significant chemical changes could occur. The Ca-phosphate now found in these sediments is of detrital origin and does not indicate salinity in the depositional environment. (ii) A previously existing small amount of Ca-phosphate may have become enriched and indicate falsely a marine environment. The dark claystones under- and overlying coal measures of the Upper Carboniferous soon after deposition were reduced due to their high content of organic material. In a lacustrine environment Fe-phosphate, if present, will be transformed under reducing conditions in the presence of H_2S into FeS, and phosphate ions are liberated.

These two disadvantages of the new method are so frequently found in sedimentary rocks that this method cannot be used extensively.

GERMAN MÜLLER
Laboratorium für Sedimentforschung,
University of Heidelberg,
Berliner Strasse 79
69 Heidelberg, Germany

References and Notes

1. B. W. Nelson, *Science* **158**, 917 (1967).
2. I thank Professor Falke and Drs. Rabitz and Fiebig for providing sample material.

28 October 1968

Coalescence of Two Immiscible Liquid Drops

Abstract. *When two immiscible liquid drops suspended in a third immiscible liquid are brought into contact, three equilibrium configurations which depend upon the spreading coefficients are possible. Experiments for a large number of systems, including three-phase emulsions, confirm the theory and indicate the mechanisms of reaching equilibrium.*

We have studied the interaction of two immiscible liquid drops brought into collision in a third immiscible liquid by shear motion or by mutual electrostatic attraction in an externally imposed electrical field or by a combination of the two effects. This report is an extension of earlier work on the coalescence of two identical liquid drops interacting under similar conditions (*1, 2*).

We have considered the equilibrium configurations to be expected when the two drops, designated as phases 1 and 3 with radii b_1 and b_3, respectively, come into intimate contact in the liquid medium (phase 2) so that, in addition to the existing 12 and 23 interfaces, the 13 interface can also form. We assume that the final equilibrium states are determined solely by the three interfacial tensions σ_{ij} $(i \neq j \neq k = 1, 2, 3)$; thus gravity, fluid motion, and forces between particles do not determine the position of equilibrium, even though, in practice, these other factors may be important in promoting its attainment.

After considering the three spreading coefficients $S_i = \sigma_{jk} - (\sigma_{ij} + \sigma_{ik})$ and adopting, without loss of generality, the convention of designating phase 1 as that phase for which σ_{12} is greater than σ_{23} so that S_1 is less than 0, we have shown that there are only three possible sets of values for S_i:

$$S_1 < 0 \quad S_2 < 0 \quad S_3 > 0 \qquad (1)$$

$$S_1 < 0 \quad S_2 < 0 \quad S_3 < 0 \qquad (2)$$

$$S_1 < 0 \quad S_2 > 0 \quad S_3 < 0 \qquad (3)$$

These three conditions lead to three different equilibrium configurations which are independent of b_1 and b_3.

1) Complete engulfing: Phase 1 is entirely absorbed into phase 3 to form a spherical drop which has two spherical interfaces (23 and 13). The external radius of this compound drop, which we define as a 2-singlet, is

$$r_{23} = (b_1^3 + b_3^3)^{1/3}$$

2) Partial engulfing: The three interfacial tensions form a closed (Neumann) triangle with the 12, 13, and 23 interfaces in equilibrium along a 123 line bounding the three phases. The geometrical details of the resulting drop, which we call a 3-singlet, are determined from capillarity equations and the interfacial tensions and initial radii of the drops.

3) Nonengulfing: The 13 interface cannot form spontaneously, and the drops remain separated as a 2-doublet.

We have confirmed the predictions by experiments with over 20 different systems. In all of these systems one of the phases is water or an aqueous solution of a surface-active agent, and the three phases are of nearly equal density. The systems reflect a wide range of values of S_i (−40 to +15 dyne cm^{-1}), b_i (10 μm to 1 mm), and phase viscosities (0.01 to 50 poise). Most of the experiments were performed in a Couette apparatus consisting of two concentric cylinders capable of counter-rotation. Pairs of liquid drops were brought into collision at velocity gradients up to 2 sec^{-1} in transversely applied electric fields up to 2 kv/cm. The apparatus included provision for viewing the drops through a microscope and taking photographs of the events (*3*).

The equilibrium configurations attained were in accord with conditions 1 to 3 except for several systems in which either S_2 or S_3 was nearly zero. Here the extent of engulfing was smaller than predicted, presumably because the driving force S_i was too small to achieve true equilibrium.

The measured geometry of the 3-singlets was in fairly good agreement with the theory (Fig. 1) for a system in which the size ratio $R_0 = b_1/b_3$ was varied over wide limits. We conclude that in this system, in which the smallest drop radius was 300 μm, the 3-phase line tension σ_{123} (*4*), which, in principle, can influence the drop geometry, was not appreciable.

Systems which correspond to conditions 2 and 3 and which were forcibly engulfed by the injection of a droplet of phase 1 into phase 3, deengulfed to form either a 3-singlet or a 2-doublet in accordance with the theory. In some cases the 3-singlets had one of the phases dispersed as a myriad of tiny lenses at the surface of the other phase.

The mechanism of engulfing, as observed by high-speed photography, can best be illustrated by the formation of a 2-singlet. When two drops are pressed together, the phase-2 film between them drains until a hole suddenly forms in

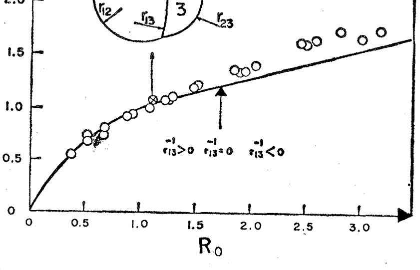
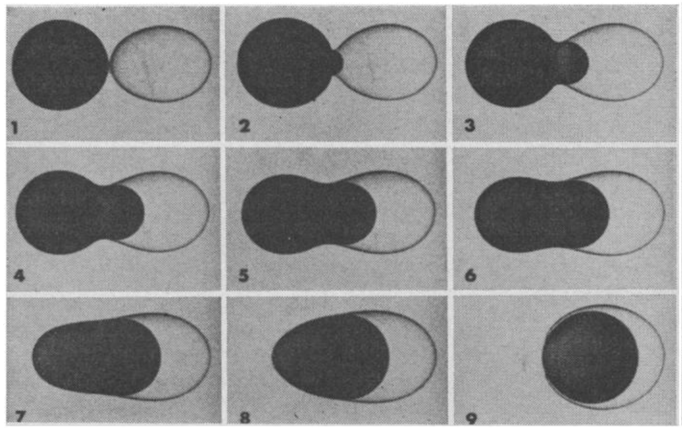


Fig. 1. Measured (points) and calculated (line) shapes of 3-singlets in the system H_2O + 10 percent (by volume) Tween 20 (phase 1), silicone oil (phase 2), and castor oil (phase 3). The arrow indicates the point at which the 13 interface changes its curvature from positive to negative. Inset is the configuration of the doublet drawn to scale for the system marked with a cross. Of the various geometrical parameters of the doublet, we have selected $R = r_{12}/r_{23}$. The quantity $R_0 = b_1/b_3$ is the ratio of the radii of the undeformed drops; R is the ratio of the final radii of curvature of the 12 and 23 interfaces.



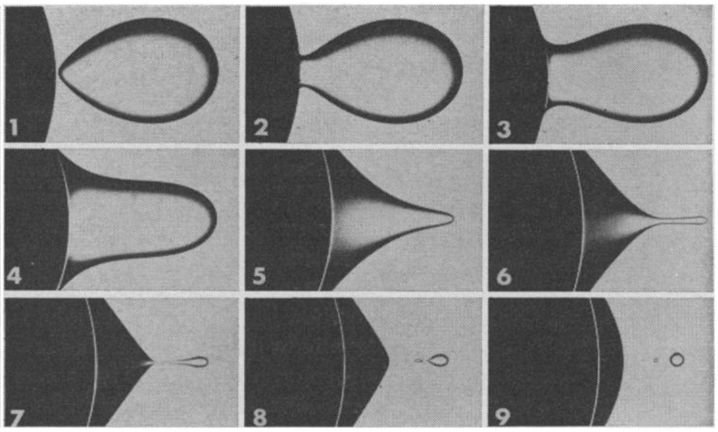


Fig. 2 (left). Photographs of the stages of complete engulfing ($R_0 = 1$) of water + 1 percent (by volume) malachite green (black drop) by a drop of polyglycol oil (Ucon oil LB-285) suspended in silicone oil. Frames 1 to 6 show the penetration of the aqueous phase into the oil phase, and frames 7 to 9 show the subsequent relaxation of the deformed water drop into the oil drop. The total elapsed time was 0.9 second. Engulfing was promoted by the application of a horizontal electrical field of 2.0 kv/cm. The diameter of the drop of polyglycol oil was 0.8 mm. The same steps were followed when engulfing was promoted by a shear field alone. Fig. 3 (right). The engulfing process for the same system as in Fig. 2 at $R_0 = 10$. Here the phase-3 drop (clear drop) spread over the drop of dyed water (phase 1) shown in part on the left. In this case $\Delta p_{13} < 0$, and no penetration occurred. Partial coalescence (*6*) left a daughter drop of phase 3 (frames 7 to 9). The diameter of the drop of polyglycol oil was 0.8 mm, and the total time was 5 seconds.

the same way as in the two-phase systems (*1, 2*). Now, however, a third interface, 13, is formed at the expanding hole, and coalescence (or engulfing) occurs by two competing processes: (i) the penetration of phase 1 into phase 3 under the action of a positive capillary pressure difference

$$\Delta p_{13} = 2(\sigma_{12}/b_1 - \sigma_{23}/b_3)$$

across the 13 interface; and (ii) the spreading of phase 3 over phase 1 under the action of S_3. Penetration is favored by low values of R_0, σ_{13}, and σ_{23}, and by high values of σ_{12}; spreading is favored by high positive values of S_3 and R_0. Figure 2 shows the steps in the engulfing process where penetration overrides spreading. Spreading predominates in the engulfing process for the same system when R_0 is large (Fig. 3) (*5, 6*).

The same equilibrium configurations are formed in three-phase emulsions in which phase 2 usually contains the emulsifying agent, the observed configurations corresponding to the three conditions cited above. We believe that measurements of the geometry of 3-singlets several micrometers in diameter may provide a more reliable method of determining the line tension σ_{123} than other methods (*4*). Interesting three-phase emulsions can be formed consisting of two incompatible polymer solutions such as 2 percent solutions (by weight) of polystyrene and polyisobutene in toluene. When dispersed in water containing an emulsifier (Dowfax 9N15), 3-singlets can be observed in a phase-contrast microscope. The compound droplets are nearly spherical and the 13 interface is nearly flat; this indicates that σ_{12} is approximately equal to σ_{23} and that σ_{13} is close to zero. Quantitative measurements of the curvature of the 13 interface may provide a method for calculating σ_{13} which is difficult by conventional methods (*7*).

Experimental variations included (i) the engulfing of droplets which react chemically with one another, for example, interfacial polycondensation of hexamethylenediamine and sebacyl chloride to produce a nylon membrane at the 13 interface in a 2-singlet (*8*); (ii) permutation of phases with predictable changes in equilibrium configurations; (iii) interaction of droplets which are soluble in one another; here the transient σ_{13} is effectively zero and penetration is thereby promoted; (iv) rotation, deformation, and burst of 2-singlets and 3-singlets in shear and electrical fields, thus providing variations of the corresponding phenomena in single droplets (*9*); (v) experiments in which one of the phases is a solid or a gas; here the engulfing processes can be complicated by buoyancy (gas bubbles) and contact-angle hysteresis (solid spheres); and (vi) interaction of drops with diffusing components which generate surface flows of the Marangoni type at the various interfaces (*2*).

These equilibrium configurations and the processes of formation are important in colloid and surface chemistry, especially in the preparation of practical emulsions. Furthermore, the analysis of engulfing and deengulfing processes can be useful in explaining biological phenomena such as fecundation, pinocytosis, phagocytosis, and in finding physicochemical therapeutic compounds able to selectively engulf cancer cells (*10*).

S. Torza
S. G. Mason

Pulp and Paper Research Institute of Canada and
Department of Chemistry, McGill University, Montreal, Canada

References and Notes

1. R. S. Allan and S. G. Mason, *Trans. Faraday Soc.* **57**, 2027 (1961); *J. Colloid Sci.* **17**, 383 (1962).
2. G. D. M. MacKay and S. G. Mason, *Kolloid Z.* **195**, 138 (1964).
3. W. Bartok and S. G. Mason, *J. Colloid Sci.* **12**, 243 (1957).
4. I. Langmuir, *J. Chem. Phys.* **1**, 756 (1933); W. D. Harkins, *ibid.* **5**, 135 (1937); F. P. Buff and H. J. Saltsburg, *ibid.* **26**, 23 (1957).
5. Complete engulfing by the penetration mechanism appears similar to the penetration of oil drops into naked *Arbacia* (sea urchin) eggs in seawater; Robert Chambers and M. J. Kopac, *J. Cell. Physiol.* **9**, 331 (1937).
6. G. E. Charles and S. G. Mason, *J. Colloid Sci.* **15**, 105 (1960).
7. V. N. Kuleznev, L. S. Krokhina, B. A. Dogadkin, *Kolloidn. Zh.* **29**, 170 (1967).
8. T. M. S. Chang, *Science* **146**, 524 (1964); ———, F. C. MacIntosh, S. G. Mason, *Can. J. Physiol. Pharmacol.* **44**, 115 (1966).
9. W. Bartok and S. G. Mason, *J. Colloid Sci.* **14**, 13 (1959); F. D. Rumscheidt and S. G. Mason, *ibid.* **16**, 238 (1961); R. S. Allan and S. G. Mason, *Proc. Roy. Soc. London Ser. A* **267**, 45 (1962).
10. L. J. Old, E. A. Boyse, H. A. Campbell, *Sci. Amer.* **219**, 34 (August 1968).
11. Supported by the Petroleum Research Fund (grant 2457-C) administered by the American Chemical Society.

12 November 1968