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THE ROTATING DISC ELECTRODE; HYDRODYNAMIC BOUNDARY
AND DIFFUSION LAYERS BY LASER INTERFEROMETRY

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It has recently become possible to build long path interferometers
to study concentration contours in electrochemical cells where the path
difference between interfering beams in a wedge-type interference cell
is 2 centimeters or greater. Such a cell has been described recently\textsuperscript{1}
and the theory presented\textsuperscript{2}. The present cell has been modified from those
previously described only in that a disc electrode of the parabolic shape
recommended by Riddiford\textsuperscript{3} to give stable flow patterns is admitted from
the top and a counter electrode from the bottom. The cell as before
consists of a teflon cylinder whose axis is at 90° to the axis of the
electrode with partially reflecting glass flats in the end and a cylinder
insert whose axis coincides with the axis of rotation of the electrode
with its sides sliced off to allow the laser beam to pass through.

From the expression for the location of wedge fringes on the inter-
ferometer wedge, 2 μt Cos φ = nλ (μ is the refractive index, t the thick-
ness of the cell, Cos φ is about one for φ, the angle of incidence close
enough to zero to give good fringes, n is the order of interference and
λ the wave-length of the light used), if λ is 6328 Å, the common gas laser
frequency, and the liquid has a refractive index of 1.3540 and t is one cm,

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n is calculated to be 42,810. This means that one fringe shift, that is when the displacement of the fringe brings it opposite where the next fringe would have been if it had remained straight, represents one part in 42,810 change in refractive index. If, however, it is a solution, only the part of the refractive index due to the solute will vary and in this case one fringe shift is one part in 240 for the solution referred to below.

When a disc is rotated in a liquid the application of the shearing force to the layers of liquid near the disc should result in dilation and the thermodynamic PAV term that describes the dilation should be proportional to the shearing force applied and hence useful in evaluating liquid viscosities. The change in density is related to the change in refractive index by the Lorentz-Lorenz expression

\[ \frac{R_M}{\mu} = \frac{M}{\rho} \frac{\mu^2 - 1}{\mu^2 + 2} \]

where \( R_M \) is the molar refraction, \( M \) the molecular weight, \( \rho \) the density and \( \mu \) the refractive index. The molar refraction of \( H_2O \) is 1.64624 and detection of one fringe shift due to change in density represents a change in refractive index from 1.33315 at 25°C to 1.33312 and consequently a dilation of one part in 14,875. Since 1/10 of a fringe shift can be detected, the limits of measurement are one part in 148,750 or this is a very accurate dilatometer.

Figure 1 contains four frames taken from a 16 mm motion picture film taken at 12 fps of a 3.18 mm diameter Ni disc in a 2 NaOH solution which is also 0.1 M in \( K_4 Fe(CN)_6 \) and also \( K_2 Fe(CN)_6 \). In the first frame a current of 20 \( \mu \) amperes or 2.5 ma/cm\(^2\) is passing and the disc is not rotating. The nickel disc is coated with catalysed polyurethane so that no current
passes except on the bottom of the disc. The disc is the anode and the
$K_3\text{Fe(CN)}_6$ being generated is more dense than the bulk solution so natural
convection is causing a reversal of the concentration gradient outside
the simple diffusion layer.

In the second frame, taken one second later, the disc is rotating at
about 250 rpm or the rim speed is about 5 cm/sec and most of the diffusion
layer has already been removed but some convective effects are still evi-
dent. The direction of rotation is such that the rim of the disc nearest
the camera is moving from right to left. The third frame shows a deflec-
tion of the fringes in the opposite direction (to the left) except for
the solution very close to the electrode. In the last frame, one second
later, a hydrodynamic shear zone has been established to the exclusion of
any recognizable diffusion layer. The total fringe shift at the centre of
the disc is again about $3/4$ of a fringe as in the diffusion layer, but
the layer is about twice as thick so the refractive index gradient is only
half as steep.

Further experiments are planned to firmly establish flow patterns
around the rotating disc and to explore the system's usefulness as a
dilatometer. It is hoped sufficient accuracy of measurement can be devel-
oped to test recently published theories.⁵

The work reported was performed in association with the Inorganic
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of California, Berkeley.
REFERENCES

4. E. A. Flood, personal communication, theory to be published.
Fig. 1. Four interferograms taken 1 second apart. Frame (a) shows a concentration gradient affected by natural convection. Frame (b) shows the result of rotating the disc at about 300 rpm, accelerating from 0 one second from the start of rotation. Frame (c) was taken one second later and frame (d) one second after (c). Frame (d) shows the diffusion layer is now too thin to observe; the effects of convection are erased and a hydrodynamic shear layer has formed.
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