Int. J. Heat Mass Transfer. Vol. 10, pp. 1633–1636. Pergamon Press Ltd. 1967. Printed in Great Britain

THE MEASUREMENT OF CONTACT ANGLES UNDER CONDITIONS OF HEAT TRANSFER WHEN A LIQUID FILM BREAKS ON A VERTICAL SURFACE

A. B. PONTER, G. A. DAVIES, W. BEATON and T. K. ROSS
Chemical Engineering Department, University of Manchester Institute of Science and Technology, Manchester

(*Received* 26 *May* 1967)

NOMENCLATURE

M = Mass, L = length, T = time, t = temperature.

A, area $[L^2]$;
K, thermal conductivity $[M\,L\,T^{-3}\,t^{-1}]$;
Q, heat transferred $[M\,L^2\,T^{-2}]$;
T, temperature $[t]$;
g, acceleration due to gravity $[L\,T^{-2}]$;
t, time $[T]$.

Greek symbols
θ, contact angle;
γ, surface free energy $[M\,T^{-2}]$;
γ^d, dispersion force contribution to the surface free energy $[M\,T^{-2}]$;
π, equilibrium film pressure $[M\,L^{-2}]$;
μ, viscosity $[M\,L^{-1}\,T^{-2}]$;
ν, kinematic viscosity $[L^2\,T^{-1}]$;
ρ, density $[M\,L^{-3}]$;
σ, surface tension $[M\,T^{-2}]$;
λ, heat of vapourization $[L^2\,T^{-1}]$;
Γ, peripheral mass flow rate $[M\,L^{-1}\,T^{-1}]$.

Subscripts
L, liquid;
S, solid;
SL, solid–liquid;
v, vapour.

INTRODUCTION

THE STUDY of liquid film flow and heat transfer to liquid films flowing over vertical surfaces has provoked a great deal of attention in recent years, considerable attention being paid to the stability of liquid films. Models have been proposed to predict liquid film breakdown and dry patch stability under heat-transfer conditions [1–5]. Most of these models have included the contact angle of the liquid at the point of breakdown. The lack of data on contact angles under these conditions has precluded any definite conclusions to be drawn. In this paper the pertinent theory relating to contact angle will be reviewed and an experimental method for measuring contact angles under isothermal and heat-transfer conditions presented, together with results for water on a copper surface over a temperature range 20–100°C.

THEORY

Consider a sessile liquid droplet on a horizontal solid surface in equilibrium with its vapour, Fig. 1. Then from Young's equation [6],

$$\gamma_S - \pi = \gamma_L \cos\theta + \gamma_{SL} \tag{1}$$

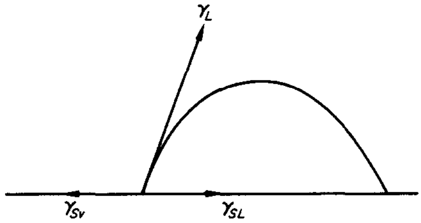

FIG. 1. Sessile liquid droplet.

where γ_S, γ_L and γ_{SL} are the surface free energies of the film free solid, liquid and solid–liquid interface respectively. π is the equilibrium film pressure and θ the contact angle. This equation allows the change in contact angle with temperature (t) to be expressed as

$$\frac{\mathrm{d}\cos\theta}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\gamma_S - \pi - \gamma_{SL}}{\gamma_L}\right). \tag{2}$$

To make a quantitive estimate of the temperature dependency of the contact angle the individual surface free energies and their change with temperature must be known. Fowkes [7] has shown, by considering the interactions of molecules in the surface regions between phases and interpreting them in terms of London dispersion forces, that the free energy of the solid–liquid interface, γ_{SL}, is given by

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d \cdot \gamma_L^d)^{\frac{1}{2}} \tag{3}$$

where γ_S^d and γ_L^d are the dispersion force contributions to the surface free energy in the solid and liquid respectively. By substituting equation (3) into equation (1) and (2)

$$\frac{\mathrm{d}\cos\theta}{\mathrm{d}t} = 2\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\gamma_S^d\,\gamma_L^d}{\gamma_L}\right)^{\frac{1}{2}} - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\pi}{\gamma_L}\right). \quad (4)$$

For some systems the dispersion forces have been determined but in general because of the difficulties in measuring the equilibrium film pressure [8, 9] equation (4) cannot be readily applied to specific systems with any confidence.

Some uncertainty exists in the reported behaviour of the change of contact angle with temperature. Davies and Rideal [10] on one hand have quoted values for $\mathrm{d}\theta/\mathrm{d}t$ on high energy surfaces of $-0{\cdot}06$°/degC whilst Fowkes and Harkins [11] quoted a value of $+0{\cdot}06$°/degC for water on low energy surfaces of paraffin wax and graphite. This latter result conflicts with the work reported by Neumann [12] who observed a steady decrease of contact angle of water and several organic liquids on a siliconed glass surface with increasing temperature. Phillips and Riddiford [16] have recently suggested that the temperature coefficient of contact angle for water on low energy surfaces should be zero.

If sufficient information is available for a particular system equation (4) can be used to obtain the contact angles over a range of temperatures. This data can then be used in models derived to predict breakdown of isothermal liquid films flowing over vertical surfaces. In the more complicated situation of liquid film breakdown initiated by heat transfer to the film, equation (4) could not be used to obtain a value for θ. In this case equilibrium conditions do not exist; the transient temperature gradients within the liquid would influence the contact angle. Insufficient data on the individual surface free energies are available to predict the effect of this even with the simplest physical model.

APPARATUS

The apparatus, illustrated in Fig. 2, consisted of a 1-l still and a cell fitted with optical flat surfaces mounted vertically above the still in which the copper specimen was positioned. This system is basically the same as that described in an earlier communication where contact angles were measured under mass-transfer conditions [13]. An electrical heating element was embedded in the copper block so that the temperature of the specimen surface could be accurately controlled to within 0·25 degC over the range 20–100°C. Care was taken in positioning the heating element to ensure a uniform surface temperature over the area of measurement. The surface was carefully prepared by polishing, to a mean surface roughness of less than 1×10^{-6} in measured on a Talysurf meter, degreasing and finally washing in distilled water.

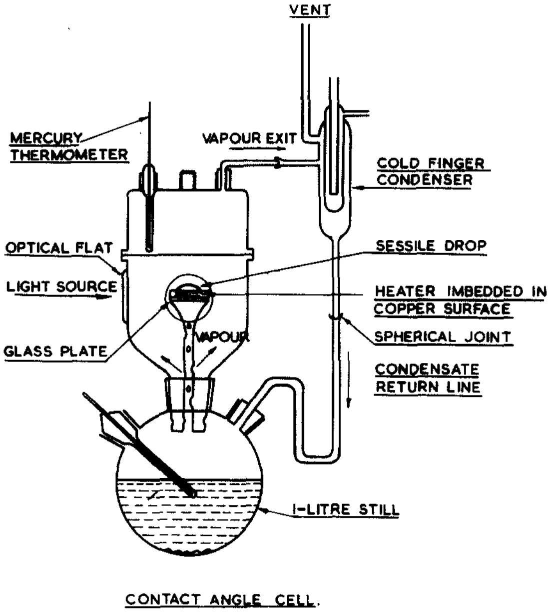

FIG. 2. Contact angle cell.

For measurement of contact angles under isothermal conditions, the temperature of the water in the still, the jacket temperature and surface temperature of the specimen were controlled at a pre-set value for each experiment. A liquid sample was then removed from the still, via the thermometer pocket and re-introduced into the cell to form a sessile drop on the specimen surface. Sufficient liquid was added to the drop to establish an equilibrium drop height [14]. When equilibrium had been reached the contact angle was measured using a travelling microscope fitted with a goniometer eyepiece. Six readings were taken at each temperature. The values were reproducible to ±0·5°. Under heat-transfer conditions the temperature of the specimen surface was controlled at a pre-set value. The temperature of the vapour space surrounding the specimen was maintained at 25°C for all measurements. A sessile liquid drop, initial temperature 25°C, was then placed on the specimen surface as before and the contact angles measured at 30-s intervals. Six sets of measurements were taken for each surface temperature, the contact angles being reproducible to ±1°. The results are shown in Figs. 3 and 4.

RESULTS AND DISCUSSION

The contact angles measured under isothermal conditions decreased steadily with increasing temperature over the whole range from 25–90°C. From Fig. 3 the graph θ vs. temperature is linear and the temperature coefficient for water on a smooth copper surface, $\mathrm{d}\theta/\mathrm{d}t$ is $-0{\cdot}1$°/degC. This value compares with that quoted by Davies and Rideal [10] for the change in contact angles on high energy surfaces of

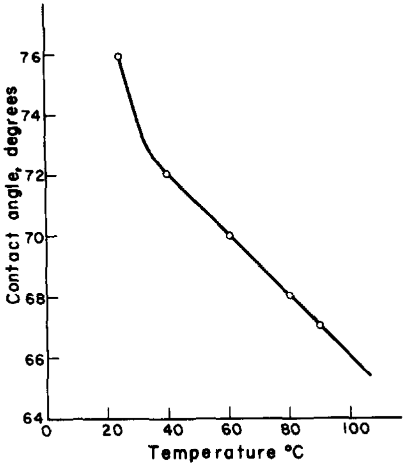

FIG. 3. Contact angle of a water drop on a smooth copper surface under isothermal conditions.

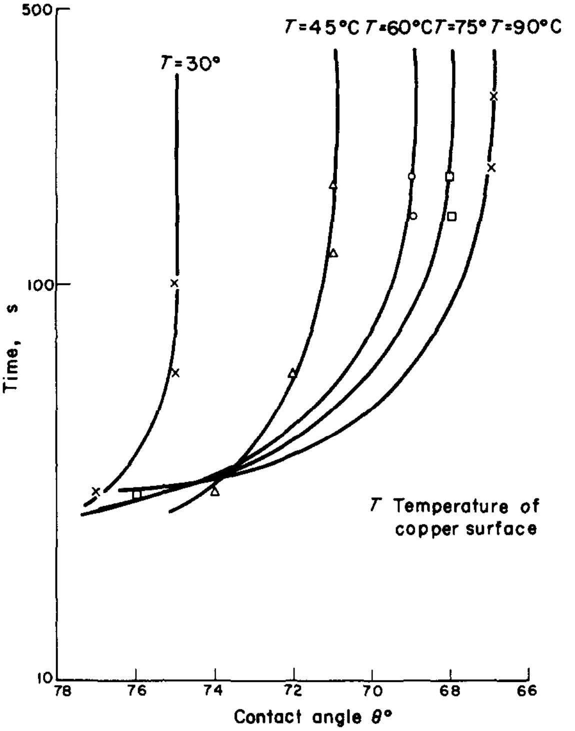

FIG. 4. Contact angle of a water drop (initial temperature 25°C) on a smooth copper surface under heat-transfer conditions.

−0·06°/degC. The change in contact angle under heat-transfer conditions is shown in Fig. 4. At low temperatures the difference in the initial contact angle measured and the equilibrium contact angle under isothermal conditions is small. This difference increases with temperature being 13 per cent at 90°C.

All models to predict dry patch formation under heat-transfer conditions based on momentum balances have included the contact angle of the sub-cooled liquid in contact with the heated surface. Hartley and Murgatroyd [3] have anticipated the influence of contact angle on the minimum wetting rate and attempted to correlate the experimental results of Norman and McIntyre [1], for water on copper surfaces, by assuming values for the contact angle within the range 20–45°. From a simple momentum balance at the point of breakdown the minimum flow rate to sustain a stable dry patch was shown to be

$$\Gamma = 1{\cdot}69\left(\frac{\mu\rho}{g}\right)^{\frac{1}{5}}[\sigma(1-\cos\theta)]^{\frac{3}{5}}. \tag{5}$$

Hsu [4] on the other hand, assumed values in the range 45–90°, whereas the values presented here are between 65–76°.

Since the contact angle measured under heat-transfer conditions rapidly approaches the equilibrium value this may be used in models to predict dry patch stability. The simple momentum and force balance models examined by Hartley and Murgatroyd can be modified, however, to account for the effect of temperature on the surface tension and for the effect of vapourization from the liquid at the surface of the film. This has been discussed by Zuber and Staub [5] who proposed an equation

$$\frac{\rho_f}{15}\left[\frac{g\,\Delta\rho}{\rho_f v}\right]^2\left[\frac{3\Gamma v}{g\,\Delta\rho}\right]^{\frac{5}{3}} = \frac{\sigma(1-\cos\theta)}{\left[\dfrac{3\Gamma v}{g\,\Delta\rho}\right]^{\frac{1}{3}}} + \frac{\partial\sigma}{\sigma t}\frac{Q/A}{K}\cos\theta + \rho_v\left[\frac{Q/A}{\rho_v\lambda}\right]^2\frac{\Delta\rho}{\rho_f}\cos^2\theta \tag{6}$$

where $\Delta\rho = \rho_L - \rho_v$.

The second term on the right hand side of equation (6) accounts for the effect of temperature on surface tension and the third term for the effect of vapourization of the liquid on the interfacial drag. For water this is very much smaller than the effect of temperature on surface tension and can be ignored [5]. The values of minimum wetting rate predicted by these models are compared in Table 1 with experimental values reported by Norman and McIntyre and values measured by the authors. It can be seen that only at high temperature differences between the surface and inlet water temperature do the predicted values approach the experimental results. This is not surprising when one compares the actual dynamics of the system with the assumptions made in the model. This was developed, for laminar flow conditions, assuming a parabolic velocity profile. Above a

Table 1

Surface temperature [°C]	Contact angle θ° (mean of 4 measurements)	$(1 - \cos\theta)$	Surface force $(1 - \cos\theta)$ [dyn/cm]	Thermal capillary force $\frac{d\sigma}{dt}\frac{Q}{KA}\,\delta\cos\theta$ [dyn/cm]	Minimum wetting rate (predicted) [lb/ft h]	Minimum wetting rate (experimental) [lb/ft h]
30	74·6	0·735	53	0·272	285	166
42	72·75	0·705	50·6	1·67	290	200
55	71·25	0·68	49·0	3·84	290	200
70	68·75	0·64	46·0	8·68	290	242
80	68	0·625	45·0	14·7	312	330

Reynolds number of 20 surface waves are apparent [15] which between the ranges $Re = 300\text{–}1120$ cause liquid circulation sufficient to induce mixing. In this range the simple models will not simulate actual flow conditions.

REFERENCES

1. W. S. Norman and V. McIntyre, Heat transfer to a film on a vertical surface, *Trans. Instn Chem. Engrs* **38**, 301 (1960).
2. W. Murgatroyd, The role of shear and form forces in the stability of a dry patch in two-phase film flow, *Int. J. Heat Mass Transfer* **8**, 297 (1965).
3. D. E. Hartley and W. Murgatroyd, Criteria for the break-up of thin liquid layers flowing isothermally over a solid surface, *Int. J. Heat Mass Transfer* **7**, 1003 (1964).
4. Y. Y. Hsu, F. T. Simon and J. F. Lad, Destruction of a thin liquid film flowing over a heating surface, N.A.S.A. Report E2144 (1963).
5. N. Zuber and F. W. Staub, Stability of dry patches forming in liquid films flowing over heated surfaces, *Int. J. Heat Mass Transfer* **9**, 897 (1966).
6. L. I. Osipow, *Surface Chemistry*. Reinhold, New York (1962).
7. F. M. Fowkes, Attractive forces at interfaces, *Ind. Engng Chem.* **56** (12), 40 (1964).
8. D. Graham, Adsorption on low energy solids, *J. Phys. Chem. Ithaca* **68**, 2788 (1964).
9. W. D. Harkins and F. H. Leeser, Surfaces of solids XIX, *J. Chem. Phys.* **18**, 556 (1954).
10. J. T. Davies and Sir Eric Rideal, *Interfacial Phenomena*. Academic Press, New York (1961).
11. F. M. Fowkes and W. D. Harkins, The state of monolayers at the interface solid–aqueous solution. *J. Am. Chem. Soc.* **62**, 3377 (1940).
12. A. W. Neumann, *Proc. Fourth Int. Cong. Surf. Activ.* Brussels (1964).
13. A. B. Ponter, G. A. Davies, W. Beaton and T. K. Ross, The measurement of contact angles under equilibrium and mass transfer conditions, *Int. J. Heat Mass Transfer* **10**, 733 (1967).
14. J. F. Padday, A new method for measuring the spreading coefficient of a liquid on a solid surface, *Proc. Second Int. Cong. Surf. Activ.* **3**, 136 (1957).
15. F. P. Stainthorp and J. M. Allen, The development of ripples on the surface of a liquid film flowing inside a vertical tube. *Trans. Instn Chem. Engrs* **43**, 85 (1965).
16. M. C. Phillips and A. C. Riddiford, Temperature dependence of contact angles, *Nature, Lond.* **205**, 1005 (1965).