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:

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


## ACKNOWLEDGMENT

The desirability of explaining the calculation of the curves of Figure 3 was pointed out in private communication by Professor R. B. Bird of the University of Wisconsin. The work referred to was performed at the Emeryville, California, laboratories of the Shell Development Company.


## 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
$\sigma$ = parameter
$\tau_w$ = shear stress at capillary wall
$G$, $H$, $K$, $x$, $\bar{\eta}_w$, and $\Phi$ and $\psi$ = functions defined in text

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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-

veloped by David and Hamann (4). The methyl borate data closely matches the correlation curve (see Figure 2).

Lennard-Jones and Kihara intermolecular potentials were fitted to the second virial coefficient-temperature data. The techniques for doing this have been described by Hirschfelder, Curtiss, and Bird (5) and Kihara (6).

Values of Lennard-Jones parameters found in the present work were $\sigma = 5.404$Å and $\epsilon/k = 422$°K. Second virial coefficients computed from these parameters deviated on the average by 1.5% from the experimental values.

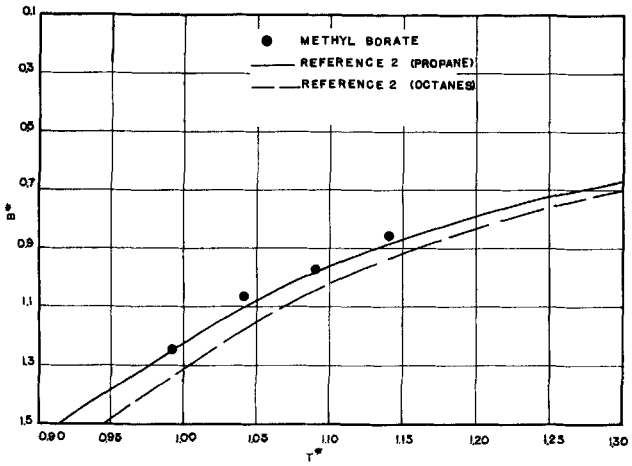


Fig. 1.

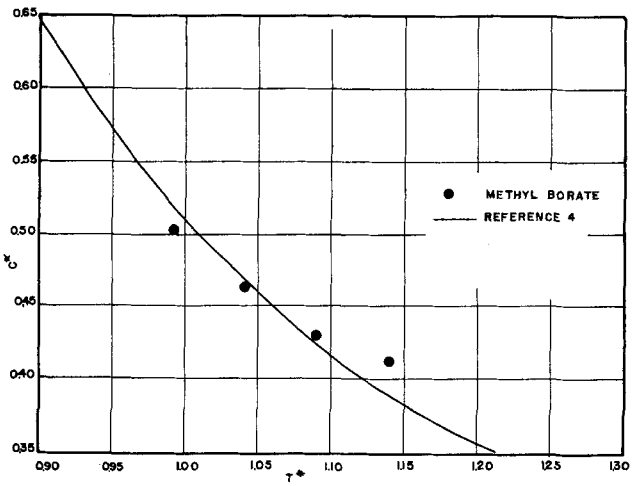


Fig. 2.

The Lennard-Jones parameters were also checked by calculating viscosity data and comparing it with experimental values (7). These viscosities were calculated from the equation (8)

$$\mu = 2.6693 \times 10^{-5} \frac{\sqrt{MT}}{\sigma^2 \Omega_\mu} \qquad (2)$$

The calculated viscosity values had average deviations of 0.61% from the experimental values.

Kihara parameters determined in the present study were $\rho_o = 2$Å $\frac{U_o}{k} = 1{,}160$°K., $l = 4.87$Å, $S_o = 20.5$(Å)$^2$, and $M_o = 22.9$(Å)$^2$. A tetrahedronal model was used for methyl borate. Values of second virial coefficients computed from the Kihara parameters deviated by 1.90% on the average from experimental second virial coefficients.

## CONCLUSIONS

1. Second and third virial coefficients have been determined for methyl borate.
2. The coefficients compared favorably with published correlations.
3. Kihara and Lennard-Jones parameters were derived for methyl borate.
4. Second virial coefficients calculated from these parameters checked experimental values with less than 2% average deviation.
5. Viscosities calculated from the Lennard-Jones parameters deviated on the average by 0.61% from experimental values.

## NOTATION

$B$ = second virial coefficient, liter/g. mole
$C$ = third virial coefficient
$M$ = molecular weight
$R$ = gas constant, liter atm./g. mole °K.
$T$ = temperature, °K.
$V$ = molal volume, liter/g. mole
$Z$ = compressibility factor
$B^*$ = $B/V_c$, reduced second virial coefficient
$C^*$ = $C/V_c^2$, reduced third virial coefficient
$M_o$ = surface integral of mean curvature of the Kihara model over the model surface, (Å)$^2$
$S_o$ = surface of Kihara model, (Å)$^2$
$T^*$ = $T/T_c$, reduced temperature
$T_c$ = critical temperature, °K.
$U_o$ = maximum potential energy
$V_c$ = critical volume, liter/g. mole
$k$ = Boltzmann constant
$l$ = characteristic dimension of Kihara model, (Å)
$\epsilon$ = parameter of Lennard-Jones potential
$\sigma$ = parameter of Lennard-Jones potential
$\rho$ = distance separating Kihara cores
$\rho_o$ = shortest distance between Kihara cores and energy minimum
$\mu$ = viscosity, g./cm. sec.
$\Omega_\mu$ = function of $kT/\epsilon$

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