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MARCH 1967

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[1] and the theory presented.[2] The present cell has been modified from those previously described only in that a disc electrode of the parabolic shape recommended by Riddiford[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 interferometer wedge $2\mu t \cos\phi = n\lambda$ (μ is the refractive index, t is the thickness of the cell, $\cos\phi$ 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 is 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 1 cm, n is

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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 present experimental set-up this means one part in 240 change from the bulk concentration of all solutes present.

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 $P\Delta V$ term that describes the dilation should be proportional to the shearing force applied and hence useful in evaluating liquid viscosities.[4] The change in density is related to the change in refractive index by the Lorentz-Lorenz expression $R_M = \frac{M}{\rho}\left(\frac{\mu^2 - 1}{\mu^2 + 2}\right)$ where R_M is the molar refraction, M the molecular weight, ρ the density and μ the refractive index. Since it is difficult to see how, in the solution considered, the dilation can occur in anything but the solvent, we will consider only the change in density of water. 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 24°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 sensitive dilatometer.

Figure 1 contains four frames taken from a 16 mm motion picture film taken at 12 fps of a 3.50 mm diameter Ni disc in a 2N NaOH solution which is also 0.1 M in $K_4Fe(CN)_6$ and 0.1M in $K_3Fe(CN)_6$ at 24°C. In the first frame a current of 20μ amperes or 2.5 ma/cm^2 is passing and the

disc is not rotating and the apex of the wedge is to the left. The nickel disc is coated with catalysed polyurethane so that no current passes except on the bottom of the disc. The disc is the cathode and the $K_4Fe(CN)_6$ 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, analogous to effects noted in other systems.[5] Since the current density is far from the limiting current density in this system, it is assumed (as found to be essentially true in acidified $CuSO_4$ solution[6] that only the electroactive species change concentration.

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 concentration gradient $\left(\frac{\partial[K_4Fe(CN)_6]}{\partial x} - \frac{\partial[K_3Fe(CN)_6]}{\partial x}\right)$ previously established has already been swept away as a much thinner diffusional layer is set up, undetectable by this apparatus. Some convective effects are still evident at the same location in this frame as in the previous one, indicating that the effect of rotation progresses, as expected, through the layers at a finite rate. That is, the previously set up processes relax at a measurable rate. 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 deflection 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 recognisable diffusion layer. The total fringe shift at the center 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. A diffusion layer must still exist, but it can be confidently stated that since it cannot be

detected by this apparatus (and hence its extent and the concentration gradient in it cannot be determined), its thickness must be less than 0.02 mm since measurements have been made in other systems at this distance.[7]

Figure 2 was produced by tracing the center of fringes in a system in which the disc is the anode and no natural convection occurs, all other conditions the same except as noted. The frames were taken at 1/4 second intervals. Frame (a) shows a well developed diffusion gradient at twice the current density in Fig. 1 (5 ma/cm^2) and the apex of the wedge is to the right. Frame (b) shows the diffusion layer set up under non-rotating conditions being swept tangentially outward in accord with Riddiford's theory.[3] Frame (c) shows an intermediate regime. In Frame (d) the diffusion layer has been established at a thickness undetectable by this apparatus. The hydrodynamic dilation shear gradient is, as expected, in the same direction as the concentration gradient previously established.

Since the effects being viewed in this work are independent of the thickness of the cell (as attested by unperturbed fringes appearing in the edges of the frames), and are the result of viewing a disc of perturbation, the usual formula $2\mu t = n\lambda$ must have a variable t. Now $t = 2d \operatorname{Sin} \frac{d}{r} \frac{w}{2}$, where d is the distance from the center of the perturbed disc of fluid and r is the radius of this disc. Scales in concentration and density units have been calculated for specific marked points, and are, of course, only applicable to that point. They can only be used as a rough guide to judge as to whether the fringe shift follows the indicated sine function.

Experiments were also performed in which a nickel rod was encased in a teflon tube. The outside diameter of the teflon was twice that of the nickel rod, and the teflon tube outside diameter was 3.5 mm. The

surface of the teflon and nickel were gently polished flat while assembled together and just prior to mounting in the interferometer. The nickel could be rotated while the teflon remained stationary, or both could be rotated at the same speed. When current was passed in the same electrolyte as above without rotation, then rotation began after an appreciable diffusion layer was present, the patterns of perturbations to the fringes were similar in both cases to the bell-shaped disc recommended by Riddiford. The configuration in which only the electrode moved showed a slightly better (i.e., more closely horizontal, that is tangential, motion of the electrolyte away from the electrode) flow pattern. It is thought that both the flow patterns and the dilation in the shear zone will have an effect on current distribution which has recently been the subject of theoretical calculations.[8]

Further experiments are planned to firmly establish flow patterns around the rotating disc and to explore the system's usefulness as a dilatometer.

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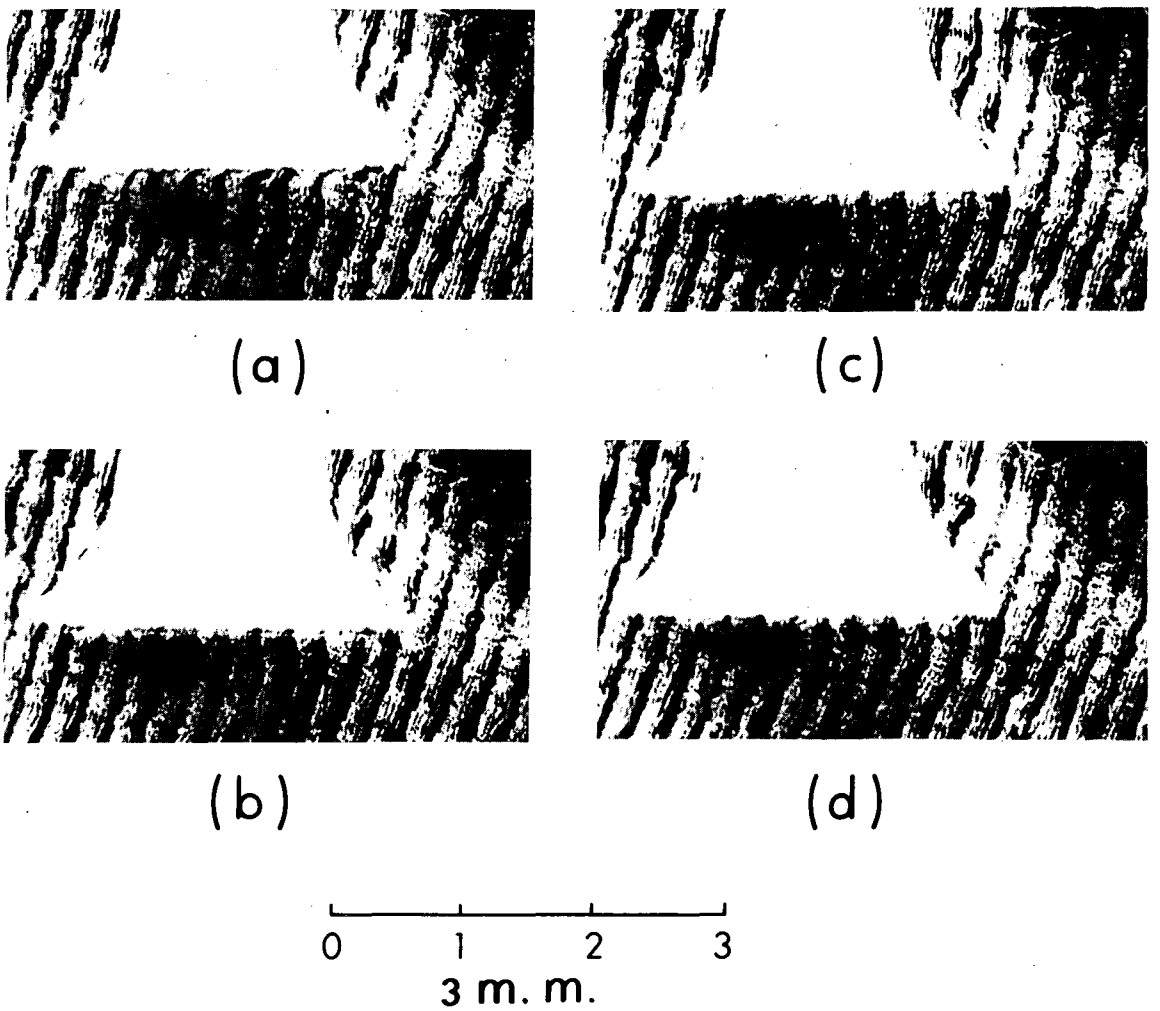

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Fig. 1. Four interferograms taken 1 second apart. Frame (a) shows a concentration gradient affected by natural convection. Frame (b) shows the result of rotating the disc at about 300 rpm, accelerating from 0 one second from the start of rotation. 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.

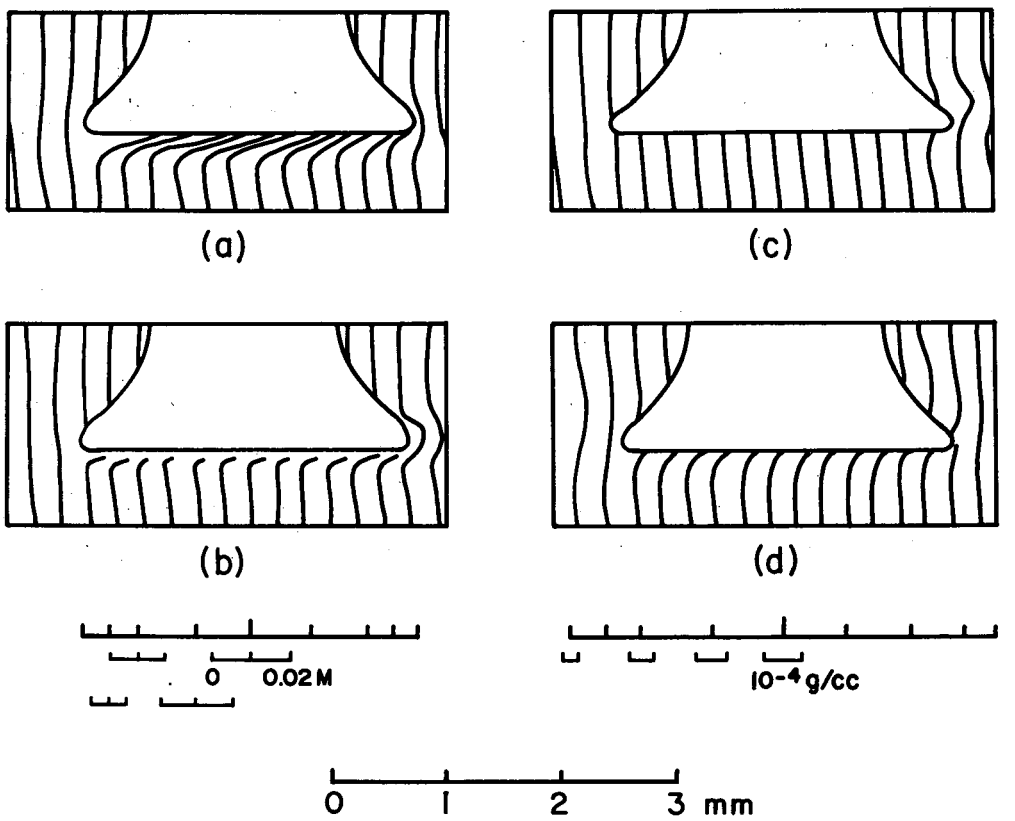

Fig. 2. Interference fringes traced from 16 mm motion picture frames. The current density is 5 ma/cm^2 in the same solution but the disc is now the anode, no convection is occurring, there is only 1/4 second between frames and the dilation in the hydrodynamic shear zone gives a fringe shift in the same direction as the oxidation of $K_4Fe(CN)_6$ in the diffusion layer.

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