285. *Dynamic Contact Angles. Part II.*[1] *Air–Solution–Solid Contact Angles in Aqueous Solutions of Decyl Alcohol and Decanoic Acid.*

By T. A. Elliott and L. Leese.

Dynamic contact angles have been measured at the air–solution–paraffin wax interface for aqueous solutions of decyl alcohol and decanoic acid. The effects of changes in surface area are considered, and methods of calculating the air–liquid interfacial tensions discussed.

That the rates of change of contact angle for an air bubble on paraffin wax immersed in an aqueous solution of a normal alcohol (C_5—C_9) vary with the chain length and concentration of the solute [1] was attributed to differences in adsorption and desorption rates of the solutes. Dynamic contact angles for both equilibrium and non-equilibrium bubbles have been measured over a range of concentrations of decyl alcohol and decanoic acid.[2,3] Rapid changes in area of the air–solution interface of these solutes, which have long adsorption and desorption times, change the surface tension. During bubble contact, changes in area of the liquid–air interface occur, and ought to affect the surface tension and the contact angle. An attempt to determine the surface tension at the air–solution interface has been made, and the effect of changes in surface area considered.

Experimental

Apparatus.—The apparatus and procedure were as described in Part I.

Purification of Materials.—Decyl alcohol and decanoic acid (B.D.H.) were fractionally distilled under vacuum, and had, respectively, d_4^{20} 0·8289, —; b. p. 231·2°, 135°/4 mm.; m. p. —, 30·5°; n_D^{20} 1·4371, —. The surface tensions measured by the vertical-plate technique for decanoic acid solutions were lower than Addison's drop-weight results.[4] Addison and Hutchinson observed similar deviations for decyl alcohol solutions and concluded that the results obtained by the vertical-plate method were true static surface tensions.[5]

Discussion and Results

In Figs. 1 and 2 are shown typical curves for both " equilibrium " (Curves *A*, *D*, *F*, *I* and *O*, *P*, *T*) and " non-equilibrium " (Curves *H*, *L*, *M* and *S*, *X*) bubbles.

(a) *Induction Times.*—These were longer for bubbles with appreciable amounts of adsorbed solute, which is in accord with the suggestion that the disjoining film is stabilised by adsorption of solute.[6]

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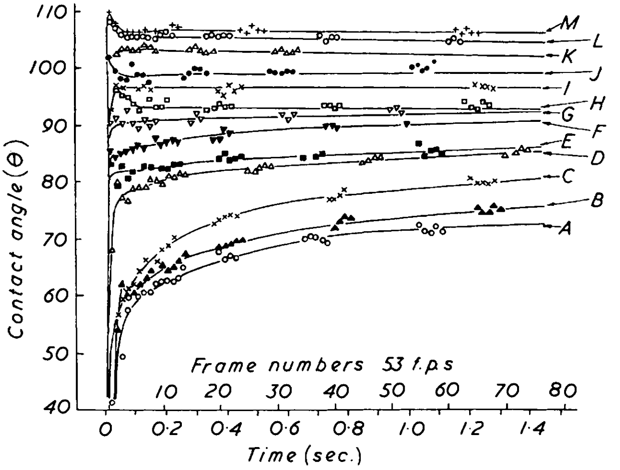
[1] Part I, *J.*, 1957, 22.
[2] Addison and Hutchinson, *J.*, 1949, 3404, 3406.
[3] Addison, Bagot, and McCauley, *J.*, 1948, 936.
[4] Addison, *J.*, 1946, 579.
[5] Addison and Hutchinson, *J.*, 1949, 3390.
[6] Bikermann, " Foams," Reinhold, New York, 1st Edn., 1953, pp. 162—169.

(b) *Contact-angle–Time Curves.*—The curves differed in several respects from those for the C_2—C_9 normal alcohol solutions: (i) The initial increase in angle for " equilibrium bubbles " was more rapid than would be expected from comparison with the octyl and nonyl alcohol solutions; (ii) the expected increase in the " long-term " effect was not observed; (iii) differences between " equilibrium " and " non-equilibrium " bubbles were very marked (cf. Curves *D* and *L*; *T* and *X*).

Effect (i) is more apparent in Fig. 3, where, for " equilibrium bubbles " in a range of C_5—C_{10} alcohol solutions ($\gamma = 50$ dynes/cm.), values of θ_{rt}/θ_{re} are plotted against time;

FIG. 1. *Decyl alcohol solutions.*



Curve	Concn. (%)	γ (dynes/cm.)	Time on jet (sec.)	$\theta_r \pm 0·5$ or $\theta_a \pm 0·5$	$\theta + 0·5$	Induction time (frames)
A	0·0024	39·8	60	73·3	80·1	10
B *	0·00127	50·0	60	87·8	89·5	4
C *	„	„	60	„	„	5
D	„	„	60	„	„	4
E	„	„	10	„	„	5
F	0·000819	56·4	60	91·2	94·2	7
G	„	„	10	„	„	12
H	0·00167	45·9	0	88·6	81·3	2
I	0·00055	61·4	60	97·5	99·0	13
J	„	„	20	102·7	102·7	2
K	„	„	10	99·3	100·1	5
L	0·00123	50·4	0	95·0	90·5	3
M	0·00055	61·4	0	104·6	101·7	1

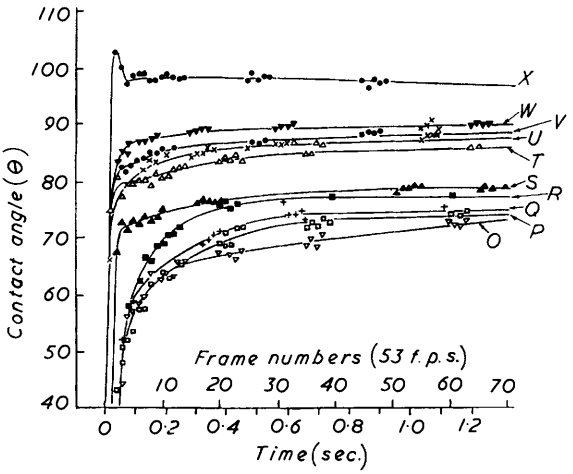
* Slow ejection technique.

θ_{rt} is the contact angle at time *t* and θ_{re} is the angle when the bubble has reached equilibrium.

Effects (i) and (ii) suggested that the bubbles were not carrying the equilibrium surface excess of solute owing to their ejection before adsorption of this excess was complete, and/or to their expansion during ejection. The effect of reducing the initial surface excess by reducing the adsorption time, while the bubbles were standing on the orifice, is shown by curves *I*, *J*, *K*, *M* of Fig. 1 and *T*, *U*, *V*, *X* of Fig. 2. Adsorption of solute during the passage of the bubble through the solution (less than 0·2 sec.) would be too slow to compensate for the decrease in surface excess caused by surface expansion.

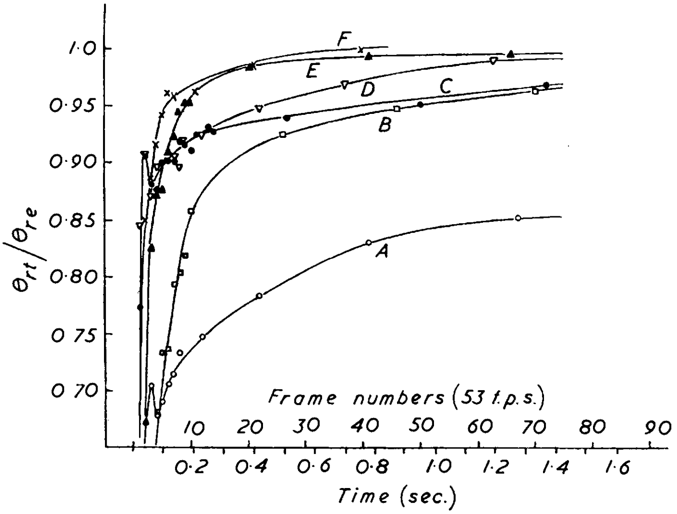
Both factors were minimised by slowly expanding the bubble almost to its maximum stable size and keeping it on the orifice for 1 min. before ejection; contact-angle–time

FIG. 2. *Decanoic acid solutions.*



Curve	Concn. (%)	γ (dynes/cm.)	Time on jet (sec.)	$\theta_r \pm 0{\cdot}5$ or $\theta_a \pm 0{\cdot}5$	$\theta_e \pm 0{\cdot}5$	Induction time (frames)
O	0·00414	38·6	60	75·5	80·9	27
P	0·00295	43·2	60	82·5	86·9	31
Q	,,	,,	10	83·0	86·5	32
R	,,	,,	20	84·1	87·4	21
S	0·00414	38·6	0	78·4	80·6	11
T	0·00170	51·2	60	88·4	90·9	3
U	,,	,,	20	89·6	90·8	2
V	,,	,,	10	89·3	89·6	3
W	0·00141	53·9	15	90·9	90·1	16
X	0·00170	51·2	0	98·6	92·8	1

FIG. 3.



Curve	Solute	Concn. (%)	γ (dynes/cm.)	$\theta_r \pm 0{\cdot}5°$	$\theta_e \pm 0{\cdot}5°$
A *	Decyl alcohol	0·00127	50·0	87·8	89·5
B	Nonyl alcohol	0·00426	50·6	84·9	87·5
C	Decyl alcohol	0·00123	50·4	87·8	89·4
D	Decanoic acid	0·00170	51·2	89·6	90·8
E	Heptyl alcohol	0·049	49·9	84·6	86·2
F	*n*-Pentyl alcohol	0·408	50·5	86·5	87·4

* The bubble was ejected slowly.

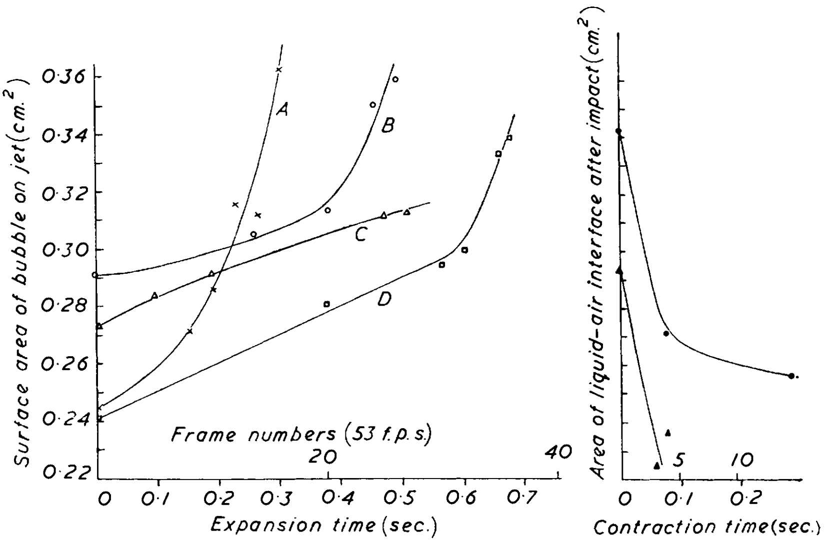
curves B and C of Fig. 1 (cf. Curves D, E, and L) were so obtained. Different rates of final ejection probably caused the discrepancy between curves B and C.

Surface expansion. Values of the surface expansion during bubble ejection were calculated from photographs of the ejection process and by the use of Guldinus's theorem.[3] Surface areas, plotted against time in Fig. 4, were used to calculate changes in Γ_{LA}, the surface excess, with time for solutions of decyl alcohol, as described below.

During ejection the surface excess is decreased by surface expansion, but is increased by contraction of the surface of the bubble when it is on the block. The calculations were extended to determine this effect (Fig. 5).

Calculation of Γ_{LA}. (*a*) Values of Γ_{LA} during bubble expansion were obtained from the experimental γ–concentration curve. It was assumed that the Gibbs adsorption equation applied for a dynamic system. The small adsorption to the surface during the expansion time (0·5 sec.) was neglected. (*b*) Values of Γ_{LA} after bubble contact were calculated (desorption during contraction being neglected) by use of three assumptions: (1) That all the solute adsorbed at the air–liquid interface remained there during contraction [Points (1), Fig. 5]; (2) that transfer of solute from the solid interface to the bubble surface occurred but only when the triple interface was outside the periphery of the circle of contact during the induction period, and that the acquired solute was uniformly distributed over the air–liquid interface [Points (2), Fig. 5]; (3) that solute was not lost from the liquid–air interface [Points (3), Fig. 5], and that solute transfer occurred from the entire solid–liquid interface covered by the bubble.

Fig. 4.



Curves A, B, C, slow ejection technique; Curve D, normal ejection technique.

In order to apply assumptions (2) and (3), Γ_{LS} was calculated.

Calculation of Γ_{LS}. If Young's [7] equation $\gamma_{SA} + \gamma_{LA} \cos \theta = \gamma_{LS}$ applies to the system, then γ_{LS} can be calculated and hence Γ_{LS}, provided γ_{SA} and $\gamma_{LA} \cos \theta$ are known.

Fox and Zisman [8] reported that adsorption at the air–solid interface of a low-energy solid does not affect the surface energy. If γ_{SA} remains effectively constant over a range of concentrations, then a graph of $\gamma_{LA} \cos \theta$ against solute concentration will have the same shape as the plot of γ_{LS} against concentration. Hence the surface excess Γ_{LS} can be calculated by use of the Gibbs equation.

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[7] Young, *Phil. Trans.*, 1805, **95**, 65.

[8] Fox and Zisman, *J. Colloid Sci.*, 1950, **5**, 514.

The Γ_{LS}-concentration curve (Fig. 6, *B*) was calculated by use of values of $\gamma_{LA,e}$ corrected for the "bag effect" reported by Addison, Bagot, and McCauley,[3] by comparison with the γ_{LA}–θ_e curve for the shorter-chain alcohols.

Values of Γ_{LA} calculated from assumptions (1) [Points (1), Fig. 5] are smaller than the equilibrium values, although "equilibrium" bubbles would be expected to have at least the equilibrium surface excess. Assumptions (2) and (3) both give values higher than the equilibrium surface excess, but the values from assumption (2) [Points (2), Fig. 5] are in closest agreement with the true equilibrium value.

The initial fall in surface excess (Fig. 5) due to expansion of the surface of the bubble on ejection is outweighed by the contraction of the surface on impact with the block. These opposing effects mutually compensate to give approximately the equilibrium surface excess on the block, and hence reduced the long-term effect which, for the shorter-chain alcohols, was attributed to the desorption of excess of solute into the bulk solution.

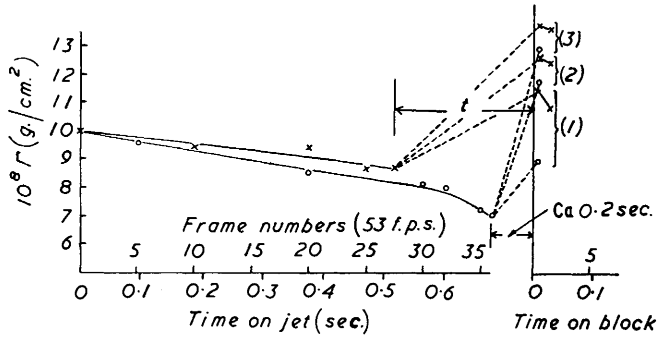


FIG. 5.

Curves *A* and *B* were derived from curves *C* and *D* (Fig. 4) respectively. The time-lapse *t* is about 0·2 sec.

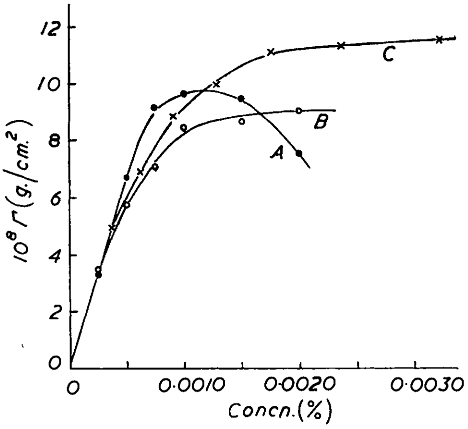


FIG. 6.

Curve *A* Γ_{LS} (calculated), *B* Γ_{LS} (corrected), *C* Γ_{LA} (calculated).

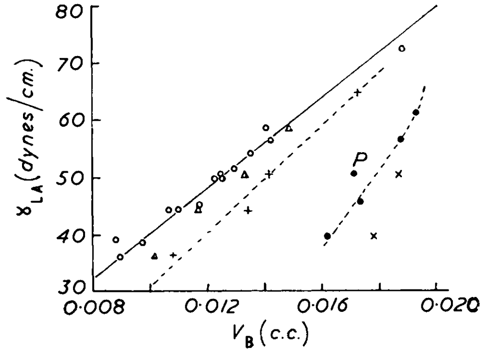
The values of γ_{LA} so obtained are given in Table 1, column (iii), for comparison with values obtained by other methods. The actual values of γ_{LA} corresponding to the calculated γ_{LA} should probably be several dynes/cm. higher to account for disorientation of the solute molecules.[2]

Determination of γ_{LA}.—From the bubble volume. In order to calculate the change in surface tension of the bubble on the block with time, it is necessary to know the surface tension at some instant. γ_{LA} on impact can be calculated from the volume of the bubble on the block, by equating this to the volume on ejection and using the normal drop-volume method, adsorption and changes in volume due to pressure change being neglected.

The full line in Figs. 7 and 8 represent bubble volumes on the orifice (*d* 0·101 cm.)

calculated from Harkins and Brown's tables.[9] The points represent experimental bubble volumes estimated (i) by calculation from observed heights and diameters of bubbles at equilibrium on the wax, the bubble being assumed to be a spherical cap with the measured contact angle, or (ii) by measurement of the dimensions of bubbles at equilibrium, and application of Guldinus's theorem. The scale factor (which is cubed in the calculation) is a source of error.

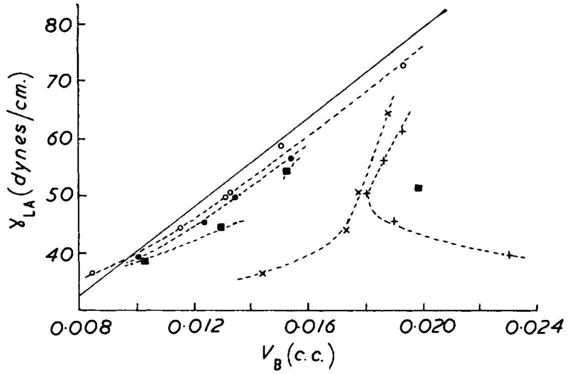
FIG. 7.



n-Alcohols	" Equilibrium bubble " volumes by (i) Calculation	(ii) Guldinus's theorem
C_2—C_8	○	
C_5	○	△
C_9	+	
C_{10}	●	×

P, C_{10} alcohol solution, $\gamma = 50$ dynes/cm.; slow ejection. The full line was derived from Harkins and Brown's tables.

FIG. 8.



Solute: normal alcohol	C_2—C_5	C_7	C_8	C_9	C_{10}
Non-equilm. bubble vol. by calcn.	○	●	■	×	+

The full line was derived from Harkins and Brown's tables.

In Fig. 7 agreement is good between calculated values [method (i)] and results obtained by use of Harkins and Brown's tables for solutions of C_5—C_9 alcohols. Slightly larger volumes were obtained by method (ii). The calculated bubble volumes give a value of surface tension of the solution within 10% of the true value. The increase in bubble volume for solutions of long-chain solutes, and comparable surface tensions, is a measure of the increase in the dynamic surface tension during the rapid expansion of the air–liquid interface on bubble ejection (Table 1).

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[9] Harkins and Brown, *J. Amer. Chem. Soc.*, 1919, **41**, 499.

" Non-equilibrium bubbles " showed an increase in dynamic surface tension for solutions of *n*-pentyl alcohol; the effect increased with the chain length of the solute. The high bubble volumes recorded for decyl alcohol solutions may be due to excess of air flowing through the neck of the bubble, which is stabilised by adsorbed solute and collapses relatively slowly.

TABLE 1. *Values of* γ_{LA} *(dynes/cm.) on bubble impact for decyl alcohol solution.*

γ_{LA} (dynes/cm.) calc. from (i) Bashforth and Adams's tables, (ii) bubble volume V_B, (iii) surface areas.

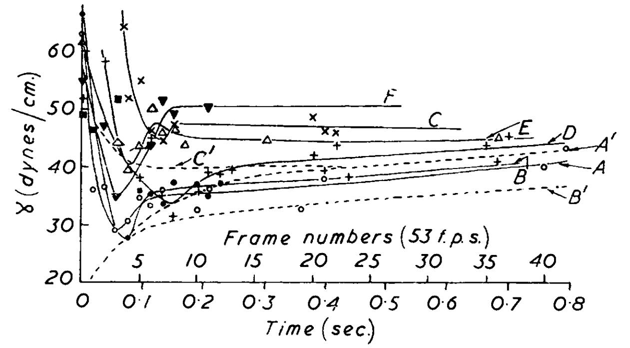
γ_{LA} (measured)	Equilm. bubbles (i)	Equilm. bubbles (ii)	Non-equilm. bubbles (i)	Non-equilm. bubbles (ii)	Non-equilm. bubbles (iii)
39·8	66·5	65	>75	>75	
45·9		69		73	
50·6		68		69	60·0 *
56·4		75		71	
61·4		77		74	
50·0	63	66			55·6 †

* " Equilibrium bubble." † Slow ejection technique.

Values * and † should probably be increased by about 8 dynes/cm. to account for the disorientation of the solute molecules.

Use of Young's equation. If γ_{SA} and γ_{LS} are constant for a particular solution, then $\gamma_{SA} - \gamma_{LS} = \gamma_{LA,\,e} \cos \theta_e$ at equilibrium. Hence $\gamma_t = {}_{LA,\,e} \cos \theta_e/\cos \theta_t$. This equation fails when $\cos \theta_e$ and $\cos \theta_t$ have opposite signs, as θ_t passes through 90°.

FIG. 9.



Curve	Solute	γ (dynes/cm.)	Time on jet (sec.)	Ejection
A	Decyl alcohol	50	60	Slow
B	,,	39·8	60	Equilm. bubble
C	,,	39·8	0	Non-equilm. bubble
D	Decanoic acid	43·2	60	Equilm. bubble
E	,,	43·2	0	Non-equilm. bubble
F	Ethyl alcohol	49·9	60	Equilm. bubble
			0	Non-equilm. bubble

A similar error occurs when γ_t is evaluated by comparison of θ_t with the appropriate curve of θ_e (receding) or θ_e (advancing) plotted against $\gamma_{LA,\,e}$. The use of the equilibrium curve assumes that the bulk concentration is such that γ_t is the equilibrium surface tension of the solution. The results so obtained (broken lines, Fig. 9) are slightly more reasonable than those obtained by the previous method.

Use of Bashforth and Adams's tables.[10] The dimensions of the bubbles were measured on enlarged photographs with a vernier microscope, and values of γ_{LA} (Points, Fig. 9) were calculated from the Tables. The full lines illustrate the trends only.

" Non-equilibrium " bubbles in decyl alcohol solution ($\gamma = 50$ dynes/cm.) gave

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[10] Bashforth and Adams, " An Attempt to Test the Theories of Capillary Action," Cambridge, 1883.

unreasonably high results; the least was 66 dynes/cm. and the equilibrium contact angle gave a value of 76 dynes/cm.

An error of 1% in the contact angle would give rise to an error of 15—20% in the value of γ_{LA}. Calculations from the equilibrium bubble dimensions for solutions of higher concentrations also gave high values for γ_{LA}. It was concluded that Bashforth and Adams's treatment did not fully account for the shape of the bubble under the conditions of these experiments.

Interpretation of Results.—Short-term effect (0—5 *frames*). Peaks which always occur in the curves for " non-equilibrium " bubbles and frequently for " equilibrium bubbles," and extend over a maximum of four frames, are attributed to mechanical effects and not to changes in γ_{LA}.

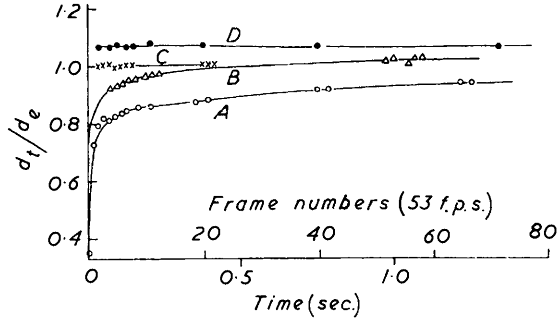

FIG. 10.

Curves A and D, $\gamma = 50$ dynes/cm. B and C $\gamma = 40$ dynes/cm.

d_t base diameter at time t; d_e base diameter at equilm. before tapping.

The energy required to overcome viscous and frictional forces during spreading of the bubble will be due to gravitational and surface forces. If the buoyancy factor is neglected, the initial velocity of recession of the liquid will depend on $F = \gamma_{LA}(\cos\theta - \cos\theta_e)$, provided that Young's equation may be applied and $\gamma_{LS} - \gamma_{SA}$ remains constant during the recession. If the contact angle exceeds the equilibrium value, F becomes a restoring force and the contact angle should vibrate about the equilibrium. Small variations would be obscured by random errors in the measurement of contact angles. Peaks were not recorded for solutions of C_5—C_8 alcohols.[11]

Vibrations in the solutions of longer-chain solutes may be due to surface expansion on ejection, which causes γ_{LA} (on impact) to exceed $\gamma_{LA,e}$. γ_{LA}, which determines the velocity of recession, is continually reduced by contraction of the liquid–air interface and possibly by adsorption of solute from the solid–liquid interface. The moving liquid possesses too much kinetic energy to be damped out immediately by the viscous forces and the reduced restoring force when the equilibrium contact angle is reached. The liquid front therefore " overshoots " and the initial contact angle is increased.

For " non-equilibrium " bubbles, the diameter of the base remains practically constant during the succeeding rapid decrease in contact angle (Fig. 10, Curves C and D), which must be caused by a change in bubble shape.

For " equilibrium " bubbles, the base diameter continues to increase as the contact angle increases (Fig. 10, Curves A and B).

Rapid changes in contact angle (5—65 *frames*). Changes in contact angle depend on differences between the value of γ_{LA} at the moment of impact and its final equilibrium value. The initial value of γ_{LA} will depend on the time allowed for adsorption equilibrium before ejection, and on surface expansion of the bubble during ejection.

Long-term effect. The times for " non-equilibrium " bubbles to give constant contact angles are of the same order as the adsorption times (20—60 sec.) for decyl alcohol and decanoic acid solutions (15 sec.).

The final contact angles of equilibrium bubbles in decyl alcohol solutions are reached sooner than expected from desorption times. The lowest value of Γ_{LA} for slowly ejected

[11] **Addison and Hutchinson, *J.*, 1949, 3396.**

bubbles (Fig. 5) corresponds to an initial value of $\gamma_{LA} = 45$ dynes/cm., comparable with an equilibrium value of 50 dynes/cm. Desorption of the excess of alcohol should require at least 200 sec. The equilibrium receding angle was reached after approximately 150 sec.

More rapid release of bubbles will involve greater rates of surface expansion and smaller initial values of Γ_{LA}; such bubbles should give static angles sooner, as confirmed.

Changes of contact angle above 90°. Results (Fig. 1) cannot be explained by changes in γ_{LA} alone. The rates of the short-term changes in contact angle are similar to rates of desorption from monolayers compressed below the normal surface area per molecule for a complete monolayer. Expansion of the bubble surface on ejection, and the slow adsorption rates of the solutes, cause the initial surface excess to be too low for a complete monolayer to be formed by compression of the liquid–air interface on bubble spreading.

Some solute is probably transferred from the solid–liquid to the liquid–air interface to bring the initial value of Γ_{LA}, for the normal equilibrium bubbles in solutions of decyl alcohol ($\gamma = 50$ dynes/cm.), below the equilibrium value.

For " non-equilibrium " bubbles the advancing contact angles which exceed 90° can be explained, provided it is assumed that γ_{LS} changes with time. It being assumed that the paraffin wax surface has been freed from solute molecules by the receding liquid, before the initial maximum contact angle is formed, the subsequent advance of the bulk liquid is across a clean solid–air interface to form a solid–liquid interface of high surface free energy. Hence the contact angle formed is equivalent to that where $\gamma_{LS} - \gamma_{SA}$ is larger than its equilibrium value.

Adsorption of solute to the clean solid–liquid interface governs the rate of change of the contact angle. (Below 90° the same mechanism will operate, but will be assisted by a fall in γ_{LA}.)

Analogous considerations apply to " equilibrium bubbles " with contact angle greater than 90°, where desorption from an overcrowded solid–liquid interface causes the slow increase in the angle.

It is considered that the contact angle formed by an air bubble at a solid–solution interface depends on the previous history of the bubble, as well as changes in interfacial tensions after impact with the solid.

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