NOTE

Kinetics of Liquid/Liquid Displacement

Cherry and Holmes (1) have recently offered a theoretical explanation of the observation (2) that the rate of spreading of certain polymers on solid surfaces is dependent upon the factor γ/η where γ and η are, respectively, the surface tension and viscosity of the polymer. In their model, the high viscosity of the polymer is the main influence controlling relaxation of the contact angle and spreading. They note, however, that with less viscous fluids, the nature of the solid surface will be more important.

In this communication we discuss the influence of the adsorptive properties of the solid surface on the movement of the three phase line formed with two fluids of normal viscosity (3). We obtain expressions giving the velocity dependence of the contact angle in terms of the rate constant of the molecular displacement process at the solid surface. This approach is complementary to the method of Washburn (4), in which the rate of capillary displacement is related to macroscopic properties of the system, including the contact angle (which may be permitted to vary (2)). The methods we use are similar to those of Cherry and Holmes, being based on the theory of absolute reaction rates as applied to transport processes (5); however, the mechanisms are very different and the final equations presented here are capable of simple verification.

Consider two mutually-saturated liquids, 1 and 2, in contact with each other and with a solid surface at a line of three phase contact (the TPL). Suppose that on the surface of the solid there are a large number of identical sites at which molecules of either liquid may be adsorbed. Since neither liquid completely wets the solid, the adsorption at the $S/1$ interface will differ from that at the $S/2$ interface, and the three phase *zone* (the TPZ) will constitute the region of transition from one adsorption condition to the other. Viewed even on a molecular scale, this transition may be somewhat abrupt; it is estimated (6) that the thickness of the fluid/fluid interfacial region in systems well below their critical temperatures may be between 2 and 5 Å, and it is reasonable to expect the TPZ to be of a similar thickness, spanning not more than one or two adsorption sites. However, the situation will not be static, for, at the molecular level, the TPZ constantly fluctuates about some mean position as adsorbed molecules of one species interchange with those of the other, either by surface migration or via the contiguous bulk phases. Nevertheless, when the system is at equilibrium the net rate of exchange will be zero.

Let the displacement of a molecule of phase 1 by one of phase 2 from a site in the TPZ define the forward, i.e. positive direction, and let the number of times this occurs in unit time along unit length of the TPL be K_+. Then application of the theory of absolute reaction rates (5) gives

$$K_+ = \left(\frac{kT}{h}\right)\frac{Z^*}{Z_+}\exp\left(\frac{-\epsilon_+}{kT}\right) \qquad [1]$$

where ϵ_+ is the activation energy for the process, and Z^* and Z_+ are the partition functions for the activated and initial states; the remaining symbols have their usual significance. The rate of molecular displacement in the reverse direction will likewise be

$$K_- = \left(\frac{kT}{h}\right)\frac{Z^*}{Z_-}\exp\left(\frac{-\epsilon_-}{kT}\right) \qquad [2]$$

At equilibrium, the net rate of exchange is zero;

$$\left.\begin{array}{ll}\text{thus} & K_+ = K_- \\ \text{and} & Z_-/Z_+ = \exp\,(\epsilon_+ - \epsilon_-)/kT.\end{array}\right\} \qquad [3]$$

It has been experimentally shown (3) that when one liquid displaces another in a uniform cylindrical capillary of such a radius, r, that gravitational distortion of the liquid/liquid interface may be ignored, then for sufficiently low rates of steady displacement, the pressure drop across the moving phase boundary is given by

$$\Delta p = \frac{2\gamma_{12}\cos\phi}{r} \qquad [4]$$

where γ_{12} is the interfacial tension of the 1/2 interface, and ϕ is the appropriate dynamic contact angle. At equilibrium, the same condition holds if ϕ is replaced by the equilibrium contact angle ϕ^0 (assumed here to be single valued):

$$\Delta p^0 = \frac{2\gamma_{12}\cos\phi^0}{r} \qquad [5]$$

In general, $\phi \neq \phi^0$, and the difference $\Delta p - \Delta p^0$ gives a measure of the additional (irreversible)

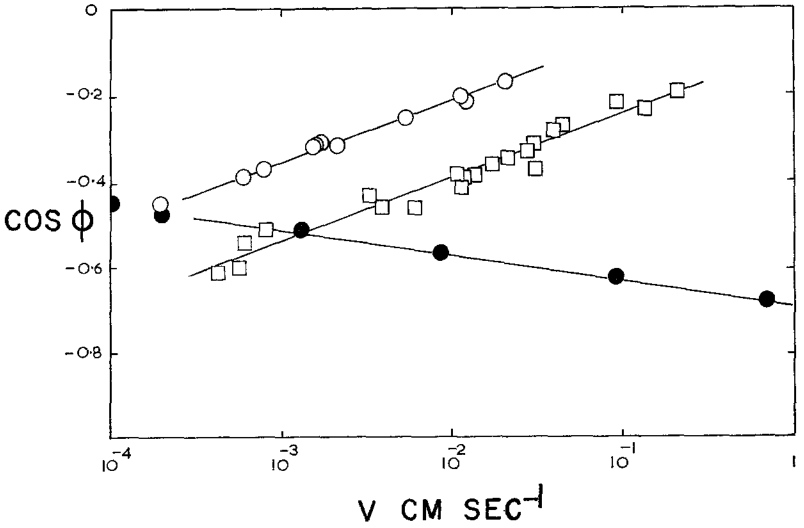

FIG. 1. Data from benzene/water displacements plotted according to [14]: ○—$B \rightarrow W$; ● — $W \rightarrow B$; (Tube A). □—$B \rightarrow W$; (Tube B).

work expended in moving the interface at some finite velocity.

The additional force needed to cause flow will not change Z_+ or Z_- (since liquids are virtually incompressible); it can be regarded simply as altering the energy barriers, ϵ_+ and ϵ_-, lowering one and raising the other. This results in movement of the TPZ in the favoured direction.

The work done by the additional force per unit displacement of unit length of the TPL is given by

$$W = \gamma_{12}(\cos\phi - \cos\phi^0) \qquad [6]$$

If this work is used entirely in raising or lowering ϵ_+ and ϵ_- then

$$W = \Delta n . \delta w \qquad [7]$$

where Δn is the number of sites affected at the two solid/liquid interfaces, per unit area of the solid surface, and δw is the work done on each site. This, of course, implies that the same amount of work is done on each site irrespective of whether or not it is initially occupied by a molecule of phase 1 or one of phase 2.

For positive W, ϵ_+, and ϵ_- will be, respectively, lowered and raised by the same amount, $W/\Delta n$, and the net displacement will be in the forward direction.[1]

$$K_{\text{net}} = \frac{kT}{h}\left[\frac{Z^*}{Z_+}\exp\left(\frac{W - \Delta n\epsilon_+}{\Delta nkT}\right) - \frac{Z^*}{Z_-}\exp\left(\frac{-W - \Delta n\epsilon_-}{\Delta nkT}\right)\right] \qquad [8]$$

$$= K_+ \exp\left(\frac{W}{\Delta nkT}\right) - K_- \exp\left(\frac{-W}{\Delta nkT}\right).$$

From [3], $K_+ = K_- = K$, say; hence

$$K_{\text{net}} = 2K \sinh\left(\frac{W}{\Delta nkT}\right) \qquad [9]$$

and the velocity of the TPL is

$$v = 2K\lambda \sinh\left(\frac{W}{\Delta nkT}\right), \qquad [10]$$

where λ is the average distance between centers of adsorption sites. Combination of [6] and [10] yields

$$v = 2K\lambda \sinh\left[\left(\frac{\gamma_{12}}{\Delta nkT}\right) \cdot (\cos\phi - \cos\phi^0)\right] \qquad [11]$$

For $(\gamma_{12}/\Delta n)\cdot(\cos\phi - \cos\phi^0) \ll kT$, [11] simplifies to

$$v = \frac{2K\lambda\gamma_{12}}{\Delta nkT}(\cos\phi - \cos\phi^0) \qquad [12]$$

so that v is a linear function of $\cos\phi$. On the other hand, if $(\gamma_{12}/\Delta n)(\cos\phi - \cos\phi^0) \gg kT$,

$$v = K\lambda \exp\left[\frac{\gamma_{12}}{\Delta nkT}(\cos\phi - \cos\phi^0)\right] \qquad [13]$$

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[1] The change in ϵ_+ and ϵ_- will be $\pm W/\Delta n$ and not $\pm W/2\Delta n$, since a forward displacement can only occur at a site initially occupied by a phase 2 molecule, and a backward displacement only at a site initially occupied by a phase 1 molecule.

whence

$$\log v = \log K\lambda - \frac{\gamma_{12}\cos\phi^0}{2.303\Delta nkT} + \frac{\gamma_{12}\cos\phi}{2.303\Delta nkT} \qquad [14]$$

and a plot of log v against cos ϕ should give a straight line of slope $\gamma_{12}/2.303\Delta nkT$.

Figure 1 shows data obtained in this laboratory (3) plotted according [14]. Contact angles were measured from single frames of a micro-cine film of a benzene/water interface, moving along a cylindrical capillary tube under the influence of known, variable, hydrostatic pressures. Velocities were also measured from the film. The rate-dependence of contact angle determined in this way had earlier been shown (7) to agree well with that obtained from application of the Washburn equation to the variation of interfacial velocity with applied hydrostatic pressure. The glass tubes used were of about 0.2 mm radius, and were treated by exposure to trimethylchlorosilane vapour in a grease-free vacuum system prior to a displacement experiment. The results shown relate to two tubes differing slightly in their surface properties. Each graph is linear over a wide range of velocities. From the slopes, $\Delta n \simeq 5.2 \times 10^{13}$ cm^{-2} for benzene displacing water ($B \rightarrow W$), and $\Delta n \simeq 2.0 \times 10^{13}$ cm^{-2} for water displacing benzene ($W \rightarrow B$). The interfacial tension, γ_{12} is 35 dyne cm^{-1} so that $W/\Delta n \gg kT$ if $(\cos\phi - \cos\phi^0) > 0.1$. The use of [14] is thus appropriate. In principle, Δn should be a constant of the system; that it is dependent upon the direction of flow is possibly the result of assumptions made in formulating [7].

Cherry and Holmes' equivalent of [12] may be deduced from their Eqs. [3], [7], and [8].

In their notation

$$v = \frac{dp}{dt} = \frac{\gamma_{LV}\, x^2 y}{\eta V}(\cos\phi_\infty - \cos\phi) \qquad [15]$$

so that, for a material of high viscosity, cos ϕ should be proportional to the TPL velocity. The bulk viscosity η appears explicitly in [15] because Cherry and Holmes invoke the Eyring theory of bulk viscous flow (5), identifying its activation energy with that of surface flow.

The model used in deriving [14] requires ϕ^0 to be single valued. As with the Hansen and Miotto theory of contact angle hysteresis (6), given sufficient time, ϕ should relax to ϕ^0. The Hansen and Miotto theory predicts $(d\phi/dv)_{v=0} = 0$, whereas the Cherry and Holmes theory gives $(d\phi/dv)_{v=0} = \eta V/\gamma_{LV} x^2 y \sin\phi$ and [12] gives $(d\phi/dv)_{v=0} = -\Delta nkT/2K\lambda\gamma_{12}\sin\phi$. The behavior of ϕ at very low velocities should, therefore, provide an indication of the mechanism operative in a given case.

The data of Fig. 1(a) are of special interest since it is possible to determine ϕ^0 (119 ± 1°) and hence calculate K(5 × 10^2 sec^{-1}) assuming $\lambda \simeq (\Delta n)^{1/2}$. The value of λ (approx. 14 Å) is perhaps more realistic than the value of (V/xy) obtained by Cherry and Holmes (3.6 × 10^{-3} cm).

In conclusion, since [12] and [14] do not contain parameters specific to the capillary system for which they were derived, they are likely to be of general application to systems of normal viscosity that show velocity dependence of the contact angle. However, the apparent success of [14] in relating the data reported here is no guarantee of the correctness of the model used. Alternative activated processes might be involved such as non-Newtonian flow in the vicinity of the TPL, viscoelastic deformation of a soft substrate, or the adsorption/desorption of an additional surface active component.

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T. D. Blake[2]
J. M. Haynes

Department of Chemistry,
University of Bristol
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[2] Present address: Department of Chemistry, University of Texas, Austin.