

obtained from a Langmuir plot, as reported for graphite<sup>2</sup>. The B.E.T. monolayer volume is 1.24 c.c. at N.T.P., Taking 20 Å.<sup>2</sup> for the effective cross-sectional area of a krypton atom, the film area is 6.67 m.<sup>2</sup> or 565 m.<sup>2</sup>gm.<sup>-1</sup>. Films of this area, which is such that contamination hazards are much less severe than before, are readily prepared by the new method. The specific surface area is some ten times greater than that of the thinner films prepared by Sykes and Thomas, and is only slightly affected by baking at 550° C. A study of the relation of film area to film thickness is under way.

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<sup>1</sup> Sykes, K. W., and Thomas, J. M., *Proc. Fourth Carbon Conf.*, 29 (Pergamon Press, 1960).  
<sup>2</sup> Ross, S., and Winkler, W., *J. Coll. Sci.*, **10**, 330 (1955).

### The Marangoni Effect and Liquid/Liquid Coalescence

THE rate of coalescence of liquid drops (phase 1) suspended in an immiscible liquid (phase 2) has been shown to increase when a third component, soluble in both phases, diffuses out of the drop<sup>1-5</sup>, and vice versa. This behaviour has been attributed to the Marangoni effect<sup>6</sup>, whereby interfacial flow is established by gradients in interfacial tension causing an increase in one case, and a decrease in the other, of the rate of thinning of the phase-2 film separating the coalescing interfaces.

We have studied the buoyant rise of a drop of water (phase 1) through cinnamaldehyde (phase 2) to a flat phase 1/phase 2 interface, using an interferometric method<sup>8</sup> to measure the rate of thinning  $-(dh/dt)$  of the intervening phase-2 film. For drops 650μ diam., the thinning followed the relation<sup>3</sup>:

$$-\frac{dh}{dt} = kh^3$$

Table 1 lists experimental values of  $k$  and the corresponding values of the mean rest time  $\bar{\tau}$  (ref. 3), which offer strong support of the foregoing hypothesis. Similar, but less complete, results were obtained from the system water/diphenyl sulphide.

Table 1

	$\bar{\tau}$ sec.	$10^3 k$ cm. <sup>-2</sup> sec. <sup>-1</sup>
1 per cent acetone in phase 1	5.3	$\geq 3$
Pure system	8.1	3.0
1 per cent acetone in phase 2	12.0	2.0

The film drainage was uniform and symmetrical in each case, and the minimum thickness of the film at rupture was < 500 Å. Lateral oscillations, or 'kicks'<sup>9-11</sup>, were observed during the rise of a drop of water through cinnamaldehyde containing 1 per cent acetone. The oscillation became more marked as the drop approached the interface and continued during the early period of film thinning. Despite the fact that kicks were observed to propel the drop distances of several diameters on the interface, the circular patterns of interference colours and rings were undisturbed, indicating that film thinning continued at a uniform rate.

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- <sup>1</sup> Johnson, H. F., and Bliss, H., *Amer. Inst. Chem. Eng. Trans.*, **42**, 331 (1946).  
<sup>2</sup> Allan, R. S., and Mason, S. G., *J. Colloid Sci.* (in the press).  
<sup>3</sup> Charles, G. E., and Mason, S. G., *J. Colloid Sci.*, **15**, 236 (1960).  
<sup>4</sup> Groothuis, H., and Zuiderweg, F. S., *Chem. Eng. Sci.*, **12**, 288 (1960).  
<sup>5</sup> Sawistowski, H. (private communication).  
<sup>6</sup> Scriven, L. E., and Sternling, C. V., *Nature*, **187**, 186 (1960).  
<sup>7</sup> Zuiderweg, F. S., and Harmes, A., *Chem. Eng. Sci.*, **9**, 89 (1958).  
<sup>8</sup> Allan, R. S., Charles, G. E., and Mason, S. G., *J. Colloid Sci.*, **16**, 150 (1961).  
<sup>9</sup> Lewis, J. B., and Pratt, H. R. C., *Nature*, **171**, 1155 (1953).  
<sup>10</sup> Haydon, D. A., *Proc. Roy. Soc.*, **243**, 483 (1958).  
<sup>11</sup> Davies, T. V., and Haydon, D. A., *Proc. Roy. Soc.*, **A**, **243**, 492 (1958).

### Formation of Calcium Chloraluminate by Interaction of Portland Cement with Sea-water and Chloride Solutions

THE effect of chloride-containing solutions on Portland cement has received relatively little attention. Batta<sup>1</sup> and Thorvaldson<sup>2</sup> noted that addition of chloride ions to solutions containing sulphate reduced or inhibited the expansion of concrete and mortar bars. Batta attributed this effect to the increased solubility of gypsum and calcium sulphoaluminate in chloride solutions.

In the present investigation prisms of dilute pastes of Portland cement I and V and of mortar were exposed to various attacking solutions, including Mediterranean sea-water, solutions containing 3 per cent sodium chloride + 0.4 per cent magnesium sulphate (artificial sea-water), 3 per cent sodium chloride + 0.4 per cent sodium sulphate, 0.4 per cent magnesium sulphate, 0.4 per cent sodium sulphate, 3 per cent sodium chloride and 3 per cent magnesium chloride respectively and water from the Dead Sea. The products after different reaction times were identified by X-ray powder methods and simultaneously the expansion of duplicate prisms was measured.

Contrary to observations of Batta and Thorvaldson, addition of chloride ions to solutions containing sulphate was found to increase expansion of cement and mortar bars in all the present experiments. Expansion in sodium chloride solution only slightly exceeded that in distilled water. A considerable increase of volume was observed in magnesium chloride solution but can probably be attributed to the accelerated hydration caused by the reaction of magnesium ions with calcium hydroxide and hydrated calcium silicates of the cement.

X-ray patterns of all samples exposed to chloride-containing solutions showed, besides many other lines, a strong one at 7.90-7.97 Å. It was invariably observed independent of any other components present and was attributed to 3CaO.Al<sub>2</sub>O<sub>3</sub>.CaCl<sub>2</sub>.10H<sub>2</sub>O (A.S.T.M. card No. 2-0081). This was confirmed by direct comparison of the X-ray patterns with that of synthetic material.

The amount of chloraluminate formed is appreciable, increasing steadily with time of exposure of the bars to chloride solutions. The variations observed in