$$X_2 = \exp(-\Delta F_0/RT)\exp(-P\Delta V/RT) = K_0 \exp(-P\Delta V/RT), \quad (29)$$

where K_0 is the equilibrium constant when $P=0$. Also

$$\beta_2 = (\lambda 2k'/\lambda_1)_2^{-1} = (\lambda/\lambda_1 2kT/h)_2^{-1} \exp\Delta F^{\ddagger}/RT) = \beta_{2,0}\exp(P\Delta V^{\ddagger}/RT, \quad (30)$$

where

$$\beta_{2,0} = (\lambda/\lambda_1 2kT/h)^{-1}\exp(F_0^{\ddagger}/RT).$$

Substituting Eqs. (29) and (30) into (28) yields

$$f = [K_0/\alpha_2 \exp(-P\Delta V/RT)] \sinh^{-1} \times [\beta_{2,0}\exp(-P\Delta V^{\ddagger}/RT)\dot{s}], \quad (31)$$

which is the equation of flow under pressure.

By applying (31) to the $\dot{s}$-f flow curves discussed earlier, the factors X_2/α_2 and β_2 are obtained. ΔV is obtained from the slope of the line in the plot of $\ln(X_2/\alpha_2)$ against P. Similarly $\Delta V^{\ddagger}$ is determined from the plot of $\ln\beta$ against P. $\beta_{2,0}$ is evaluated by extrapolating the β_2 values obtained at various pressures to $P=0$. Finally, in (30), $\Delta F^{\ddagger}$ is readily calculated for $\lambda \cong \lambda_1$.

APPLICATION TO LUBRICANT

Figure 18 shows the theoretical and experimental flow curve for Calresearch 60R–588 grease (obtained from the California Research Corporation) under a pressure of 339 atm. The shear rate $\dot{s}$ is determined by Eq. (25) and the stress f by the relation $f = r\Delta P/2L$. The reproducibility of the experimental result is within a range of two percent. The theoretical flow curve was calculated from Eq. (27). The factors $X_1\beta_1/\alpha_1$, X_2/α_2, and β_2 were determined using Eyring's well-known method.[35]

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