An Assessment of Interactions at the Polytetrafluoroethylene–Water Interface from Dynamic Contact Angle Studies

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Summary At very low interfacial velocities, the free energy per unit area of the P.T.F.E.–water interface includes both dispersive and polar components, while at higher velocities only the dispersive forces need be considered.

WE have measured the dynamic advancing contact angle, θ_A, for the water-saturated air–P.T.F.E. system at 22°. The P.T.F.E. surface was prepared from a high-purity sample, supplied by Prof. N. K. Adam through the courtesy of Imperial Chemical Industries, Ltd., by a method essentially similar to that described by Zisman and Fox.[1] The experimental technique has been described elsewhere.[2,3]

The dependence of θ_A upon dr/dt, the linear velocity with which the water–air interface is caused to advance over the solid surface, is shown in the Figure. At very small velocities, θ_A is sensibly constant at $\theta_{A,\min} = 109 \pm 1°$, this value being in good agreement with the static value of 108° found by Zisman and Fox[1] at 20° using the sessile-drop technique. Above dr/dt *ca.* $0{\cdot}6$ mm min^{-1}, θ_A increases until, when dr/dt exceeds 7 mm min^{-1}, it again becomes independent of the interfacial velocity, now having the higher value $\theta_{A,\max} = 115 \pm 1°$.

According to Young's equation,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \qquad (1)$$

where γ_{SV}, γ_{SL}, and γ_{LV}, respectively, are the free surface energies per unit area of the solid–vapour, solid–liquid, and liquid–vapour interfaces, θ being the equilibrium contact angle. If, as has been suggested elsewhere,[4] Young's equation is also valid under dynamic conditions provided the appropriate non-equilibrium values of the interfacial free energies are used then, since there is no reason to suppose that any of the three interfaces in the present system is modified by the presence of an adsorbed film, or that either γ_{SV} or γ_{LV} is dependent on dr/dt, it follows that $\theta_{A,\min}$ and $\theta_{A,\max}$ should be interpretable in terms of an increase in γ_{SL} as dr/dt is raised from zero to 7 mm min^{-1}. This increase, given by γ_{LV} ($\cos\theta_{A,\min} - \cos\theta_{A,\max}$), amounts to 7·6 erg cm^{-2} at the experimental temperature.

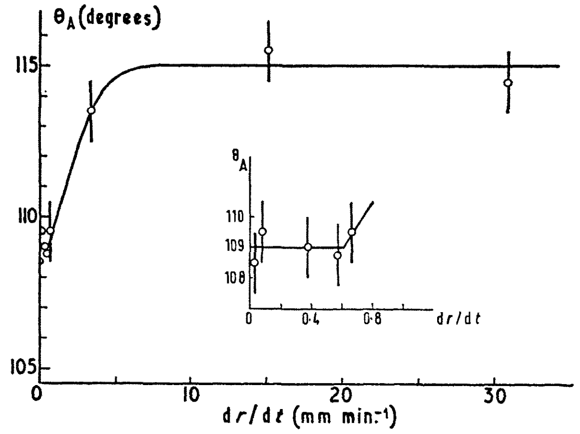

FIGURE. *The dynamic advancing contact angle,* θ_A, *for the P.T.F.E./water/saturated air system at 22°, as a function of dr/dt, the linear velocity of the water/saturated air interface.* (*Inset. Expansion of the low-velocity region.*)

If it be further assumed that, in the static or low-velocity region, γ_{SL} is determined solely by dispersive interactions then, following Fowkes,[5]

$$\cos\theta_A = -1 + 2\,(\gamma^d_{SV}\gamma^d_{LV})^{0\cdot5}/\gamma_{LV} \qquad (2)$$

where γ^d_{SV} and γ^d_{LV}, respectively, are the dispersive components of γ_{SV} and γ_{LV}. By considering systems wherein purely dispersive forces act across the solid–liquid or liquid–liquid interfaces, Fowkes has assessed γ^d_{SV} for P.T.F.E. as 19·5 erg cm^{-2}, and γ^d_{LV} for water as 21·8 erg cm^{-2}, at 20°. Applying these values in equation (2) with $\gamma_{LV} = 72\cdot8$ erg cm^{-2}, θ_A is calculated to be 116°, *i.e.* 8° higher than the static value observed by Zisman and Fox, but very close to our observed value for $\theta_{A,\max}$.

Bearing in mind the markedly polar nature of the C–F bond ($\mu = 1\cdot5$D), and the relative immobility of the C–F bonds in the surface of the polymer as compared to the ability of water molecules to assume preferred orientations at a solid–liquid interface, we suggest that for the static (equilibrium) case, or when the water–air interface is caused to advance slowly, γ_{SL} is determined by both dispersive and polar interactions, these latter causing the hydrogen atoms in the first water layer to tend to be directed towards the external (negatively charged) fluorine atoms in the surface. In the dynamic situation, it would then appear that, for $dr/dt \leqslant 0\cdot6$ mm min^{-1}, there is ample time for water molecules to assume their preferred orientation immediately behind the advancing water–air interface such that $\theta_{A,\min}$ is very close to the equilibrium value. At higher interfacial velocities, there is insufficient time, this leading to a measure of disorientation, the degree of which increases until, for $dr/dt \geqslant 7$ mm min^{-1}, the water molecules being laid down are completely disoriented. Interactions still obtain across the solid–liquid interface, however, since $\theta_{A,\max} \neq 180°$, and the agreement between $\theta_{A,\max}$ and θ calculated from equation (2) strongly suggests that these interactions are purely dispersive.

On this view, it follows that similar arguments should be applicable to other systems in which a polar liquid is placed upon a low-energy solid surface where the latter comprises markedly polar and unshielded, or incompletely shielded, bonds. It also follows that dynamic contact-angle studies should be made in such cases, and that caution should be exercised when attempting to assess static contact-angle measurements in terms of purely dispersive interactions.

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