6. *Dynamic Contact Angles. Part I. Changes in Air–Solution–Solid Contact Angles with Time.*

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The impact of air bubbles and subsequent changes in contact angle on paraffin wax surfaces, immersed in solutions of normal aliphatic alcohols, have been recorded photographically. The rates of change of the contact angles with time depend on the chain length of the solute molecules and on the concentration of the solution. A qualitative explanation of the results is given in terms of the surface properties of the solutes.

WARK and Cox [1] have established the importance of the equilibrium contact angle at a mineral–solution–air interface in froth flotation. However, equilibrium angles cannot be obtained in practice. Adam [2] suggested that, because of hysteresis, receding angles are important in flotation; Philipoff [3] calculated that the time of contact between a bubble and a mineral particle in a flotation cell is of the order of 0·01 sec. only, which may be too short to permit the attainment of the equilibrium contact angle. Furthermore, Sven-Nilsson [4] noticed that a short period elapses before true contact between an air bubble and a solid surface becomes established. After true contact, the angles will vary with the solid–liquid, liquid–air, and air–solid interfacial tensions. Addison [5] has shown that air–solution interfacial tensions vary with time at freshly formed surfaces, and it was expected that changes in contact angle would depend on the surface properties of the solute. It therefore appeared that a study of changes in contact angle with time, immediately after bubble impact, would be of value.

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[1] Wark and Cox, *J. Phys. Chem.*, 1933, **37**, 797, 805, 815.
[2] Adam, " Physics and Chemistry of Surfaces," Oxford University Press, London, 1941, p. 193.
[3] Philippoff, *Mining Eng.*, 1932, **4**, 386.
[4] Sven-Nilsson, *Kolloid Z.*, 1934, **69**, 230.
[5] Addison, *J.*, 1945, 98.

Bubbles on a paraffin wax surface were studied, since it is generally accepted that treated mineral particles in a flotation cell carry a hydrocarbon-like surface.[6] Normal aliphatic alcohols were used as solutes.

EXPERIMENTAL

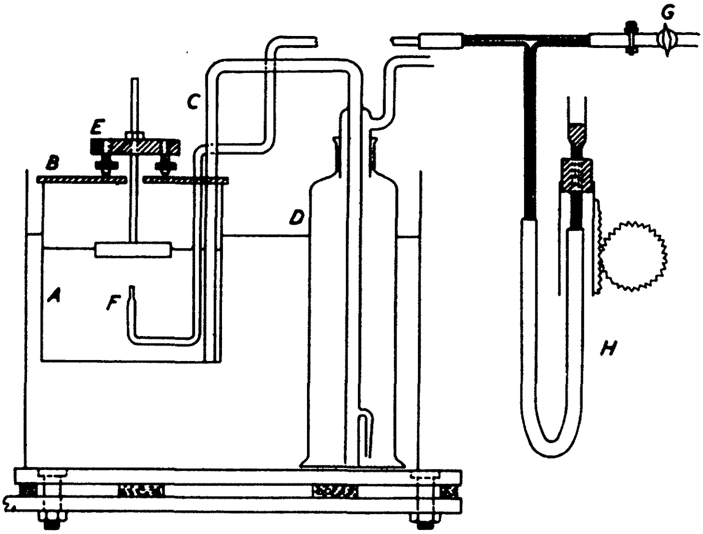
Apparatus.—The apparatus was as shown in Fig. 1.

Optical cell. The solution was contained in a glass cell *A*, with optically plane sides (8 cm. edge) and a Perspex cover *B*. A delivery tube *C*, leading to a Pyrex Dreschel bottle *D*, which served as a reservoir, passed through one corner of the cover. The cell and reservoir were enclosed in a tank maintained at 20° ± 0·01°.

Block. The block (4 × 4 × 0·5 cm.) of paraffin wax was supported by a threaded brass rod screwed into a levelling table *E*, which rested on the cover of the cell.

Before each experiment, a smooth plane face was produced on the block by polishing, first with filter paper, and then with a lens tissue,[7] until a high gloss was obtained. Attempts to prepare a surface by pressure [8] were unsuccessful.

FIG. 1.



Gas supply. Air was used, since it is used in froth flotation, and the solutes and paraffin wax are inert to oxygen under the experimental conditions. Air from an aspirator (12 l.) was passed through concentrated sulphuric acid, concentrated potassium hydroxide solution, and through a simple manostat and a Dreschel bottle containing distilled water, then, saturated with water vapour, through a Y-tube, one branch of which led to the reservoir *D* and the other to jet *F* (orifice diam. 0·101 cm.).

Anti-vibration mounting. In order to minimise vibration, the air supply to jet *F* was first led *via* rubber pressure tubing to a length of glass capillary tubing clamped to the wall. From this capillary, pressure tubing (with a glass tap *G* inserted) led to a pressure regulator, *H*, and finally to the jet *F*. The thermostat and the clamps for the jet and pressure regulator were mounted on a platform insulated by " Sorbo " rubber pads from a shelf fixed to a main wall of the building.

Pressure regulator. A bubble could be produced at the orifice by an increase in pressure controlled by a device *H* resembling a manometer. The height of mercury in the vertical arm of a capillary T-piece, let into the air line, was adjusted by using the focusing mount of a microscope. If the volume of air between the glass tap and the jet was too great, fine control of the pressure was not possible.

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[6] Taggart, " Elements of Ore Dressing," Chapman and Hall, London, 1951, p. 248 *et seq.*

[7] Mitchell and Elton, *J.*, 1953, 843.

[8] Bartell and Shepard, *J. Phys. Chem.*, 1953, **57**, 212.

The jet was isolated from the rest of the apparatus by closing the tap and by placing a screw clip immediately before the horizontal arm of the T-piece. No grease was used on the glass tap. The bubble could be kept stationary on the orifice or smoothly ejected when required.

Lighting. The bubble, when on the surface, was silhouetted by a parallel beam of light, passing through a ground-glass screen and then through the thermostat bath, which acted as a heat filter.

Camera. A Keystone A12 cine-camera, mounted on a tripod, and carrying a 1 in. *f*/2·9 T.T.H. lens with a 1 in. extension tube and reflex focusing, was placed in front of the optical cell, to photograph through the plane glass front of the thermostat tank. In these circumstances the object distance was approximately 1 in., and the image was approximately natural size.

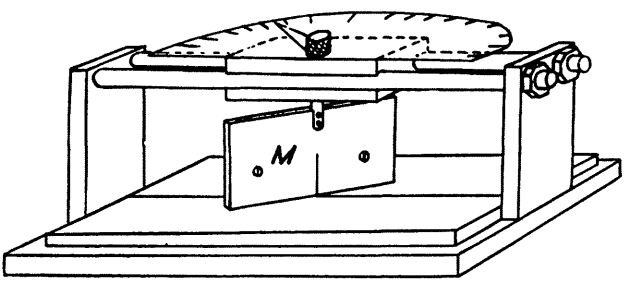
The actual film speed at a nominal 64 f.p.s. (frames per sec.) was 53 f.p.s., and at a nominal 10 f.p.s. the speed was 11 f.p.s. Values quoted are corrected.

The film used was Ilford F.P.3 cine negative film, developed in fine-grain developer.

Procedure.—Cleaning. All the glass apparatus was washed with concentrated nitric acid, tap water, and distilled water; it was considered to be clean when water ran freely from the surface. The apparatus was then left immersed in distilled water until needed.

Filling the cell. First, the reservoir was rinsed three times with the experimental solution, filled, stoppered, and placed in the thermostat. The cell was then rinsed several times with solution, and the freshly polished block, which had been kept under a stream of tap water, was placed in the cell. The cell was put in the thermostat and the jet and delivery tube set in position. The solution was blown from the reservoir into the cell, and allowed to stand for 1 hr., in order that equilibrium between the solute and the surface might be established.

FIG. 2.



Position of the orifice and levelling the block. The cross-wire of a travelling microscope was set parallel with the liquid surface, and the paraffin surface and the orifice were aligned with the horizontal wire. Small variations in the distance between the orifice and the block (1·0—2·0 cm.) had no detectable effect on the behaviour of the bubble. However, the distance was maintained at 1·5 ± 0·1 cm. throughout. The distance between the orifice and the liquid surface when the block was in position was 1·9 ± 0·1 cm.

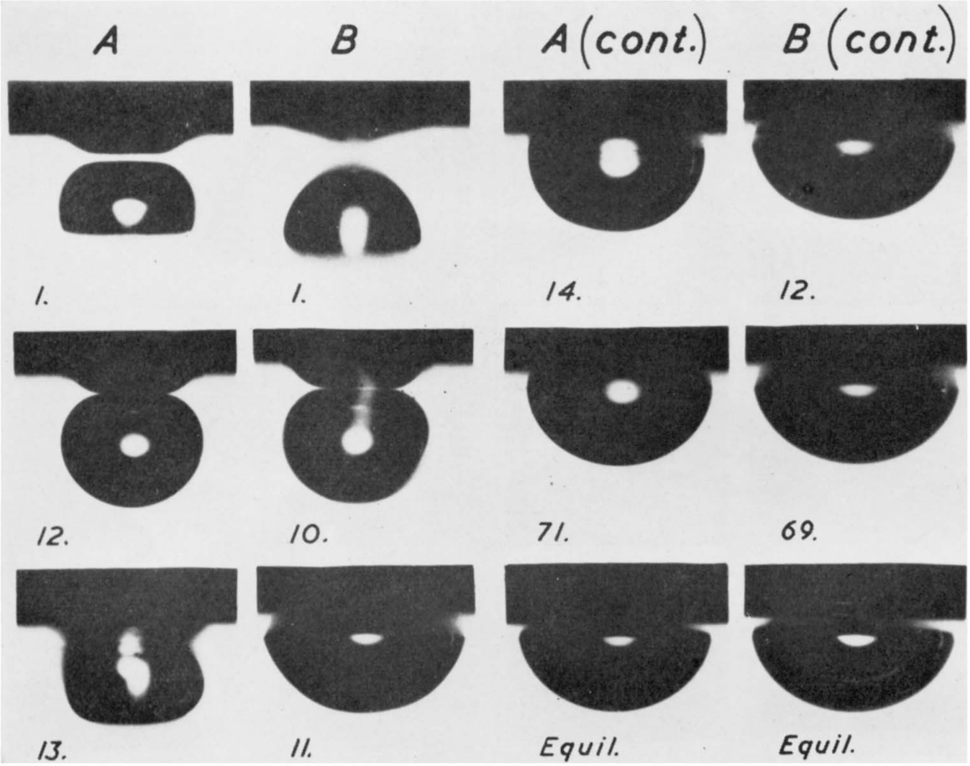
Production of bubbles. (i) " Equilibrium bubbles " were produced by allowing a bubble to stand on the orifice for one minute to allow adsorption equilibrium to be established before ejection.

(ii) " Non-equilibrium bubbles " were produced by driving air rapidly through the orifice and immediately ejecting the bubble.

Photography. The camera was aligned and focused on a stationary bubble on the surface of the block. This bubble was removed by tilting the block. A second bubble was released, and its impact on the block, and the subsequent changes in contact angle, were photographed at a rate of 53 f.p.s. (f/5·6) for 3 sec. Slower changes were recorded at 11 f.p.s. (*f*/11).

Measurement of angles. Measurements were made on prints with bubble images 2·5—3 cm. in diameter (magnification, × 8, linear), with the device shown in Fig. 2.

A metal mirror *M*, attached to a sliding carriage, could be rotated about a vertical axis, moving a pointer over a fixed protractor. With the pointer set at 90°, a photograph was placed so that the base of the bubble coincided with the front mirror surface. The base was defined by the intersections between the curved edges of the bubble and its reflection in the solid surface. The position of the carriage was adjusted so that the centre of the mirror, *Changes in contact angle with time for* n-*nonyl alcohol solution.*



γ = 64·7 dynes/cm. Film speed 53 f.p.s. Numerals are frame numbers.
A, Equilibrium bubble; *B*, Non-equilibrium bubble.

[*To face p.* 25.

which was marked by a line, fell on one of the points of intersection. By rotating the mirror, and observing the reflection of the bubble, the angle of the normal to the bubble was obtained. The pointer was fixed so that the angle of the tangent was read off directly. Errors in aligning the mirror with the base of the bubble were eliminated by using the mean value of the angles obtained for both edges of the bubble. Contact-angle measurements were reproducible to within ±1°. Each quoted value of θ_e and of θ_r, which are the equilibrium and receding angles respectively, is the average of five measurements. The mean deviation is $<0{\cdot}5°$.

Purification of Materials.—Paraffin wax. This was a sample of "Gurr's Filtered Paraffin Wax," which was further purified by distillation under reduced pressure. The product melted at 56—57°.

Alcohols. The alcohols used were pure absolute ethyl alcohol, *n*-pentyl alcohol (B.D.H. Laboratory Reagent), and *n*-heptyl, *n*-octyl, and *n*-nonyl alcohols (L. Light and Co. Ltd.). Each alcohol (250 ml.) was dried (Na_2SO_4) and distilled into five fractions. The first and last fractions were discarded. The refractive indices and densities at 20° of the other fractions agreed well with each other and with published [5,9] values (see Table).

n-Alcohol	d_4^{20}	B. p.	n_D^{20}	*n*-Alcohol	d_4^{20}	B. p.	n_D^{20}
Ethyl	0·7895	78·4°	1·3596	Octyl	0·8250	195·5°	1·4291
Pentyl	0·8153	137·5	1·4102	Nonyl	0·8280	211·5	1·4329
Heptyl	0·8225	175·9	1·4237				

Surface-tension measurements. Surface tensions were measured with a modified vertical plate apparatus.[10] The beam was returned to zero by a torsion head, and readings were reproducible to within ±0·05 dyne/cm. Surface tensions of all solutions were measured before and after their use in the cell; no differences were found between the two values.

DISCUSSION AND RESULTS

From photographs of air-bubble contact with the paraffin wax surface immersed in a solution, changes in contact angle with time can be measured. In Fig. 3, values of contact angle are plotted against time for bubbles in pure water and in solutions of *n*-pentyl alcohol. All values in Figs. 3—7 refer to equilibrium bubbles. The results can be considered in three sections: (*a*) the delay between impact and the establishment of the first measurable contact angle ("induction time"); (*b*) the initial rapid change in angle; and (*c*) the slow change in angle.

(a) *Induction Time.*—The time scale is defined by the speed of the film. Frame 1, when the bubble was first photographed in contact with the paraffin surface, was equivalent to 1/53 sec. (0·019 sec.) after impact, and other times were evaluated by counting frames from this point on the film. The lapse of a time interval between the first impact of the bubble on the surface and the attainment of the first measurable contact angle was common to the behaviour of all the bubbles studied (Plate).

In pure water, bubbles did not remain in contact with the block on impact, but rebounded from the surface two or three times. This was attributed to the restoring force of surface tension acting on the considerable deformation of the bubble caused by the impact. When the bubble settled on the surface, air–solid contact was established in less than 1/53 sec.

Bubbles in solutions of alcohol were deformed much less, and settled down more quickly, than bubbles in pure water. However, they remained on the paraffin surface without apparent change in shape, and with a zero contact angle, for periods of time which varied widely, and in a random manner, for different bubbles. A progressively closer approach of the bubble to the surface was indicated by the thinning and disappearance of the line dividing the bubble from its reflection in the surface (Plate). Contact between air and surface appeared to take place at the edge of the bubble. The time between apparent and true contact, when an air bubble is pressed against a solid surface, was called

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[9] Vogel, *J.*, 1948, 1815.

[10] Minnassian-Saraga, *J. Chim. phys.*, 1955, **52**, 80—94.

FIG. 3. n-*Pentyl alcohol solution.*

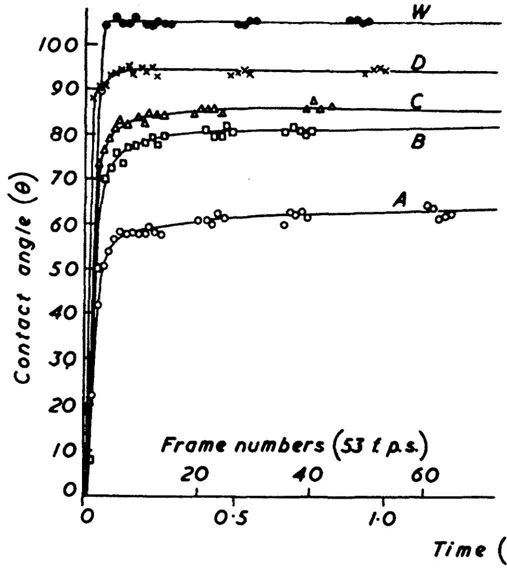
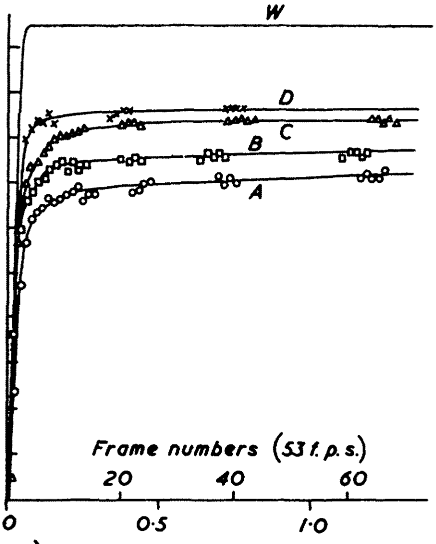


FIG. 4. n-*Heptyl alcohol solution.*



Curve	Concn. (%)	γ_{LA} (dynes/cm.)	$\theta_r \pm$ 0·5°	$\theta_a \pm$ 0·5°	Indctn. time (sec.)
A	1·28	36·2	69·9°	71·1°	0·11
B	0·637	44·3	81·5	83·9	0·42
C	0·408	50·5	86·5	87·4	0·26
D	0·204	58·7	93·7	96·1	0·056
W	—	72·2	105·2	107·0	<0·019

Curve	Concn. (%)	γ_{LA} (dynes/cm.)	$\theta_r \pm$ 0·5°	$\theta_a \pm$ 0·5°	Indctn. time (sec.)
A	0·108	39·2	72·8°	74·8°	0·057
B	0·071	45·2	80·3	82·0	0·15
C	0·049	49·9	84·6	86·2	0·19
D	0·028	56·4	86·4	88·0	0·25

FIG. 5. n-*Octyl alcohol solution.*

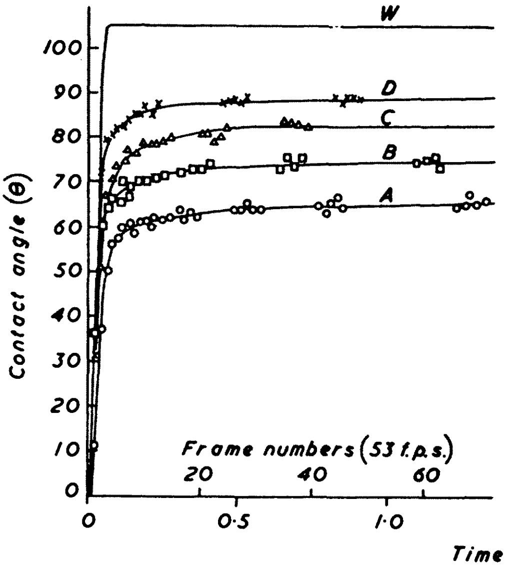
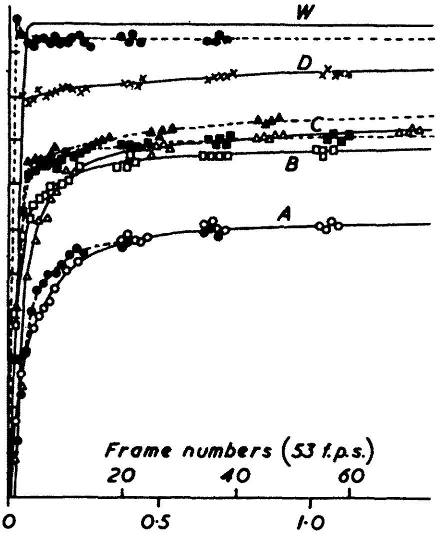


FIG. 6. n-*Nonyl alcohol solution.*



Curve	Concn. (%)	γ_{LA} (dynes/cm.)	$\theta_r \pm$ 0·5°	$\theta_a \pm$ 0·5°	Indctn. time (sec.)
A	0·0324	38·7	70·7°	73·5°	0·28
B	0·0216	44·2	77·7	81·0	0·15
C	0·0130	51·5	82·8	82·3	0·28
D	0·108	54·2	88·1	89·6	0·19

Curve	Concn. (%)	γ_{LA} (dynes/cm.)	$\theta_r \pm$ 0·5°	$\theta_a \pm$ 0·5°	Indctn. time (sec.)
A	0·00976	36·2	66·6°	69·3°	0·23
B	0·00626	44·2	81·9	85·9	0·26
C	0·00426	50·6	84·9	87·5	0·38
D	0·00142	64·7	98·0	100·7	0·23

by Sven-Nilsson[4] the "induction time." Evans[11] showed that the induction time depended on the rate of drainage of a thin film of liquid trapped between the bubble and the surface, the film finally rupturing at a point on the periphery of the circle of contact.

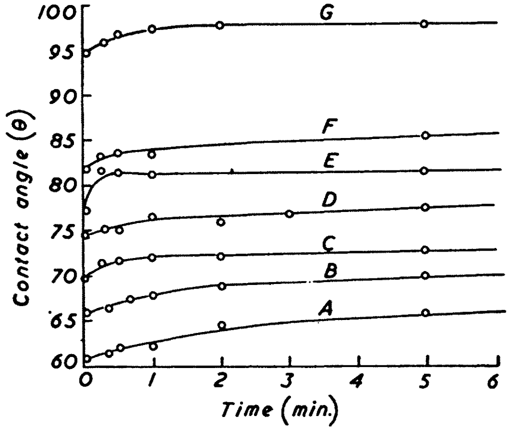
The relatively long induction times found for bubbles in alcohol solution suggest that the disjoining films are stabilised by the presence of solute molecules. This is in accordance with the known effect on foams of surface-active molecules.[12]

Gillespie and Rideal,[13] in studying the related problem of the coalescence of drops at liquid–liquid interfaces, showed that the induction time for a single drop is predictable only statistically. The number of bubbles studied in the present work was insufficient for a quantitative interpretation of the induction effect.

In order to facilitate comparison of rates of change of contact angle induction times have been omitted from Figs. 3—7. The zero of the time axis is taken as the frame preceding that on which the first measurable contact angle occurs. This gives rise to a maximum possible error in the axis of 1/53 sec. Induction times varied between 1 and 23 frames (0·019 to 0·435 sec.); values for individual curves are given below the graphs.

FIG. 7. *Long-term effects. " Equilibrium " bubbles*

Curve	*n*-Alcohol	γ_{LA} (dynes/cm.)
A	Nonyl	36·2
B	Octyl	38·7
C	Heptyl	39·2
D	Octyl	44·2
E	Nonyl	44·2
F	„	50·6
G	„	64·7



(b) *Initial Rapid Change in Angle.*—Fig. 3 shows that for the pure water system the contact angle rose sharply (within 2 or 3 frames) to a value (105°) which was constant and was in agreement with the value 104° ± 2° obtained by Bartell and Ray[14] for the receding angle on a comparable paraffin wax surface. When the block was tapped, the angle increased to the equilibrium value. Contact angle–time curves resembling those given by pure water were obtained with " equilibrium " bubbles in solutions of *n*-pentyl alcohol. However, the time taken to reach a constant value of the contact angle increased with the increase in the concentration of the solutions. Again the contact angles rose to the equilibrium values when the block was tapped.

The behaviour of " non-equilibrium " bubbles did not differ significantly from that of " equilibrium " bubbles.

(c) *Slow Change in Angle.*—This slow change was readily detected for longer-chain alcohols.

Chain-length Effect.—" Equilibrium " bubbles. In Figs. 4, 5, and 6, are shown the contact angle–time curves for solutions of *n*-heptyl, *n*-octyl, and *n*-nonyl alcohols. The curves obtained by employing " equilibrium " bubbles resemble the curves for *n*-pentyl alcohol solutions in shape, but this time for the large initial increase in angle is greater

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[11] Evans, *Ind. Eng. Chem.*, 1954, **46**, 2420.

[12] Bikermann, " Foams," Reinhold, New York, 1st Edn., 1953, pp. 162—169.

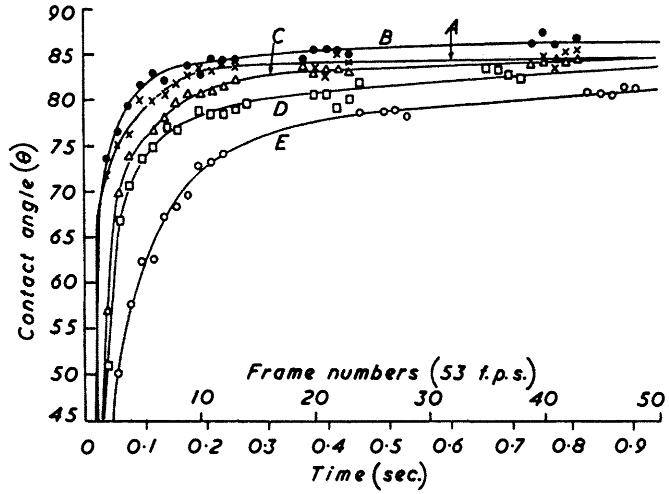
[13] Gillespie and Rideal, *Trans. Faraday Soc.*, 1956, **52**, 173.

[14] Bartell and Ray, *J. Colloid Sci.*, 1953, **8**, 216.

for the alcohols of longer chain length. For *n*-octyl and *n*-nonyl alcohols in medium and high concentrations, the secondary slow change in contact angle was considerable (5—8°), and required up to 5 minutes for completion in *n*-nonyl alcohol solutions. This slow change is illustrated in Fig. 7.

The effect of increase in chain length of the solute on the rate of change of the contact angle is shown in Fig. 8. The changes of contact angle with time are given, for " equilibrium " bubbles, in a series of alcohol solutions of approximately equivalent values of surface tension. The volumes of the bubbles at the moment of release from the orifice were approximately the same, and the buoyancies and the velocities on impact on the paraffin surface should be similar. Differences in their subsequent behaviour are therefore attributable to differences in the surface properties of the solutes.

FIG. 8. *Chain-length effect.*



Curve	*n*-Alcohol	Concn. (%)	γ_{LA} (dynes/cm.)	$\theta_r \pm 0{\cdot}5°$	$\theta_e \pm 0{\cdot}5°$
A	Ethyl	9·700	49·9	84·7	87·8
B	Pentyl	0·408	50·5	86·5	87·4
C	Heptyl	0·049	49·9	84·6	86·2
D	Octyl	0·0130	51·5	82·8	82·3
E	Nonyl	0·00426	50·6	84·9	87·5

" Non-equilibrium " bubbles. The " non-equilibrium " bubble contact angle–time curves (broken lines, Fig. 6) of *n*-nonyl alcohol show marked deviations from the " equilibrium " bubble curves for the same solutions. The angles increase more rapidly during the initial stages of change, and are greater throughout. The differences between the two types of curve increase with decrease in the concentration of alcohol, and in *n*-nonyl alcohol solution ($\gamma = 64{\cdot}7$ dynes/cm.) an angle greater than the equilibrium angle is reached in less than 1/53 sec. The angle afterwards decreases to the equilibrium value.

Interpretation of Results.—A qualitative interpretation of the foregoing results is suggested, based on the relationship between the contact angle and the surface tensions of the three interfaces involved, and taking into account the changes which take place at the air–liquid interface as the bubble makes true contact with the solid surface.

For a system in equilibrium, the contact angle is given by the expression $\cos\theta = (\gamma_{SA} - \gamma_{SL})/\gamma_{LA}$, where γ_{SA}, γ_{SL}, and γ_{LA}, represent the solid–air, solid–liquid, and liquid–air interfacial tensions, respectively.

The angles obtained in this series of experiments were probably receding or advancing angles, and some term taking into account the hysteresis of the contact angle should be included. However, in this qualitative discussion, it will be assumed that the solid surface is smooth.

" *Equilibrium* " *bubbles*. The contact angle–time curves obtained should resemble those given by pure water, but should rise to a lower final value of contact angle. Bartell and Ray [15] plotted $\cos \theta_r$ against γ_{LA} for droplets on paraffin wax for a series of solutions, and found a linear relation. Receding contact angles measured in the present study gave a similar result, but the graph deviated from a straight line for small values of γ_{LA}. Points lay on the same line, irrespective of the chain length of the alcohol in the solution. The spreading coefficient of a liquid on a solid is given by $\sum = \gamma_{LA}(\cos \theta - 1)$. Sumner [16] suggested that, for finite values of θ, the expression represents a " recession " coefficient for the liquid. Rate of recession of liquid, *i.e.*, rate of spreading of air, then depends on $\sum_A = \gamma_{LA}(1 - \cos \theta)$, and on the viscosities of the fluid phases. As $\cos \theta$ increases when γ_{LA} decreases, $\sum_A$ will fall as the concentration of alcohol increases. Rate of spreading, and rate of increase of contact angle, will therefore be expected to fall with fall in γ_{LA}. This generalisation was confirmed by the experimental results.

The viscosities of the gas and of the solutions are practically unaltered by changing the solute, and the relationship between γ_{LA} and $\sum_A$ is the same throughout the series of alcohols studied. Air bubbles, in solutions with the same equilibrium values of γ_{LA}, would be expected to spread over a solid surface at the same rate. Thus (Fig. 8) the differences between the values of contact angles obtained by using solutes of various chain length, are caused by the different properties of the solute molecules at freshly formed, rather than at static surfaces.

Surface-area changes. Addison and Hutchinson [17] showed that the surface tension of a solution of a long-chain alcohol could be depressed by rapidly decreasing the area of the air–liquid interface. This was due to the low desorption rates of the molecules. The times for the contact angles of " equilibrium " bubbles to reach equilibrium in the present series of experiments are comparable with the desorption times recorded by Addison and Hutchinson,[18] who showed that rates of desorption decreased with increase in chain length.

Measurements of surface area indicate that there is a contraction of the air–liquid interface when the air spreads on the solid surface. The slow rise in angle shown in Fig. 7 may then be caused by a gradual increase in γ_{LA}, and possibly in γ_{LS}, produced by desorption of solute molecules in excess of $\Gamma_{equ.}$, the equilibrium value of the Gibbs surface excess. This increase in Γ may be produced by the rapid compression of the adsorbed layer at the air–liquid interface. The surface concentration of solute in excess of $\Gamma_{equ.}$ will be greater in alcohol solutions of higher concentrations, and the subsequent desorption will also be slower.

" *Non-equilibrium* " *bubbles*. No information is available on variations of γ_{LS} or γ_{SA} with time, but Addison *et al.* have shown that γ_{LA} decreases markedly at a freshly formed solution–air interface in an alcohol–water solution. It might therefore be expected that the contact angle of a freshly formed air bubble on a solid surface would fall.

However, an appreciable time (0·1 sec.) elapses between the formation of the bubble on the orifice and its attachment to the solid surface. In solutions of short-chain alcohols the minimum time for a bubble to form on the jet and to reach the solid surface is sufficient for the adsorption of $\Gamma_{equ.}$. Hence no difference can be expected between bubbles formed at different rates, except for an increase in volume caused by the more rapid flow of the gas through the orifice.

For the long-chain alcohols, with longer adsorption times, it would be expected that the contact angle of a " non-equilibrium " bubble would approach the value for pure water, and then fall back to the equilibrium value. This behaviour was shown in *n*-nonyl alcohol solution when γ_{LA} was equal to 64·7 dynes/cm., but not in any solution of lower γ_{LA}.

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[15] Bartell and Shepard, *J. Phys. Chem.*, 1953, **57**, 460.
[16] Sumner, " Wetting and Detergency Symposium," A. Harvey (Publ.), London, 1937, p. 16.
[17] Addison and Hutchinson, *J.*, 1949, 3395.
[18] *Idem, ibid.*, p. 3401.

For " non-equilibrium " bubbles a combination of adsorption of fresh solute molecules, and compression of the air–solution interface, will increase the rate of accumulation of $\Gamma_{\text{equ.}}$. Contact angle–time curves intermediate between that for pure water and those for " equilibrium " bubbles will be obtained. Since adsorption is more rapid, and desorption is slower, in more concentrated solutions, " equilibrium " and " non-equilibrium " bubble curves will be closer together than for dilute solutions.

For a quantitative study of the effects of desorption rates on the changes of contact angle with time, a detailed knowledge of the relationship between solute concentration and desorption rate is required. This is available for decyl alcohol only,[17] and a study of the decyl alcohol–water system will be given in a later paper.

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