

distortion of  $\sim 5^\circ$  from a planar skeleton at the nitrogen atom. On the other hand, an increase of comparable magnitude may well be due to the crystal field effects discussed by Rowlands and Whiffen<sup>5</sup>.

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### Equilibrium at the Solid-Liquid Interface

Ward and Brooks<sup>1</sup> in 1952 provided the only experimental justification for the much used assumption of concentration equilibrium at the interface during solid dissolution investigations. Using both Lamm scale and Rayleigh interferometer measurements of concentration gradients they calculated interfacial concentrations equal to the saturation values for the dissolution of salicylic acid and of *n*-butyl acetate in water. They also reported probable saturation for the benzoic acid-water system although the calculated concentration at the interface varied somewhat with the experimental method. It appears that a more appropriate instrument for such measurements would be the Mach-Zender interferometer, which permits the direct measurement of concentrations in the vicinity of a solid surface<sup>2</sup>. For the present work an interferometer was constructed similar to that described by Caldwell for diffusion studies<sup>3</sup>. The continuous light source was replaced, however, by a high-intensity, short-duration spark discharge<sup>4</sup> to provide better photographic resolution of the rapidly changing concentrations in the vicinity of the interface. This instrument was then used to investigate the dissolution in water of benzoic acid and of acetanilide.

The diffusion cells constructed for this investigation had two separate compartments arranged so that each was intersected by one of the interferometer light beams. The upper (reference) compartment was then filled with distilled water only, while the lower one contained both the solid under investigation and the water solution in which that solid was slowly dissolving. Powders of the appropriate solids were compressed into blocks in a hydraulic press under an applied pressure of approximately 10,000 lb./in.<sup>2</sup>. The compressed solids were then carefully machined to fit into the cells and to provide flat, horizontal interfaces. Distilled water was permitted to fill the cell and overflow slowly. The water flow was then halted and a series of interferograms taken at convenient time intervals.

Fig. 1 is a typical set of interferograms. Parallel and vertical fringes on these photographs indicate a region of pure solvent. The number of fringes crossed while traversing downwards along a vertical path towards the interface gives the 'fringe shift' ( $F.S.$ ) at any location. The concentration may be evaluated from the fringe shift at any point and the reference concentration as follows:

$$C - C_r = \frac{\lambda_0}{Lk} (F.S.)$$

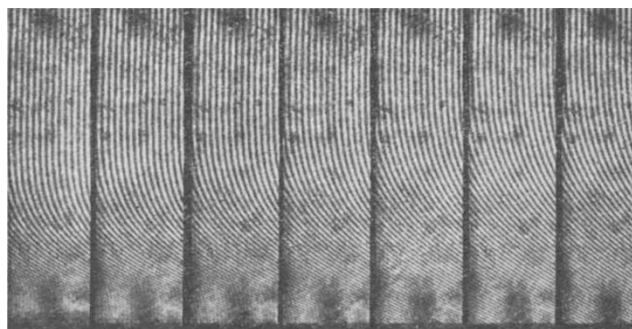


Fig. 1. Interferograms for dissolution of benzoic acid in water. Time of contact: a, 2,340 sec; b, 2,820 sec; c, 3,360 sec; d, 4,020 sec; e, 5,040 sec; f, 5,820 sec; g, 6,300 sec

where  $\lambda_0$  is the wave-length of the light beam in vacuum,  $L$  is the optical path length, and  $k$  is the concentration coefficient of refractive index. In this investigation the reference concentration,  $C_r$ , was always zero.

Interfacial concentrations were determined by measuring the maximum fringe shift from the undisturbed region to the interface by means of a Hilger microcomparator. Table 1 lists typical interfacial concentrations as well as saturation concentrations and calculated interfacial fluxes for both systems. The fluxes were obtained from the time-dependent concentration profiles measured for each system.

Table 1. INTERFACIAL CONCENTRATIONS AT 25-25° C

System	Measured interfacial concentration (g/l.)	Measured saturation concentration (g/l.)	Interfacial flux (g/cm <sup>2</sup> -sec)
Benzoic acid-water	3.273	3.370	$1.9 \times 10^{-7}$
Acetanilide-water	6.366	6.390	$1.83 \times 10^{-7}$

Because the observed interfacial concentrations are slightly less than the saturation values, it should be noted that the measured concentrations are distance averaged values along the optical path. Although care is taken to make the solid surface parallel to the interferometer beam, the camera cannot detect depression of the far side of the solid. The effect of any such surface misalignment or irregularity will be to reduce the apparent interfacial concentration by a slight amount. Thus, the measured deviations from equilibrium must represent a maximum value for this quantity with the possibility that the true deviation is somewhat smaller.

An interfacial transfer coefficient,  $\beta$ , was evaluated in the manner proposed by Drickamer<sup>5</sup>:

$$\text{flux, } J = \beta (C_{\text{satn}} - C_i)$$

For the conditions in Table 1,  $\beta$  assumes a value of  $1.93 \times 10^{-3}$  cm/sec for benzoic acid in water and  $7.51 \times 10^{-3}$  cm/sec for acetanilide in water. Since these parameters are nearly a thousand times greater than the respective diffusion coefficients, they far exceed the limits set by Drickamer for no measurable effect at the interface. Thus it is unlikely that a measurement of net mass flux between phases would detect any interfacial effect for either system, even if the departure from equilibrium reported for benzoic acid is realistic.

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