CHAPTER VI

PRESSURE DEPENDENCE OF THE VISCOSITY OF
SUPERHEATED STEAM
Unlike other gases, the viscosity of superheated steam decreases with increase of pressure, in contradiction to the prediction of the Enskog theory for dense gases. In this paper, the unusual pressure dependence of the viscosity of steam is explained by considering steam at elevated pressures to be a mixture of dimers and monomers.

The viscosity of most gases increases with increase of pressure or density due to collisional transfer of momentum and can be accounted for approximately by the Enskog theory for dense gases\(^1\). However, the viscosity of superheated steam at a particular temperature decreases with the increase of pressure\(^2-4\). The negative pressure coefficient of viscosity decreases with increase of temperature. Helium also shows an initial decrease of viscosity with the increase of pressure\(^5,6\), and this effect is more pronounced at the lower temperatures.

Because of hydrogen bonding, \(\text{H}_2\text{O}\) shows association which increases with increase of pressure and decrease of temperature. The viscosity of associated molecules may
Fig. 1. Dimer-monomer interaction.

$r_{\text{min}}$ corresponds to the value of $r$ for which

\[ \frac{d\phi(r)}{dr} = 0 \]

with $\langle \theta \rangle = 0$
Table 1.

Calculated and experimental values of the viscosity of superheated steam at elevated pressures.

<table>
<thead>
<tr>
<th>T°C (in atm.)</th>
<th>P</th>
<th>( x_2 )</th>
<th>12-6-3 model</th>
<th>( \eta_{dm} \times 10^7 )</th>
<th>( \eta_p \times 10^7 )</th>
<th>L-J(12:6) model</th>
<th>( \eta_p \times 10^7 )</th>
<th>exp t.</th>
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Contd.
where $\phi(r)$ is the potential energy between two $H_2O$ molecules separated by distance $r$, $\sigma$ is the value of $r$ for which $\phi(r) = 0$, $\epsilon$ is the depth of the potential well, $\delta$ is given by

$$\delta = \frac{1}{4} \frac{\mu^2}{\epsilon \sigma^3} \zeta (\theta_1, \theta_2, \phi);$$

$$\zeta = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi \quad \ldots \quad (6)$$

where $\mu$ is the dipole moment of $H_2O$, $\theta_1$, $\theta_2$ are the angles of inclination of the axes of the two dipoles to the line joining the centres of the molecules and $\phi$ is the azimuthal angle between them. The maximum value of $\delta$ is 2, consequently,

$$\delta_{\text{max}} = \frac{1}{2} \frac{\mu^2}{\epsilon \sigma^3} \quad \ldots \quad (7)$$
the monomer to be placed (fig. 1) in two extreme positions corresponding to $\theta = 0$ and $\theta = \pi/2$.

For $\theta = 0$,

$$(\delta_{dm})_{\text{max}} = \frac{2\varepsilon}{\varepsilon_{dm}} \left(\frac{\sigma}{\sigma_{dm}}\right)^3 \left(\frac{r_{dm}}{r_{\text{min}}}\right)^3 \delta_{\text{max}}, \quad \ldots (9)$$

and for $\theta = \pi/2$,

$$(\delta_{dm})_{\text{max}} = \frac{\varepsilon}{\varepsilon_{dm}} \left(\frac{\sigma}{\sigma_{dm}}\right)^3 \delta_{\text{max}} \left[\frac{r_{\text{min}} + \frac{1}{2}(r_{\text{min}}d)}{r_{\text{min}}} \right] \ldots (10)$$

The average of the two values of $(\delta_{dm})_{\text{max}}$ is taken as the correct value. With $\sigma = 2.71 \text{ Å}$; $\varepsilon/k = 506 \text{ °K}$; $\delta_{\text{max}} = 1.2$, we have $\sigma_{dm} = 3.15 \text{ Å}$; $\varepsilon_{dm}/k = 668 \text{ °K}$; $(\delta_{dm})_{\text{max}} = 1.44$.

The force parameters for the dimer-dimer interaction can be obtained from the combination rules\(^9\), i.e.,

$$\varepsilon_{dd} = \frac{(\varepsilon_{dm})^2}{\varepsilon} \quad ; \quad \sigma_{dd} = 2 \sigma_{dm} - \sigma;$$

$$(\delta_{\text{max}})_{dd} = \frac{(\delta_{dm})_{\text{max}}^2 (\sigma_{dm})^6}{\delta_{\text{max}} (\sigma_{dd})^3} \quad \ldots (11)$$

By knowing the force parameters for the monomer-monomer, dimer-monomer, dimer-dimer interactions, it is possible to calculate the mixture viscosity $\eta_{dm}$ on the Chapman-Enskog\(^8\)\(^9\) theory from the calculated mole fractions.
of the dimers and the monomers. The values of \( \eta_{dm} \)
calculated at different pressures and temperatures are
shown in column 4 of table 1. The values of \( \eta_{dm} \) at zero
pressure are the viscosity of the monomer at that tempera-
ture. The values of \( \eta_c \) were calculated from eqn. (3)
from the experimental second virial coefficient data. The
values of \( \eta_p \) obtained from the sum of \( \eta_{dm} \) and \( \eta_c \)
are given in column 5. The experimental values of \( \eta_p \) as
obtained by Kestin and Wang are also shown in column 7.
The results are shown in fig. 2.

Mason and Monchick have shown that the visco-
sity is not sensitive to the dipole forces. Consequently
we have also applied the Lennard-Jones (12:6) model to
explain the observed pressure dependence of the viscosity
of steam. The zero-pressure viscosity data were fitted
d graphically to a Lennard-Jones (12:6) potential to give
the best values of \( \sigma \) and \( \epsilon/k \) as 2.845 Å and 635 °K,
respectively. The parameters for the dimer-monomer and the
dimer-dimer interactions were obtained from eqn. (3) and
the combination rules. The values of \( \eta_p \) obtained are
shown in column 6 of table 1.

Since the force parameters on the 12-6-3 and
the Lennard-Jones (12:6) models cannot represent well the
zero-pressure viscosity data of steam, the quantity
Discussion.

It may be seen from column 5 of table 1 that by considering steam at elevated pressures to be a mixture of dimers and monomers, it is possible to explain the unusual pressure dependence of the viscosity of superheated steam. Further, in agreement with the experimental results, the slope of the viscosity-pressure curve decreases with the increase of temperature. The agreement between the experimental and the calculated values of \( \eta_0 - \eta_p \), for temperatures below 270°C is satisfactory in view of the approximations made in our calculations. There is some uncertainty in the viscosity data at 270°C, as Kestin and Wang\(^2\) have observed the viscosity-pressure curve at that temperature to be almost horizontal, whereas Kestin and Richardson\(^3\) found a negative slope for the viscosity-pressure curve even at 280°C. At the higher temperatures the theoretical viscosity-pressure curve shows a change of sign which has not been observed experimentally. This change occurs at lower pressures as the temperature is raised. It is expected that at sufficiently high temperatures the viscosity of steam will show a regular increase with the increase of pressure. This can be explained by
the predominance at the higher temperature of the effect of collisional transfer over that of dimerization, which also explains the temperature dependence of the slope of the viscosity-pressure curve. However, due to the approximations involved in the calculations the results obtained should be considered as more qualitative than quantitative.

It may also be seen from table 1 that although the agreement is slightly better on the 12-6-3 model, it is also possible to explain the pressure dependence of the viscosity of steam on the Lennard-Jones (12:6) model. This perhaps supports the observation of Mason and Monchick\(^{10}\) about the insensitivity of viscosity to the long-range dipole forces.

References.


