

These results cannot be taken as applying to metal in forms other than filings; X-ray photographs of a piece of hammered copper wire, for example, showed little change after several weeks at room temperature.

We hope to publish elsewhere a more detailed account of this work.

HELEN D. MEGAW.

Material Research Laboratory,
(Philips Lamps, Ltd.),
Mitcham Junction, Surrey.

H. LIPSON.
A. R. STOKES.

Cavendish Laboratory,
Cambridge.
June 22.

¹ Wood, *J. Sci. Instrum.*, **18**, 153 (1941); *Nature*, **151**, 585 (1943).

² Brindley, *Proc. Phys. Soc.*, **52**, 117 (1940).

³ Stokes, Pascoe and Lipson, *Nature*, **151**, 137 (1943).

⁴ Smith and Stickley, *Phys. Rev.*, **64**, 191 (1943).

⁵ Wood, *Proc. Roy. Soc. A*, **172**, 231 (1939).

⁶ *Proc. Phys. Soc.*, **54**, 487 (1942).

⁷ *J. Inst. Metals*, **69**, 149 (1943).

⁸ "Handbook of Chemistry and Physics" (Chemical Rubber Publishing Co., Cleveland, Ohio, 24th edition, 1940), pp. 1656-61.

Energy of Viscosity as a Measure of the Cohesion of Liquids

THE viscosity of a liquid can usually be represented by

$$\eta = A.e^{E_{\text{visc.}}/RT},$$

where η is the viscosity; A is a constant; $E_{\text{visc.}}$ is the energy of viscosity; R is the gas constant; T is the absolute temperature. In connexion with other work, it was deduced that the energy of viscosity should equal the work of cohesion for unassociated and non-metallic liquids. The work of cohesion has been defined by Harkins¹ as the energy required to form a surface in a liquid and is equal to twice the surface energy. Now if both the energy of viscosity and the work of cohesion are expressed as calories per mole, they are nearly equal for unassociated liquids.

At 20° C. Substance	$E_{\text{visc.}}$ cal./mole	Work of cohesion cal./mole
<i>n</i> -octane	2,040	1,928
<i>n</i> -hexane	1,815	1,920
Benzene	2,515	2,322
Acetone	1,668	1,676
Carbon tetrachloride	2,510	2,290
1,2 dibromoethane	2,790	3,056
1,2 dichloroethane	2,320	2,394

For associated and some polar substances the energy of viscosity is greater than the cohesive work. The factor connecting the two quantities varies between 1.5 and 3.5.

At 20° C. Substance	$E_{\text{visc.}}$ cal./mole	Work of cohesion cal./mole
Methyl chloride	1,592	948
Methyl alcohol	2,475	1,076
Ethyl alcohol	3,290	1,380
<i>n</i> -propyl alcohol	4,390	1,610
Water	4,150	2,020

The values of $E_{\text{visc.}}$ were obtained by graphical differentiation of the $\ln \eta$ versus $1/T$ curves, while the work of cohesion was calculated as twice the surface energy of one mole occupying the surface according to the equation:

$$E_s = 2.39 \times 10^{-8} \gamma V^{2/3} N^{1/3},$$

where E_s is the surface energy in calories per mole; γ is the surface tension in dynes per cm.; V is the molar volume; N is Avogadro's number.

Now if the energy of viscosity equals the work of cohesion, it should be proportional to the energy of attraction between molecules. According to prevailing views², the attraction between non-polar molecules is inversely proportional mainly to the sixth power of the distance separating the molecular centres. The attraction between polar molecules is said to be inversely proportional to the third power of that distance. The relationship between $E_{\text{visc.}}$ and the distance between the molecular centres was tested by plotting $\log E_{\text{visc.}}$ against $\log 1/r$, where r is the separation of the molecular centres and can approximately be deduced from the molar volume. The slope of the curve of $\log E_{\text{visc.}}$ v. $\log 1/r$ should have a value of 6 for non-polar substances and a value of 3 for polar substances. *n*-Pentane gave a value for the slope of approximately 5.52; 1,2 dibromoethane a value of 5.75; carbon tetrachloride a value of 6.03. On the other hand, methyl chloride, which is a polar substance, gave a slope of 2.89.

Thus $E_{\text{visc.}}$, the energy of viscosity, equals the work of cohesion in the case of unassociated substances and is quite generally a measure of the attraction between molecules.

L. GRUNBERG.

Dr. Rosin Industrial Research Co.,
Wembley.

A. H. NISSAN.

Department of Oil Engineering
and Refining,
University of Birmingham.

¹ Harkins *et al.*, *J. Amer. Chem. Soc.*, **43**, 35 (1921).

² London, *Trans. Farad. Soc.*, **33**, 8 (1937).

Existence of Time-Dependence for Interfacial Tension of Solutions

It has been known for some time^{1,2} that the surface tension (air-liquid boundary) of aqueous solutions of long-chain compounds decreases slowly over a period of many days before an equilibrium value is reached. This slow decrease cannot be attributed to diffusion of the solute to the surface, for with the usual values of the diffusion coefficient the calculated time of the change should be a very small fraction (about 10^{-7} - 10^{-8}) of the observed time³. With a solute in the aqueous phase, adsorbed at an oil/water boundary, the interfacial tension has been found to reach its equilibrium without a time-lag³, and it has been commonly assumed that interfacial tension (as distinct from surface tension) is not subject to this slow change.

We have measured interfacial tensions at the interface between water and solutions in hexane of long-chain amphipathic substances. Experiments by a precision drop-weight method⁴ showed that the interfacial tension varied with time. The variation has been studied by means of measurements made by the pendent-drop method⁵, which allows continuous readings to be made without disturbing the surface.

The interfacial tension has been found to fall, rapidly at first and then more slowly, reaching an equilibrium value after some days. This fall is much slower than can be explained by diffusion to the surface. With lauric acid as the solute, a diffusion