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CONTACT ANGLE HYSTERESIS ON AQUAGELS

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I. Summary

Micrographic studies of drops of methylene iodide on agar aquagel surfaces reveal substantial contact-angle hysteresis, which is virtually independent of agar concentration. Maximum advancing and minimum receding angles obey the relation $\cos\theta_A + \cos\theta_R = 2\cos\theta_E$ where θ_E is the equilibrium contact angle made by methylene iodide on a plane liquid water surface. These observations, and consideration of the microstructure of gels, are at variance with theories of hysteresis based on surface contamination, surface roughness, and surface heterogeneity. A new theory of contact angle hysteresis on solids is presented which, by analysis of molecular energetics, ascribes the phenomenon solely to the lack of free lateral mobility of the molecules in solid surfaces.

II. Introduction

When a drop of liquid is brought into contact with the surface of a solid (or of another liquid with which it is immiscible), it will either spread without limit on that surface, or retain its identity as a drop, attaining an apparent equilibrium configuration on the surface such that a characteristic angle is formed between the tangent to the liquid surface at its point of contact with the substrate, and a line parallel to the substrate surface at that point. This so-called contact angle is usually considered to be determined solely by the magnitudes of the free energies of the three interfaces defining the line of contact at which the angle is measured.

When the three phases under consideration are fluid (e. g. , liquid-liquid-gas), the three interfacial free energies manifest themselves as contractile tensions acting tangentially to the surfaces at all points. Under these circumstances, a single two-dimensional force-balance is adequate to establish an equilibrium value for the contact angle in terms of these surface tensions. The relation for the case where one fluid boundary is plane constitutes the well-known Young equation:

$$\cos\theta = \frac{\gamma_{L_2} - \gamma_{L_1L_2}}{\gamma_{L_1}} \quad (1)$$

where L_1 represents the drop phase, L_2 , the planar substrate, γ , the corresponding surface and interfacial tensions, and θ the contact angle between the two liquids.

When the substrate phase is solid, however, it is not possible unequivocally to assign to the solid surface, or to the solid-liquid interface, a "tension" quantitatively equal to the free surface or interfacial energy, nor is there any assurance that tensions which might exist at these phase boundaries are necessarily confined to the boundary surfaces. Hence, even if it were possible to measure directly solid-gas and solid-liquid free surface energies (which of itself is extremely difficult), there is little reason to expect that the contact angle in such a system would be determined by Equation (1).

Further evidence of the difficulties of applying the Young equation to solids is the almost universal observation that the contact angle made by a (non-spreading) liquid on a solid is not single-valued. That is, a liquid cannot be made to advance over the surface of a solid until the contact angle exceeds a certain critical value, nor to recede from the surface until the angle is reduced below another (lower) critical value. Both the "advancing" and "receding" angles, and all values between these limits, are apparently "equilibrium" values, in that there will be no net movement of the liquid with time if it is caused by external forces to reside on the solid at any angle between these limits. This phenomenon of "contact angle hysteresis" appears to be an inherent property of solid surfaces.

The causes of contact angle hysteresis have been the subject of study and speculation for many years, but the phenomenon continues to remain unresolved. The many theories which have evolved to explain hysteresis can be grouped into three major categories: (1) those which presumptively accept the validity of the Young equation as applied to solids, and which account for hysteresis in terms of variations in the interfacial free energies; (2) those which

overtly accept the validity of Young's equation, and explain hysteresis in terms of surface geometry; and (3) those which eschew Young's equation, and seek an explanation in terms of the atomic or molecular structure of the solid surface. In the first category fall the theories of (a) surface-decontamination by the advancing liquid (1, 12), and (b) reorientation of the solid surface-atoms or molecules on contact with the liquid (8). In the second, falls the theory of surface roughness (4, 10, ~~13~~). In the third, falls the theory of submicroscopic solid surface inhomogeneity (i. e., molecular-scale variations in free surface energy or liquid-adsorptivity)(2, 5). It is unfortunately true that, of these theories, those capable of direct experimental verification (i. e., surface-contamination, roughness) have not been demonstrated to be universally correct, and the others defy direct confirmation with currently available analytical tools.

This marked disparity in wetting behavior of solids on one hand and liquids on the other prompted the authors to inquire into the wetting characteristics of an intermediate category of substances which possess properties akin to both liquids and solids, namely gels. A gel can be considered as a captive liquid, imprisoned in a tenuous, three-dimensional fibrous network with the macroscopic properties of an elastic solid. By suitable selection of the gelling agent, it is possible to produce a stable gel in which neither the thermodynamic (i. e., activity, free surface energy) nor kinetic (i. e., diffusivity, "microviscosity") properties of the dispersion medium are significantly different from that of the pure liquid phase. It was believed that, by examining the contact angle between a liquid and a gel surface, it might not only be possible to ascertain whether contact angle hysteresis were attributable to microscopic or macroscopic molecular immobility in a solid surface, but also to compare directly the measured contact angles on the gel surface with the single-valued contact angle for the liquid pair in the absence of the gelling agent. In other words, a gel is unique among "solids" in that its free surface energy can be determined with very small

margin for error.

To this end, aquagels were prepared using agar (in varying concentrations) as the gelling agent. Agar, being a high-molecular weight polysaccharide of high purity, was selected because of its lack of capillary activity, and its virtual freedom from capillary active contaminants, and because of its ability to produce stable gels at relatively low concentration levels when its effect on the chemical potential of water would be minimal. The non-spreading organic liquid selected for the drop-phase was methylene iodide, because of its availability in high purity, its relatively low volatility, and the presence in the literature (3, 7) of accurate data on surface- and interfacial tensions, and contact angles, for the methylene iodide-water-air system.

III. Experimental

Weighed quantities of agar agar (U.S.P.) were dispersed in specified volumes of hot (about 90°C) distilled water with strong agitation. The resulting sols (with agar concentrations varying between 0.35% and 2% by weight) were vacuum filtered while hot to remove incompletely dissolved material, and then cooled to about 40°C with continued stirring. The liquids were then poured into a rectangular (3 x 10 x 10 cm) glass cuvette, and allowed to gel. Chlorosilane-treatment of the interior walls of the cuvette minimized meniscus-development at the gel-glass boundary, but it was found necessary to cut away a thin layer of the gel near the optical windows of the cell to obtain an undistorted view of the plane gel surface.

Methylene iodide (C.P.) was introduced onto the gel surface by means of a B-D Yale 1/4 cc. ~~hypodermic~~ ^{hypodermic} syringe equipped with a 27 gauge hypodermic needle whose end had been flat-ground. The syringe was mounted over the surface of the gel in the cuvette in an adjustable holder.

Profiles of drops on the gel surfaces were recorded photomicrographically. Illumination was provided by a Zeiss microscope illuminator and collimator, and photographs of the back-lighted drop-silhouettes taken on 3 1/4 x 4 1/4 inch Eastman Contrast Process

Ortho cut film, using a camera described by Hauser and Michaels (9), equipped with a 48 mm. microscope objective. Magnification was approximately 20 X.

Drops were caused to advance over or recede from the gel surfaces by adding or removing liquid from the drop via the hypodermic, and then allowed to equilibrate for periods varying from 5 to 139 minutes. To prevent evaporation of water from the gels during the observations, the vapor phase above the gel was kept saturated by placing a small, water-wet plug of absorbent cotton in the free space at the top of the cell.

Contact angles were measured directly on the photographic negatives by means of a straightedge and protractor, with an estimated precision of about $\pm 2^\circ$. The arithmetic mean of the angles measured at both sides of the drop profile was considered to be the best value, although the difference between the two measurements seldom exceeded the limit of precision. Between three and six independent observations were made of advancing and receding drops on each gel studied, and the average of these reported as the final result.

All measurements were made at an ambient temperature of $24 \pm 1^\circ\text{C}$.

IV. Results

The measured advancing and receding contact angles, and the corresponding hysteresis values, are presented in Table I for the various concentrations of gel examined. There were no consistent variations in contact angle with time of equilibration, and it is deduced that the reported values are essentially time-independent.

In Table I are presented the values obtained by Fox (7) for the boundary tensions and contact angles for the mutually saturated system air-water-methylene iodide at 25°C . These values are internally consistent, and in agreement with Young's equation.

Typical photographs of an advancing and receding drop are shown in Figures 1 and 2. In some instances, a small amount of syneresis of the gel occurred in the course of the measurements,

Table I
 Contact Angles and Hysteresis for Methylene Iodide on
 Agar Aquagels ($24 \pm 1^\circ\text{C}$)

Agar Conc., wt. %	Mean Advancing Angle ($^\circ$)	Maximum Advancing Angle ($^\circ$)	Mean Receding Angle ($^\circ$)	Minimum Receding Angle ($^\circ$)	Mean Hysteresis ($^\circ$)	Maximum Hysteresis ($^\circ$)
0.35	48 ± 5	52	26 ± 1	25	22 ± 6	27
0.50	71 ± 4	78	32 ± 5	30	39 ± 9	48
0.50 (replicate)	53 ± 5	66	32 ± 4	28	21 ± 9	38
0.75	86 ± 3	91 (?)	34 ± 5	25	52 ± 8	66
1.0	67 ± 4	77	--	--	--	--
1.0*	68 ± 1	69	30 ± 2	28	38 ± 3	41
2.0	68 ± 2	72	26 ± 8	13 (?)	42 ± 10	59
Mean Values:	66 ± 4	72 ± 8	30 ± 4	25 ± 4	36 ± 8	47 ± 11

Table II
Capillary Characteristics of the Methylene Iodide-
Water-Air System at 25°C*

Surface tension of water (saturated with methylene iodide)	71.9 dynes/cm
Surface tension of methylene iodide (saturated with water)	49.8 dynes/cm
Interfacial tension water-methylene iodide	41.1 dynes/cm
Contact angle measured through air	146.2°
Contact angle measured through water	137.6°
Contact angle measured through methylene iodide	75.9°

* Data of Fox (7)

leading to the formation of a very thin annular ring of water at the drop base. This is shown in Figure 3. While this ring obscured the gel-drop contact point, estimation of the gel-drop contact angle did not appear to be significantly interfered with by its presence.

V. Discussion

Examination of Table I indicates that, despite the lack of reproducibility of the contact angles (particularly the advancing angles), there is unquestionably a high degree of contact angle hysteresis on agar aquagel surfaces, irrespective of agar concentration. Within the limits of reducibility, it is also apparent that there is no consistent dependency of contact angle or hysteresis on agar concentration, at least in the range of 0.5 - 2.0 per cent agar. It is possible that there may be reduced hysteresis (and reduced advancing angle) with the 0.35% gel; however, this concentration corresponds nearly to the minimum quantity of agar required to produce a coherent gel, and it is not unlikely that such a weak gel may exhibit some gross fluidity. Furthermore, distortion of the surface of a gel of such low modulus by even very small drops of methylene iodide could cause the apparent contact angle to be less than the true value. Hence, there is little evidence from the data to indicate that the contact angles are dependent on agar concentration over the entire range studied.

It will be noted that the scatter of the mean advancing and receding angle values is appreciable. This observation has frequently been reported in the literature, and evidently reflects the fact that the contact angle measured after advancing (or receding) of a drop can but rarely be as great (or as small) as the limiting angle at which advancing (or receding) begins. It may, therefore, be considered more justifiable to employ in any analysis the maximum advancing and minimum receding angles measured in any one system, rather than the average values. These limiting values are reported in Table I, and the average of these will be used in the subsequent discussion.

The mere fact that substantial hysteresis of the contact angle is observed on these dilute aquagels is, in the opinion of the authors, of considerable theoretical significance, since it at once casts serious doubts upon several of the current hypotheses of the hysteresis phenomenon. Firstly, it appears very unlikely that hysteresis on a dilute gel surface could have its origins in surface roughness, since a gel surface must be virtually as smooth or regular (on a microscopic as well as macroscopic scale) as the surface of the solution from which it forms. Secondly, theories which attribute hysteresis to (a) removal by the advancing liquid of adsorbed contaminants on the solid surface, or to (b) reorientation of the solid surface molecules contacted with the advancing liquid (such orientation persisting after recession of the liquid), are difficult to defend in the light of the present observations. Even if surface active contaminants were present in the gel (which is not likely), inasmuch as both the surface and interior of the gel are composed virtually entirely of water molecules of unrestricted mobility on a micro-scale, one would expect that such contaminants would be freely diffusible throughout the entire gel. It would thus be difficult to conceive of a localized "decontamination" of the gel surface by receding methylene iodide which would persist for anything like two hours. By the same token, in view of the nearly unrestricted rotational freedom of water molecules in the gel surface, it appears improbable that any preferred orientation of these molecules which occurs on contact with liquid methylene iodide would remain for any sensible period of time after removal of the drop phase.

Of the remaining theories of hysteresis, those relating to microscopic surface inhomogeneities appear at first hand to be most tenable, as applied to a gel surface. The surface of a gel certainly contains molecules (or segments of molecules) of the gelling agent, and it is entirely reasonable that the attractive forces between such molecules and those of overlying liquid will be different from those between the liquid component of the gel and the drop phase. On the other hand, there are certain aspects of gel structure and composition, and of the results of this investigation, which

materially weaken this argument. It is generally believed that the process of dissolution of a linear macromolecule such as agar in a suitable solvent involves the formation of a shell or lysosphere of solvent molecules about the solute molecule. As a consequence of this solvation, the exterior of the solute molecule appears and acts little differently from the bulk liquid phase. The fact that agar has little detectable effect upon the surface tension of water is experimental evidence supporting this picture. This may be construed to mean that areas of the gel surface where agar molecular segments are present are energetically about the same as those areas containing only water. The observed lack of dependence, in this study, of contact angle and/or hysteresis on agar concentration over more than a five-fold concentration range also speaks against a surface heterogeneity hypothesis, since one would normally expect the degree of heterogeneity to increase with increasing agar concentration (in the concentration range studied), with subsequent change in contact angle and hysteresis. Finally, there is, in all probability, the same degree of surface-heterogeneity associated with an agar solution slightly above its gelation temperature as there is below it, yet there appears to be no contact angle hysteresis (nor departure from Young's relation) on agar sols.

It consequently is the opinion of the authors that the hysteresis phenomenon on gel surfaces is in some way associated with the macroscopic immobility of macromolecular segments in the surface, rather than with constitutional properties of these segments per se, nor their area-density. An alternative theory of the hysteresis phenomenon is therefore proposed, which has its origin in this premise.

The "average" maximum advancing (θ_A) and minimum receding (θ_R) angles of methylene iodide on agar gels determined in this study are 72° and 25° respectively. By employing the surface- and interfacial tension data of Fox (7), and solving Young's equation for the methylene iodide contact angle on a hypothetical plane water surface, an "equilibrium" contact angle (i. e., the angle which would be made between the two liquids if the boundary tensions were

in static balance) can be calculated. This angle, designated as θ_E , is found to be 52° . Now, in a liquid-solid system, the only surface to which a true contractile tension can be unequivocally assigned is that of the liquid. The component of that tension acting in the plane of the solid surface at the contact-line between solid and liquid (in units of force per unit length of drop-periphery) is given by $\gamma_L \cos\theta$. For the advancing, receding, and equilibrium contact angles cited above, the corresponding planar force components are:

$$F_A = \gamma_L \cos\theta_A = 15.4 \text{ dynes/cm}$$

$$F_R = \gamma_L \cos\theta_R = 45.1 \text{ dynes/cm}$$

$$F_E = \gamma_L \cos\theta_E = 30.2 \text{ dynes/cm}$$

If, on advancing (or receding), the force-contribution from the liquid surface must be reduced below (or increased above) that required to maintain equilibrium for the liquid-liquid case, the difference between these two values can be interpreted as an "extra force" acting on the plane of the gel surface which must be provided to cause the liquid to move. The corresponding values of this "extra force" are:

$$F_E - F_A = 14.8 \text{ dynes/cm}$$

$$F_E - F_R = -14.9 \text{ dynes/cm}$$

The implications of these calculations are provocative, inasmuch as they indicate that whatever agency is responsible for hysteresis requires application of a force in the plane of the gel surface of about equal magnitude (but opposite sign) to cause the liquid phase to advance or recede on the substrate. A corollary of this observation is the relation:

$$\cos\theta_A + \cos\theta_R = 2\cos\theta_E \quad (2)$$

From (2), one is tempted to generalize that the "true equilibrium" contact angle between a liquid and a solid is the invercosine of the arithmetic mean of the cosines of the advancing and receding angles. Unfortunately, extensive testing of this relationship for solid-liquid systems is impossible since the boundary free energies γ_{SL} and γ_S are not accessible; confirmation of this equation for a large number of different gel-liquid systems might, however, lend substance to its generality.

In the search for a tenable explanation for the source of this "excess force", and hence of hysteresis, it is informative to look into the microstructure of agar aquagels, and of their free surfaces. Agar is composed of semi-rigid polysaccharide chains of appreciable length which, in an aquagel, are solvated by water, randomly scattered throughout the liquid phase, and bonded to one another relatively infrequently and irregularly. It is reasonable to assume that the gel surface can be represented as a two-dimensional network structure of analogous geometry. If one postulates that the actual volume of a given mass of hydrated agar is about four times that of the dry solid, then a 0.5% agar gel will contain roughly 2% by volume of macromolecular substance with its "firmly bound" water, the remainder of the volume being "normal" liquid water. In any surface (granting absence of positive or negative adsorption), the area density of hydrated agar will be $(0.02)^{2/3}$, or roughly 7% of the surface layer. Since the diameter of a hydrated agar chain is of the order of 20 Angstroms, the surface may be envisioned as random "checkerboard" composed of islands of water molecules averaging about 400 Angstroms in width and breadth, separated from one another by 20 Angstroms tubular "rafts" of hydrated agar (see Figure 4).

In each one of these "islands" there reside of the order of 16,000 water molecules, a number probably large enough for these areas to behave as a normal liquid water surface. Hence, if the edge of a drop of methylene iodide were to reside on such an area, there is no reason to believe that the contact angle would be anything but the "equilibrium" value, θ_E , of 52° . An advancing drop would traverse these areas at this angle, as would a receding drop.

When, however, the edge of a drop, after advancing or receding, reaches an agar "raft", an unusual situation develops. While in the island areas the advancing drop encounters no significant resistance to the movement of either water or methylene iodide molecules in the plane of the surface, when an agar chain is encountered, such unrestricted lateral movement is impeded. If it is postulated that mere restriction of lateral mobility of the substrate molecules

is sufficient to pose a barrier to forward (or backward) movement of the drop-edge, then additional energy will be required for the drop edge to traverse the raft, and the observed hysteresis of the contact angle reconciled. The immediate corollary to such a postulate is that, for all contact angles greater or less than the "equilibrium" value, the three-phase contact line must lie on elements of the agar network, and thus be highly irregular on a molecular scale, as indicated in Figure 4. This condition has been predicted by proponents of the surface heterogeneity theory, such as Devaux (5), and Doss and Rao (6). If this situation does obtain, then the macroscopic contact angles may not bear much relation to the local contact angle at the three phase boundary (if, indeed, one can talk intelligently about "contact angles" on a molecular scale); were, however, the length of the true contact line to be a constant multiple of the apparent geometric line, then the term $\gamma_L (\cos\theta - \cos\theta_E)$ would still be a good measure of the "excess force" required for traverse of the barrier. Since the length of the actual contact line per unit length of apparent contact should be independent of the network area-density, the observed lack of dependence of the contact angle on agar concentration is not unexpected.

That lateral immobility of substrate molecules may by itself be sufficient to produce a barrier to drop advancement or recession can, it is believed, be justified by means of a simple molecular model, illustrated in Figure 5. There are at least three stepwise processes involving movements of nearest or next-nearest molecular neighbors whereby a liquid may advance on (or recede from) a substrate. In Process A, a molecule in the free liquid surface adjacent to the most advanced liquid-substrate molecular pair may move to the next unpaired substrate molecule; this is a next-nearest-neighbor movement through the low-density (gas) phase. In Process B, the most advanced liquid molecule at the substrate surface moves to the next unpaired substrate molecule, with the nearest liquid surface molecule taking its place; this is a nearest-

neighbor movement through the gas phase. In Process C, the most advanced liquid-substrate molecular pair moves into the nearest neighbor position, while the adjacent substrate molecule recedes into the second molecular layer; simultaneously, a liquid molecule and substrate molecule move into the space just vacated at the liquid-substrate boundary. This process is a nearest-neighbor movement through two high-density phases.

In the transition of Process A, a molecule must move a rather substantial distance through a zone of low force-field intensity, and thus must be provided with a relatively large surplus of energy to make the jump successfully. In Process B, the jump-distance is smaller, and the mean force field intensity during the transition higher, hence the required energy surplus is less. In Process C, the jump-distances are of the same order as in B; however, the force field intensities during the transitions are never much less, and in some cases greater than they are in the initial and terminal positions. The energy surplus required in C would, therefore, be expected to be significantly less than those in either A or B. Clearly, however, C requires unhindered lateral mobility of adjacent surface molecules of the substrate--a privilege accorded only to liquids. On gels or solids, advancement or recession may proceed via B if the bonding forces between liquid and substrate molecules are of the same order as those between adjacent liquid molecules, and via A only, if they are much greater. The "energy surpluses" required for the type A and B advancement are provided by suitable increases (or corresponding decreases for recession) in the contact angle above the "equilibrium" value determined by the boundary energies, and are directly responsible for contact angle hysteresis.

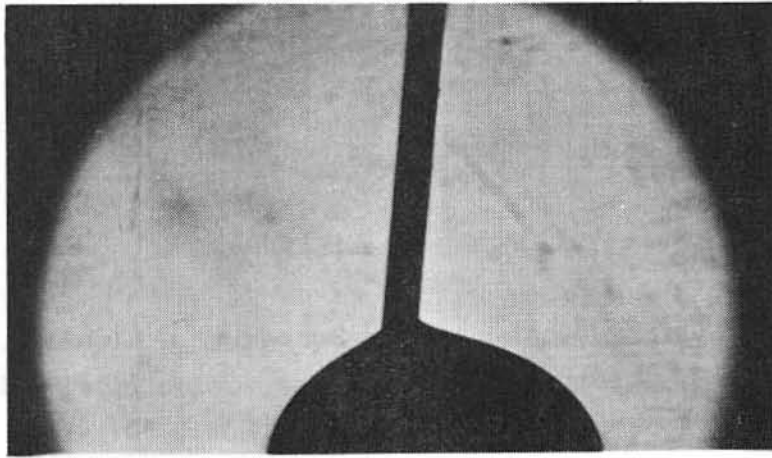
Summarizing, it is deduced from the observations herein reported that advancement or recession of liquid-on-liquid occurs primarily by migration of molecules into or out of the liquid-liquid interface without the formation or disruption of molecular pairs at the drop periphery. This is a process of low "surplus energy" demand, and hence contact angles in liquid-liquid systems are determined by

the boundary free energies. In liquid-solid systems, where unrestricted lateral mobility of molecules of the solid is improbable, movements of higher surplus energy demand are necessary; these manifest themselves as hysteresis of the contact angle.

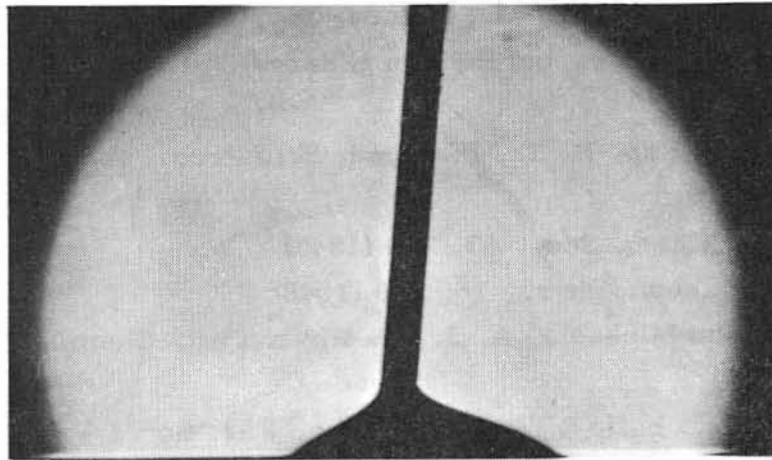
It is concluded, from the results of this investigation, that the phenomenon of contact angle hysteresis is not confined solely to conventional solid surfaces, but also exists on the surfaces of agar gels whose microscopic properties are essentially those of liquid water. Wetting studies will naturally have to be performed on a number of different gel-systems, not only to establish whether the phenomenon is a general one, but also to test the soundness of the hypotheses herein presented.

Literature Citations

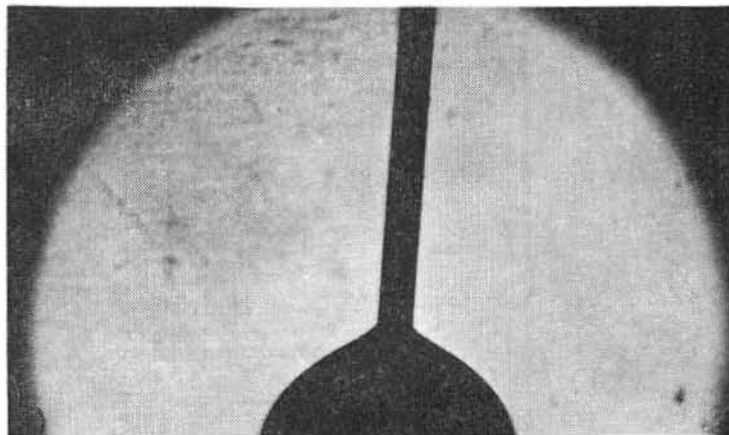
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1.)



2.)



3.)

Representative Microphotographs of Methylene Iodide on Agar
Aquagels (0.75% Agar)

- 1.) Advancing Drop
- 2.) Receding Drop
- 3.) Advancing Drop, Showing Ring of Gel Exudate at Base

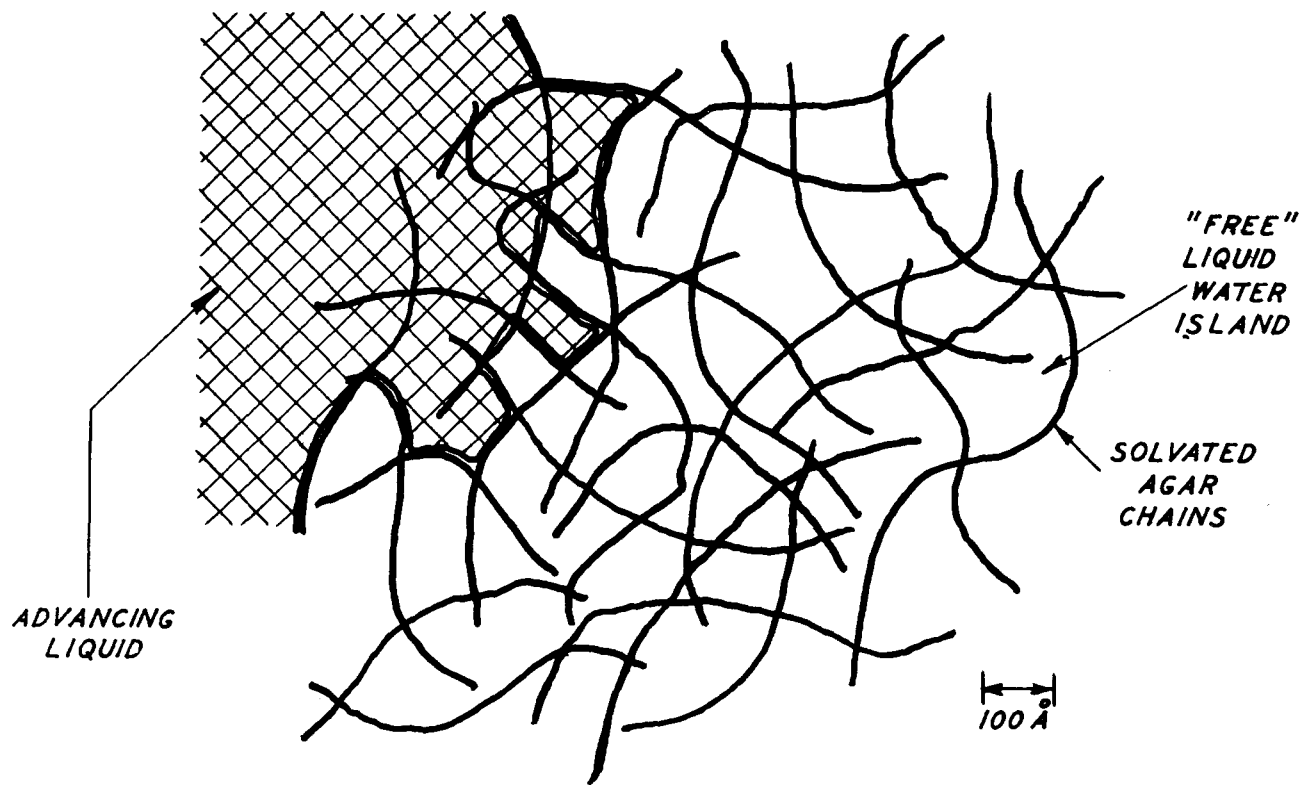


FIGURE 4

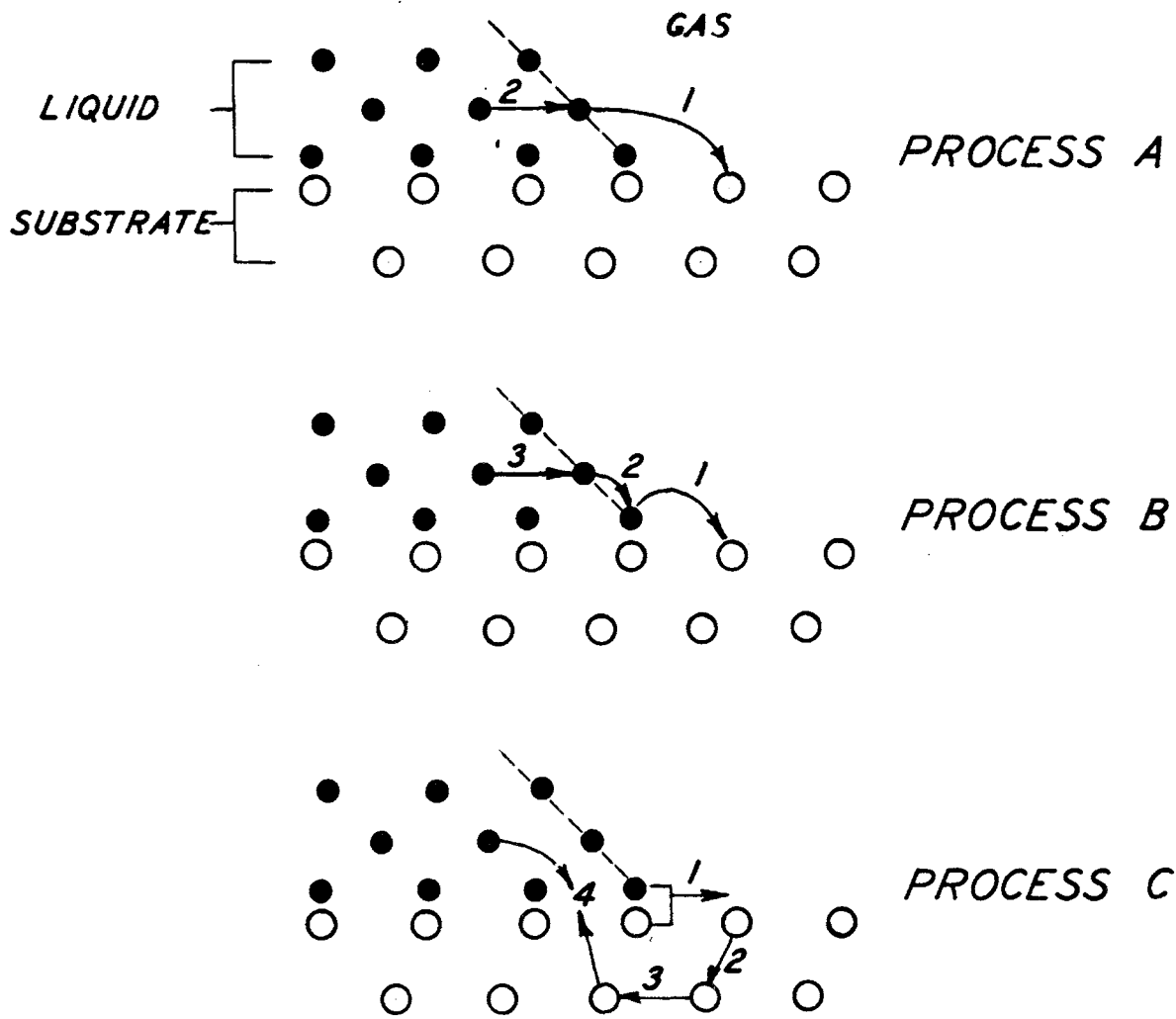


FIGURE 5