stresses gives the viscosity which is to be compared to the Newtonian viscosities of other liquids.

Smallwood[28] has applied Eq. (14) in the form

$$\eta = A f e^{(a-bf)/T} \tag{15}$$

to the experimental data of Mooney[30] on the viscosity of raw rubber as a function of temperature and shearing stress. A graphical evaluation of the constants gave: $A=1.65\cdot 10^{-4}$, $a=5100$, $b=1.28\cdot 10^{-5}$. Using these constants the equation gave good agreement with experiment for shearing stresses between 840,000 and 1,880,000 dynes/cm² and at temperatures of 70 to 140°C.

The constant a is equal to $\Delta E_{\text{vis}}/R$, so that $\Delta E_{\text{vis}}=10.1$ kcal. Raw rubber consists of linear polymers of isoprene of the order of 1000 isoprene units per chain. Such a chain would not move a whole chain length per unit flow process, but probably only the length of several isoprene units as Smallwood has suggested. The energy of vaporization of isoprene at 25° is 5.7 kcal./mole. At the higher temperatures of these experiments this energy would be less, and also the energy of vaporization per isoprene unit in rubber would be somewhat less than the energy of vaporization for an isolated isoprene molecule. If we assume then that the energy of vaporization of rubber per isoprene unit is about 4 kcal. and that $n=4$ for this molecule, the energy of activation for flow per isoprene unit would be 1 kcal. This leads to the conclusion that during the flow process, the rubber molecule moves about 10 isoprene units.

The constant b is equal to $\lambda_2\lambda_3\lambda/2k$ and substituting the experimental value we have

$$\lambda_2\lambda_3\lambda/2k = 1.28\cdot 10^{-5},$$
$$\lambda_2\lambda_3\lambda = 3.51\cdot 10^{-21}\ \text{cc.}$$

Now assume the length of the isoprene unit, λ_2, is 5A and the thickness, λ_3, is 4A. The last paragraph showed that $\lambda=10\lambda_2$, or $\lambda=50$A. These values give $\lambda_2\lambda_3\lambda=1\cdot 10^{-21}$ cc, in fair agreement with the above experimental value. The factor of 3.5 might mean, as Smallwood suggests, that a bundle of 3 or 4 hydrocarbon chains moves as a unit.

Equation (14) represents the viscous behavior of a non-Newtonian liquid, or more accura[tely] of a non-Newtonian state of flow. The equa[tion] has, however, both upper and lower limits [of] applicability. On the side of very small stre[sses] the equation is not valid when $f\lambda_2\lambda_3\lambda/2kT<1$ and on the side of large stresses the wh[ole] development is invalid when $f\lambda_2\lambda_3\lambda/2=\Delta E_a$.

Flow in Crystals

When a liquid crystallizes the viscosity usu[ally] increases by a factor of approximately 10^{12}. Th[e] energy of activation for flow is obviously m[uch] greater in the crystal, and it seems likely th[at] the regular structure of the crystal requir[es a] *whole* molecule-sized hole, and therefore *all* th[e] energy of vaporization (sublimation) to activ[ate] the flow process, compared to the $\frac{1}{3}$ or $\frac{1}{4}$ th[e] energy of vaporization in the case of liqu[ids]. Since the best of fusion is relatively sm[all] ΔE_{vis} for the crystal should be about 3 o[r 4] times ΔE_{vis} for the liquid, if the two entrop[ies] of activation for flow are the same.

The only substance for which viscosity mea[s]urements on both liquid and crystal are avail[able] is menthol, shown in Fig. 11. The slope of th[e] liquid line gives $\Delta E_{\text{vis}}=12{,}000$ cal. and the slo[pe] of the crystal line gives $\Delta E_{\text{vis}}=34{,}000$ c[al.] Since the entropies of activation for flow w[ill] probably be different for liquid and crys[tal] the approximate ratio of 3 between the t[wo] values of ΔE_{vis} is satisfactory. The energies [of] vaporization of liquid and crystalline ment[hol] have never been measured.

The high viscosities of glasses and crys[tals] differ in an important respect. High viscosity [of] a glass is accompanied by a correspondin[gly] small vapor pressure, while the vapor pres[sure] of a crystal is relatively high. Fig. 12 illustr[ates] this point. When a liquid is cooled the flui[dity] and the vapor pressure both decrease as [dis]cussed in an earlier section. At the freezing p[oint] the liquid may crystallize decreasing the flui[dity] enormously (by a factor of about 10^{12}), w[hile] the vapor pressure remains unchanged. H[ow]ever, if the liquid supercools, the fluidity a[nd] the vapor pressure continue to decrease with[out] any discontinuity (dotted line in Fig. 12), a[nd] only when the vapor pressure has become exce[ed]ingly small does the fluidity become very sm[all].

Conclusion

The conc ... ticle can ... antitative ... ively in c ... application

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