diagrammatically in the accompanying graph. It has been found that there is a large temperature variation of $\chi_\perp - \chi_{||}$, the difference between the principal susceptibilities. It varies from $46\cdot4 \times 10^{-6}$ at about $90°$ K. to $36\cdot8 \times 10^{-6}$ at about $700°$ K. On the other hand, $\chi_\perp$, the susceptibility at right angles to the symmetry axis, has been found to vary quite slowly with temperature, namely from $-45\cdot01 \times 10^{-6}$ at $90°$ K., to -43×10^{-6} at $566°$ K. Details of these investigations will shortly be published elsewhere.

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Viscosity of Ordinary Liquids at High Rates of Shear

THE viscosity, η, of a fluid can be represented by[1]

$$\eta = \left(\frac{N}{V}\right)^{2/3} \cdot \frac{c.(2.\pi.m.k.T)^{1/2} R.T}{E_T} \cdot e^{\frac{E_{\text{visc.}}}{R.T}}, \quad (1)$$

where N is Avogadro's number; c is a packing factor; m is the mass of a molecule; k is Boltzmann's constant; $E_{\text{visc.}}$ is the energy of activation of viscous flow; V is the molecular volume; E_T is the sum of the potential and the kinetic energy of the molecules. We have found that E_T can be expressed as the sum of the latent heat of vaporization ($\triangle E_{\text{vap.}}$) and a multiple of $R.T$ ($d.R.T$). It has been shown[2] that $E_{\text{visc.}}$ equals the work of cohesion for non-associated liquids, and from this fact it was deduced that $E_{\text{visc.}}$ equals the bond energy between two interacting molecules. Further, it has since been deduced that $\triangle E_{\text{vap.}} = b.E_{\text{visc.}}$, where b is a factor depending on the mean co-ordination. Thus both $\triangle E_{\text{vap.}}$ and $E_{\text{visc.}}$ depend on the number of bonds per mole, formed by the interaction of the molecules.

The number of closed bonds, N', will, apart from the mean co-ordination, be a function of the co-ordination frequency, z, that is, $N' = f(z)$, and to a first approximation $N' \propto 1/z$. In a stationary liquid the molecules are in thermal agitation and z will have a certain value, depending on the temperature. In a liquid under flow, 'agitation of flow' will be superimposed on the thermal agitation. If z_1 is the co-ordination frequency in the stationary liquid and z_2 that frequency in the moving liquid, then f, the ratio of the number of closed bonds in the moving liquid, n, to that in the stationary liquid, N', will be given by

$$f = \frac{n}{N'} = \frac{z_1}{z_2} \quad . \quad . \quad . \quad (2)$$

For z_2 one may write $z_1 + z_3$, where z_3 is the increase in co-ordination frequency due to viscous flow. If the molecular layers are moving with relative velocity v_r and the intermolecular distance is λ, then $z_3 = v_r/\lambda$. It is to be noted that z_3 according to this definition is also equal to the rate of shear in the liquid. So long as $z_1 \gg z_3$, the factor f will be practically equal to 1 and $\triangle E_{\text{vap.}}$, $E_{\text{visc.}}$ and η will be independent of

the rate of shear. When z_3 approaches values comparable with z_1, f will no longer be unity, and both $\triangle E_{\text{vap.}}$ and $E_{\text{visc.}}$ will be reduced to a fraction f of their value. Then equation (1) becomes

$$\eta = \left(\frac{N}{V}\right)^{2/3} \cdot \frac{c.(2.\pi.m.k.T)^{1/2} R.T}{f.E_{\text{vap.}} + d.R.T} \cdot e^{\frac{f.E_{\text{visc.}}}{R.T}} \quad . \quad (3)$$

To evaluate $f: z_3$, the rate of shear, is given by the experimental conditions; z_1 can be obtained approximately from the coefficient of self-diffusion, D; D will be approximately of the same order of magnitude as the coefficient of diffusion observed in solutions. Using the Stokes-Einstein relation, one obtains

$$z_1 = \left(\frac{N}{V}\right) \frac{k.T}{6.\pi.\eta} \cdot \quad . \quad . \quad . \quad (4)$$

Using equations (3) and (4), the viscosity of n-pentane at $36°$ C. and at high rates of shear was calculated (see graph). One can see that the viscosity of n-pentane will reveal its dependence on the rate of shear at a value of approximately 5×10^6 sec.$^{-1}$ of the latter.
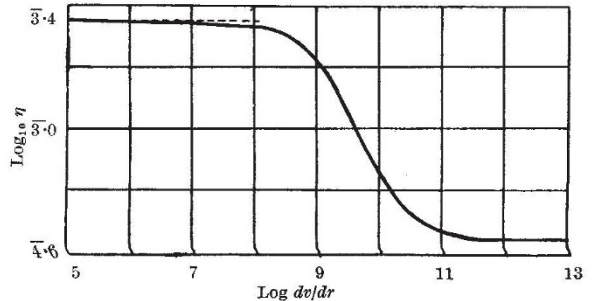
From equation (4) one can deduce that

$$z_1 \times \eta_0 \times V = \text{constant,}$$

at constant temperature and very nearly

$$z_1 \times \eta_0 \times M \sim \text{constant,} \quad . \quad . \quad . \quad (5)$$

where η_0 signifies the 'Newtonian' viscosity and M the molecular weight. The value of z_3 at which the viscosity will become markedly dependent on the rate of shear will be about 10^3 times smaller than z_1. Let $(dv/dr)_{\text{lim.}}$ be the value of the rate of shear at which the effect can be observed, then one may write

$$(dv/dr)_{\text{lim.}} x\eta_0 = \frac{\text{constant}}{M} = \text{limiting shear stress.}$$

For n-pentane at $30°$ C. the limiting shear stress is found to be about 10,000 dynes/cm.^{2}.

From the theoretical considerations brought forward, one may conclude that at high rates of shear the viscosity of 'Newtonian' liquids may be expected to become a function of the rate of shear. The value of the rate of shear at which the effect becomes perceptible depends on the relative magnitude of the thermal agitation of the molecules and the 'agitation of flow'.

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