173. *Calculated Surface Tensions of Some Organic Substances in the Solid State.*

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The applicability of the contact-angle method for the estimation of surface tensions of solids is discussed. Values for the surface tensions of four solid organic substances near their melting points are calculated from contact-angle data, and found to be slightly lower than those of the corresponding liquids.

WHEN a drop of liquid is placed on a smooth solid surface, it may exhibit a variety of contact angles, depending on, *inter alia*, whether the liquid is advancing or receding over the surface, and whether or not the liquid and the solid phase are mutually saturated. In the system liquid–solid–air, when all phases are in equilibrium (*i.e.*, mutual saturation, adsorption, etc., have occurred) an equilibrium contact angle θ_E will be obtained, given by

$$\cos \theta_E = (\gamma_{SA} - \gamma_{LS})/\gamma_{LA} \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where γ_{SA} is the equilibrium free-surface energy (surface tension) of the solid–air interface, and γ_{LS} and γ_{LA} are the corresponding values for the liquid–solid and liquid–air interfaces.

It is not possible to use equation (1) to predict the value of θ_E in a given system, since no reliable method exists for determining either γ_{SA} or γ_{SL}. It has, however, been suggested by Loman and Zwikker (*Physica*, 1934, **1**, 1181), and more recently by Elton (*J. Chem. Physics*, 1951, **19**, 1066), that measurements of contact angles might lead to information concerning γ_{SA} and γ_{SL}.

It has been found that for two mutually saturated liquids an empirical rule due to Antonoff (*J. Chim. physique*, 1907, **5**, 372) often holds, *viz.*, that the interfacial tension between two immiscible phases is equal to the difference between the individual surface tensions of the (saturated) phases. There is, unfortunately, no theoretical basis for this rule at present, but it is true for the large majority of liquid pairs. If this rule is assumed to hold at a liquid–solid interface we obtain the equation, for mutual saturation of all phases,

$$\gamma_{SL} = |\gamma_{SA} - \gamma_{LA}| \qquad \qquad \qquad (2)$$

From (1) and (2) if $\gamma_{SA} > \gamma_{LA}$ we obtain

$$\cos \theta_E = 1 \qquad \qquad \qquad (3)$$

the case corresponding to complete wetting of the solid by the liquid; and for $\gamma_{LA} > \gamma_{SA}$ we obtain

$$\gamma_{SA} = \gamma_{LA}(1 + \cos \theta_E)/2 \qquad \qquad \qquad (4)$$

By this equation a value for the surface tension at the solid–air interface can be calculated. Loman and Zwikker (*loc. cit.*) determined the contact angles of water and mercury drops on various polished geological specimens, and obtained in each case agreement to about 5% between the values of γ_{SA} for a given specimen, using the two reference liquids. Elton (*loc. cit.*) calculated values for the surface tension of (saturated) paraffin wax from contact angles of glycerol, glycol, and water, obtaining values in close agreement with each other, and of about the same magnitude as those for other long-chain hydrocarbons in the liquid state, the agreement presumably indicating that saturation with the different liquids produces little change in the solid–air tension. Fox and Zisman (*J. Colloid Sci.*, 1952, **7**, 109) determined contact angles of a large number of liquids against solid polytetrafluoroethylene, but the calculated values of γ_{SA} varied widely. No evidence was given, however, that mutual saturation was ensured in this case, although, even if this were so, the variation might be real, owing to alteration of the surface tension of the solid on saturation with the various liquids. Furthermore, deviations from Antonoff's rule might be occurring.

The investigation reported here was designed to attempt to clarify the situation concerning the applicability of equation (4) in various ways.

(a) *Use of Antonoff's rule.* Various organic solids were used, with water as the reference liquid. All the solids had low melting points, and their surface tensions, and interfacial tensions against water (mutually saturated in each case), were determined just above the melting points, in order to check that Antonoff's rule applied for the liquid–liquid–air system. The substances chosen for study, *viz.*, *n*-hexadecane, *n*-octadecane, diphenyl ether, and acetophenone, had convenient m. p.s (15—30°) and fairly low mutual solubility with water, and were regarded as unlikely to undergo the kind of interaction with water which leads to deviation from Antonoff's rule (*e.g.*, substances containing hydroxyl groups, or substances which tend to hydrolyse—acids, esters, carbon disulphide, methylene iodide, etc.—tend to deviate from Antonoff's rule with water). As seen from the agreement between the last two columns in Table 1, Antonoff's rule was obeyed in

TABLE 1.

System	Temp.	γ_{OA}	γ_{WA}	$\gamma_{WA} - \gamma_{OA}$	γ_{WO}
COMePh–H_2O	25°	36·1	49·9	13·8	13·8
Ph_2O–H_2O	30	38·1	69·4	31·3	31·2
$C_{18}H_{38}$–H_2O	30	26·6	63·0	36·4	36·4
$C_{16}H_{34}$–H_2O	25	28·1	69·0	40·9	40·6

each case. It was very difficult to remove small traces of heptadecanol from the octadecane used in these experiments, and the results quoted for this substance must be

accepted with some reserve. In particular, γ_{WA} in this case is lower than might be expected if the hydrocarbon were completely pure. However, the results are of interest in showing the relation between the surface tension of this substance in the liquid form and the calculated value for the solid, and are therefore included.

(b) *Mutual saturation.* Very careful precautions to ensure mutual saturation were taken (see Experimental section).

(c) *Value of the surface tension.* Measurements of the surface and interfacial tensions of the liquid–liquid–air system were made at three temperatures just above the m. p. of the organic substance, to enable extrapolation of its surface tension in the liquid form to a temperature just below the m. p. at which γ_{SA} was calculated from contact-angle measurements. This enabled comparison of the calculated surface tension of the solid with the surface tension of the liquid at the same temperature.
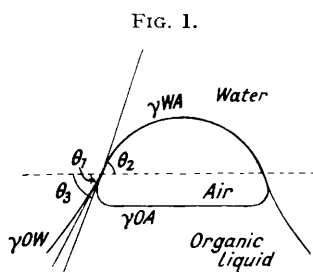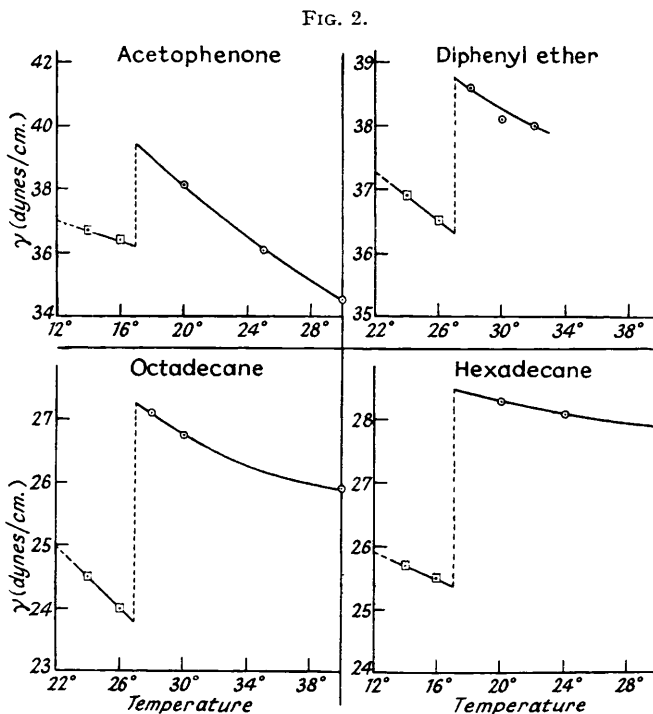
FIG. 2.

FIG. 1.

(d) *Preliminary check by use of liquid–liquid–air systems.* As a check on the calculation of an unknown surface tension from known tensions and measured contact angles, some measurements were made in liquid–liquid–air systems, where all the surface and interfacial tensions are directly measurable. The systems diphenyl ether–water–air and acetophenone–water–air were studied by a method in which a free air bubble at a liquid–liquid interface is observed. The mutually saturated liquids (saturated also with respect to air) were placed together in a square-section optical glass cell in the thermostat, and an air bubble released in the (lower) organic layer. This rose to the interface and was held there, and when equilibrium was reached, after several hours, the bubble was of shape shown in Fig. 1. By the usual method we obtain

$$\gamma_{WO} \cos \theta_1 + \gamma_{OA} \cos \theta_3 = \gamma_{WA} \cos \theta_2$$

Hence, if the surface tensions γ_{OA} and γ_{WA} are known, and $\theta_1, \theta_2, \theta_3$, are determined from a photograph of the bubble, a value for the interfacial tension γ_{WO} can be obtained and compared with the measured value. As seen from Table 2, which gives typical results for several bubbles, calculated and measured values of γ_{WO} were in good agreement,

indicating that the method of calculation from contact angles is certainly valid for a liquid–liquid–air interface.

The results for contact angles and the calculated surface tensions of the various saturated solids at temperatures just below their m. p.s are given in Table 3, all tensions being in dynes/cm., and these are shown in relation to the surface tensions of the corresponding saturated liquids in Fig. 2. The general form of the surface tension–temperature graph is the same for all four substances. In each case the surface tension of the solid, at or near its m. p., as calculated from equation (4), is found to be 2—3 dynes/cm. lower than the corresponding liquid tension. The loss in surface energy is presumably part of the general loss in energy occurring on solidification.

TABLE 2.

System	Temp.	γ_{WA}	γ_{OA}	θ_1	θ_2	θ_3	γ_{WO} Calc.	γ_{WO} Found
COMePh–H_2O ...	25°	49·9	36·1	49·0	56·0	56·5	13·2	13·8
	25	49·9	36·1	39·0	51·0	55·0	14·4	13·8
	25	49·9	36·1	33·0	41·0	44·0	13·9	13·8
Ph_2O–H_2O	30	69·4	38·1	25·0	49·5	65·5	31·3	31·2
	30	69·4	38·1	52·0	85·5	110·0	31·0	31·2

TABLE 3.

System	Temp.	θ_E	γ_{LA}	γ_{SA} (calc.)	System	Temp.	θ_E	γ_{LA}	γ_{SA} Calc.
COMePh (S)–H_2O (L)	16°	64·5	51·0	36·4	$C_{18}H_{38}$ (S)–H_2O (L)	26°	105·0	65·0	24·0
Ph_2O (S)–H_2O (L)...	26	88·5	71·1	36·5	$C_{16}H_{34}$ (S)–H_2O (L)	16	106·0	70·5	25·5

These results indicate that, provided proper attention be paid to the attainment of mutual saturation, and to ensuring that the system is one likely to obey Antonoff's rule, reasonable results for the surface tension of an air–solid interface may be obtained. A check on the numerical values of the results obtained must await the formulation of an independent method of determining such tensions, but it is submitted that results of the kind presented here will give at least a rough guide to the magnitude of the surface tensions of low-energy solids of the kind studied.

Solids with high surface tensions (metals, ionic crystals, etc.) will present difficulties, however, since in order for a liquid to show a non-zero contact angle, it must have a surface tension greater than that of the solid. Few liquids of very high surface tension are available, except mercury, which is very difficult to obtain surface pure and may show differences in surface tension for different degrees of contamination. Furthermore, no advantage is obtained by replacing the air with another liquid and measuring angles in a liquid–liquid–solid system, since a calculation similar to that given above shows that in order to obtain a non-zero angle in such a system, the surface tension of the solid must be between those of the two liquids, so it is again necessary to find one liquid with a surface tension higher than that of the solid.

EXPERIMENTAL

Materials.—*n*-Hexadecane and *n*-octadecane were samples kindly supplied by Messrs. Shell Mex and B.P. Ltd., and were purified by mechanically stirring them at 2° above their m. p.s with several changes of concentrated sulphuric acid until no further darkening of the latter occurred. (The octadecane, which contained a little heptadecanol, required 30 hours' stirring, with frequent changes.) They were washed several times with dilute sodium carbonate solution, followed by distilled water, dried ($CaCl_2$), filtered, and fractionally frozen eight times, some 10% being poured off each time. The resulting colourless crystalline solids had m. p.s : hexadecane 17·9°, octadecane 28·1°.

Diphenyl ether was a pure sample, manufactured by Messrs. L. Light and Co.; it was distilled, and the middle fraction fractionally frozen as described above; m. p. 28·0°. Acetophenone was purified in the same manner and had m. p. 17·9°.

Tap-water was found to be preferable to distilled water owing to its freedom from grease, and was used throughout.

Temperature Control.—In all the experiments described below, ranging from 15° to 40°, a water thermostat giving control to $\pm 0\cdot01°$ was used. The whole thermostat was mounted on an anti-vibration platform, since the drops and bubbles used in the surface-tension and contact-angle experiments were very sensitive to vibration.

Surface Tensions and Interfacial Tensions of the Liquids.—The pendant-drop method (Andreas, Hauser, and Tucker, *J. Phys. Chem.*, 1938, **42**, 1001) was used. The organic liquid was vigorously stirred mechanically with water for 10 hours in the thermostat at the temperature of measurement. When the two liquids were mutually saturated, a sample of either could be blown over, *via* all-glass connections, into a drop-forming pipette, suspended in a square-section optical glass cell in the thermostat. The air in the cell was kept saturated with respect to both liquids by the presence of saturated liquid in the cell. The profiles of the drops so formed were photographed with a Leitz " Makam 1 " camera on a microscope fitted with a 4″ objective. The thermostat stirrer was switched off for a few moments while the exposure was made to eliminate vibration. Measurements were made on the photographs of (1) D_e, the diameter of the drop at its greatest width, (2) D_s, the diameter at a distance equal to D_e above the base of the drop. The surface tension of the drop-forming liquid was then calculated from the equation $\gamma = g\rho D_e^2/H$, where g is the gravitational constant, ρ the excess density of the liquid, and H is a function of D_s/D_e given in tabular form by Fordham (*Proc. Roy. Soc.*, 1948, *A*, **194**, 1).

Contact-angle Determinations.—The solid organic surfaces were prepared by solidification of the liquid saturated with water. Solidification in air gave a crystalline surface too rough to give reproducible results. For this reason the organic substance was solidified between two cylindrically curved pieces of glass. The glass attached to the concave face of the solid was carefully removed and the surface polished with clean strips of paper (see MacDougall and Ockrent, *ibid.*, 1942, *A*, **180**, 151) until microscopic examination showed a smooth surface. The solid, still attached to the other piece of glass, was placed concave side downwards in the cell, with its axis in line with that of the microscope, and covered with water saturated with the organic substance. An air bubble was then placed on the solid, allowed to come to equilibrium, and photographed, the angle of contact being directly measured on an enlarged photograph. With experiments carried out in this way the angle obtained was found to be independent of the size of the bubble (sizes used, 0·05—0·3 cm.) provided it was allowed to come to equilibrium, indicating that the angle obtained was a true equilibrium one. The method of placing an air bubble under the plate was preferred to placing a liquid drop on the plate in air, owing to the smaller risk of contamination. The measured angles were reproducible to about $\pm 0\cdot5°$; the values given in Table 3 are the means of a large number of determinations.

Cleaning of Apparatus.—All glass apparatus was thoroughly cleaned in alcohol–nitric acid, washed many times in distilled water, and dried in an electric oven before use.

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