

the viscosity of water increases with pressure, and that below this temperature, initially the pressure effect is negative but at about 1,000 kg/cm² the viscosity relative to 1 atm. exhibits a minimum. Presumably at this pressure the structured regions occurring in water have been partially destroyed and the behaviour is more like that of a "normal" liquid.

Horne and Johnson¹ have recently published results obtained with a rolling-ball viscometer in the range 1–2,000 kg/cm² and in the temperature range 2° to 20° C. The results disagree with the low temperature measurements of Bett and Cappi². While Cappi's results suggest that the rate at which the negative coefficient changes between 20° C and 2° C is fairly uniform, Horne and Johnson's results indicate a gradual change until 4° C is reached, and below this temperature the pressure coefficient is shown to increase abruptly. This is apparent in Fig. 1 where it can be seen that Cappi's 10° C isotherm has a steeper slope than the 4° C and 6.2° C isotherms of Horne and Johnson, while Cappi's 20° C isotherm corresponds to the 10° results given by Horne and Johnson.

The temperature of 4° C is significant for water because at this point the effect of thermal expansion becomes greater than the contraction due to the thermal destruction of ordered regions of molecules. This gives rise to the well known minimum in the specific volumes at this temperature. Horne and Johnson's results indicate that at 4° C there is a sudden increase in the effect of pressure on viscosity while Cappi's observations show no sign of this.

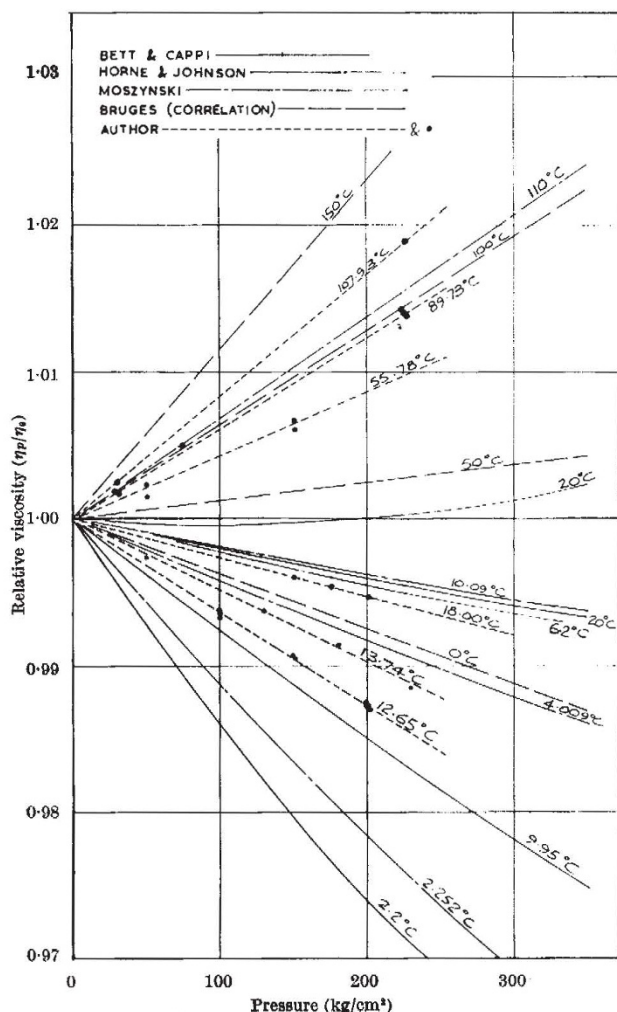


Fig. 1. Relative viscosity of water.

I have made preliminary measurements using a rotating cylinder viscometer, which has been previously described³, at pressures up to 230 kg/cm² and at temperatures between 12.5° C and 108° C. At low temperatures it can be seen that these results are in agreement with those of Bett and Cappi rather than with those of Horne and Johnson. At higher temperatures measurements are in agreement with other workers, including those of Moszynski⁴.

Discrepancies such as these present problems in the setting up of formulae representing the properties of water. The anomalous behaviour of water at low temperatures is not correctly indicated by published tables of values, examples of these being the Skeleton Tables of the International Steam Conference⁵ and the more recent correlation of Bruges, Latto and Ray⁶. There appears to be a need for more measurements at low temperatures and up to 1,000 kg/cm² to remove any doubts which may still exist.

JON WONHAM

Department of Mechanical Engineering,
University of Glasgow.

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¹ Horne, R. A., and Johnson, D. S., *J. Phys. Chem.*, **70**, 2182 (1966).

² Bett, K. E., and Cappi, J. B., *Nature*, **207**, 620 (1965).

³ Wonham, J., *Proc. Inst. Mech. Eng.*, 1965–66, **180**, Pt. 3J.

⁴ Moszynski, J. E., *J. Heat Transfer*, **83**, 111 (1961).

⁵ Sixth Intern. Conf. on the Properties of Steam, Suppl. on Transport Properties, publ. in *Engineer*, **219** (1965).

⁶ Bruges, E. A., Latto, B., and Ray, A. K., *Intern. J. Heat Mass Transfer*, **9**, 465 (1965).

Wettability and Adhesion of Polyethylene

THE linear relationship found experimentally by Barbarisi¹ between bond strength and $(1 + \cos \theta)$, where θ is the contact angle for epoxy-polyamide adhesive on polyethylene, is of technological importance and merits more careful analysis.

The relationship was arrived at on the basis of the well-known equation between the reversible work, W , required to separate liquid from 1 cm² of a solid surface, leaving adsorbed film on the surface in equilibrium with the liquid, and the contact angle

$$W = \gamma_{LV}(1 + \cos \theta) \quad (1)$$

where γ_{LV} is the surface tension of the liquid. This equation indicates that for a given liquid, the greater the degree of wetting of a surface, the stronger is the bond; a chosen solid which is completely wetted by the liquid will give $W = 2\gamma_{LV}$ (experimentally found bond strengths are invariably much less than theoretical values)².

Low energy solids, for example, polymers, can be characterized by their critical surface tension γ_c , a quantity which was found empirically by Zisman and co-workers³. The precise significance of γ_c is still uncertain, but Fowkes⁴ has shown that it is almost equal to γ_s^d —the dispersion force contribution to the surface tension of the solid. For polyethylene $\gamma_c = 31$ dyne/cm and $\gamma_s^d = 35$ dyne/cm. Because the surface tension of polyethylene will come from dispersion forces, it is justifiable in this case to write

$$\gamma_s = \gamma_s^d \approx \gamma_c \quad (2)$$

Only in the absence of better information is it reasonable to approximate γ_c for γ_s when dispersion forces are known to dominate.

Barbarisi¹ makes the statement that contamination on the surface (of polyethylene) will in general lower the value of γ_c , that is, reduce the ability of a liquid to wet the solid, and therefore recommends pretreatment of the surface. The following arguments demonstrate that

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the untreated surface used by Barbarisi is typical of polyethylene and that the treatments given increase γ_c above the literature value of $\gamma_c = 31$ dyne/cm.

Fowkes⁴ has shown that the angle of contact is related to the dispersion force contributions, γ_s^d and γ_{LV}^d , to the surface tensions of solid and liquid

$$\cos \theta = \frac{2(\gamma_s^d \gamma_{LV}^d)^{\frac{1}{2}}}{\gamma_{LV}} - \frac{\pi}{\gamma_{LV}} - 1 \quad (3)$$

where π is the spreading pressure (Zisman has shown that for low energy surfaces $\pi \approx 0$ if $\theta > 0$). For the epoxy-polyamide adhesive used by Barbarisi $\gamma_{LV} = 41.7$ dyne/cm. Equation (3) can therefore be used to calculate the expected contact angle for the adhesive on polyethylene, provided γ_{LV}^d can be obtained. The maximum value of γ_{LV}^d is γ_{LV} , and on the basis of comparison with the contribution of γ_{LV}^d to γ_{LV} of other organic liquids⁴, a minimum value of about $0.75 \gamma_{LV}$ or 30 dyne/cm is reasonable. When $\gamma_{LV} = \gamma_{LV}^d = 41.7$ dyne/cm, equation (3) gives $\theta = 33.3^\circ$ and, when $\gamma_{LV}^d = 30$ dyne/cm, $\theta = 56.6^\circ$. The values of θ given by Barbarisi are 35.4° on untreated polyethylene and 18.5° on polyethylene wiped with acetone and treated with acid (unknown) for 5 min at 70° . The untreated surface therefore most resembles polyethylene—a conclusion reached without invoking the concept of γ_c .

The empirical linear relation found by Zisman and co-workers³ can be written as

$$\cos \theta = 1 + b\gamma_c - b\gamma_{LV} \quad (4)$$

where $-b$ is the slope of $\cos \theta$ against γ_{LV} plots; γ_c will equal γ_{LV} when $\theta = 0$. This shows that the contact angle exhibited by a given liquid on different solids will depend on b as well as on γ_c . Equation (4) can be used to estimate the surface tension of a liquid which gives $\theta = 35.4^\circ$ on polyethylene, for Zisman³ established that $b = 0.026$. The result, $\gamma_{LV} = 38.1$ dyne/cm, compares favourably with $\gamma_{LV} = 41.7$ for epoxy-polyamide adhesive. It also indicates that the untreated surface is that of polyethylene. (It is also clear that the surface tension of the adhesive arises essentially from dispersion forces: $\gamma_{LV}^d \approx \gamma_{LV}$.)

The increased adhesion due to successive treatments of polyethylene must therefore be due to changes in its surface. (On the rough assumption that b does not alter, a surface giving $\theta = 19^\circ$ has $\gamma_c \approx 40$ dyne/cm.) The most comparable case found involves the results of de Bruyne⁶. The failing stress of epoxy resin/polyethylene bonds increased with decrease in the contact angle of water on surfaces oxidized with chromic acid, a trend which Zisman⁵ attributed to an increase in γ_c .

The considerations discussed help to give insight into factors involved in adhesion to plastics. It must, however, be mentioned that thermodynamic arguments give little direct information about the magnitude of shearing forces parallel to the surface required to break adhesive bonds, and that with polymers, part of the energy required to break an adhesive bond may be expended in causing deformation of the solid².

E. A. BOUCHER

School of Chemistry,
University of Bristol.

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¹ Barbarisi, M. J., *Nature*, **215**, 383 (1967).

² Eley, D. D., and Tabor, D., in *Adhesion* (edit. by Eley, D. D.), chapter 1 (Oxford University Press, 1961).

³ Zisman, W. A., *Contact Angle Wettability and Adhesion* (edit. by Gould, R. F.), chapter 1 (Amer. Chem. Soc., Washington, D.C., 1964).

⁴ Fowkes, F. M., *Ind. Eng. Chem.*, **56**, 40 (1964), reprinted in *Chemistry and Physics of Interfaces* (edit. by Ross, S.), chapter 1 (Amer. Chem. Soc., Washington, D.C., 1965), and references therein.

⁵ Zisman, W. A., *Ind. Eng. Chem.*, **55**, 19 (1963).

⁶ de Bruyne, N. A., *Nature*, **180**, 262 (1957).

CHEMISTRY

Band Width of the OH-stretching Vibration in Solid Alcohols

THERE have been many theories¹ advanced to explain the extremely broad OH-stretching vibration (ν OH) in hydrogen bonded molecules. None of these theories fully explains the ν OH band width for all types of hydrogen bonded systems and many of the theories cannot be tested experimentally. We wish to report experimental evidence that the OH-stretching vibration in solid alcohols is not inherently broad, and that the breadth normally observed results from crystal interactions through nearest neighbour or first order coupling between OH groups along the hydrogen bond chain. Spectra of single crystals were obtained in a diamond window high pressure cell with techniques previously described². Low temperature spectra were obtained in a conventional Dewar cell.

It has been well established³ that intermolecular interactions associated with crystallinity can best be detected by isotopic dilution and mixed crystal studies. Fig. 1 shows such pertinent spectral data for various degrees of deuteration of solid *n*-decanol. With increasing dilution by *n*-decanol-OD, the ν OH sharp-broad doublet coalesces, and at high dilution becomes a singlet. At the same time, ν OD changes from a narrow singlet at low concentration to a sharp-broad doublet at high concentration analogous to the shape of ν OH in the pure OH compound. These deuteration studies leave no doubt that the appearance of two bands was caused by crystal splitting. Another equally important point is that the decoupled singlet OH band is quite narrow. In the lower spectrum of Fig. 1 we measured a half-band width of $30\text{--}40\text{ cm}^{-1}$ even though the deuteration was not sufficient to decouple completely the OH vibration.

The sharp-broad character of the coupled doublet is seen more clearly in Fig. 2. This shows polarized spectra of single crystals of *n*-decanol at both low and high pressure. At low pressure, the bands are completely separated by polarization into a sharp band at $3,410\text{ cm}^{-1}$ and a broad band near $3,320\text{ cm}^{-1}$. At high pressures, both ν OH components shift to lower frequencies, but the broad, lower frequency component shows a greater shift.

The explanation of these experimental observations can be seen with the aid of Fig. 3. Here we have assumed a

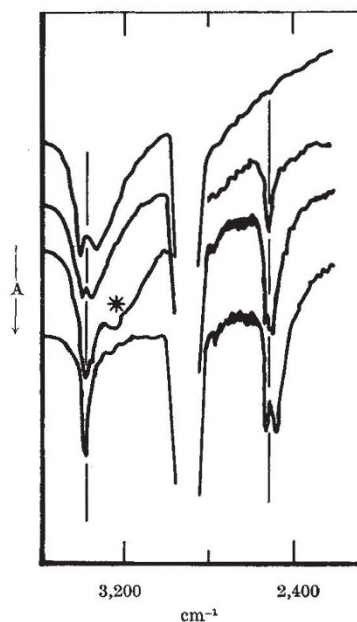


Fig. 1. Infra-red spectra of low temperature solids of deuterated *n*-decanol. OH/OD: 100/0, 85/15, 45/55, 25/75. *Water.