COMMUNICATIONS TO THE EDITOR

ADSORPTION AT THE DROPPING MERCURY ELECTRODE

Sir:

Despite the large quantity of work which has been carried out with capillary-active substances as maximum suppressors in polarographic analysis, a detailed consideration of their effect on the diffusion current itself has apparently not been made. One may find references in the literature[1,2,3] to interference with the diffusion current, brought about by the use of capillary-active materials, but no satisfactory explanation has been offered.

Polarograms prepared from solutions which contained various concentrations of purified horse albumin at *p*H 8 and which were 1×10^{-4} *M* in the dye *p*-hydroxyphenylazophenylarsonic acid, 0.15 *M* in sodium chloride, and 0.02 *M* in veronal indicated that the diffusion current was suppressed to approximately 90% of its true value at a protein concentration of 1×10^{-6} *M* and to an asymptotic value of about 25% at 1×10^{-5} *M*.

It seems likely that the albumin, a capillary-active substance, is adsorbed on the growing mercury drops, decreasing the surface available for reaction with the reducible molecules or ions and so decreasing the diffusion current. If so, the fractional change of free surface and the consequent fractional change in instantaneous diffusion current should at any stage in the life of the drop be a function of the change in the concentration of protein. At moderately high concentrations of protein, however, a monomolecular layer would be formed and an asymptotic diffusion current would be attained corresponding to the remaining free surface between the adsorbed protein molecules. (Even in closest packing these large molecules might well leave holes large enough to permit the smaller molecules of reducible material to reach the electrode.) These considerations are in qualitative agreement with the experimental results; furthermore, for protein concentrations C_p giving diffusion currents i_d not too close to the asymptotic current for a given constant dye concentration, they lead to a theoretical relation similar to the equation $\log i_d = -k_1 C_p + k_2$ which was found empirically.

As the concentration of a reducible substance is increased beyond a critical value, the "diffusion current constant" decreases and the current approaches a saturation value. It might be expected that an electrode covered over to a given extent, say with a monomolecular layer of adsorbed large molecules, would reach saturation at the same concentration of reducible substance as a normal electrode, but that the saturation current would be reduced; *i. e.*, with a given protein concentration, the diffusion current should be reduced by a constant fraction, which is independent of the dye concentration. A series of polarograms of the same system, this time with the protein absent or held constant at a comparatively high concentration, showed a 70% reduction of the saturation current, in the presence of protein, but no change in the concentration of dye required to reach saturation.

The probable relation of these results to the phenomenon of maximum suppression is being explored. A more detailed account of the work will be published later.

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[1] Salac, *Kvas*, **64**, 383 (1936).

[2] Brdicka, *Z. Elektrochem.* **48**, 278, 686 (1942).

[3] Kolthoff and Barnum, THIS JOURNAL, **63**, 520 (1941).

THE INFRARED SPECTRUM OF SPRUCE NATIVE LIGNIN

Sir:

Initial work on an extensive study of the applications of infrared spectroscopy to the problem of lignin structure has resulted in the establishment of the spectrum of Brauns' spruce native lignin by several independent methods of sample preparation. Typical curves (obtained with a Perkin–Elmer Model 12-B recording spectrometer using a sodium chloride prism) are shown in Fig. 1.

The film method of sample preparation warrants a brief description. By filling a shallow cup comprised of a metal ring and salt plate base with ethyl alcohol, adding a small proportion of dioxane solution, and allowing evaporation to take place slowly, the lignin was deposited as a strongly adherent clear film. The films thus obtained were dried for sixteen hours in a vacuum desiccator before use. Of particular value is the fact that dioxane is sufficiently transparent to permit its use as a solvent in the important carbonyl (1650–1850 cm.$^{-1}$) and hydroxyl (3000–3700 cm.$^{-1}$) regions, as shown in Curve A.

Two important points have been established: (1) The infrared spectrum of native lignin in film form is essentially unchanged by as much as ten hours of heating at 100°. (2) The broad band centered at 3350 cm.$^{-1}$ for film and Nujol dispersion and the shift of this band to higher frequency in dioxane solution is indicative of strong hydrogen bonding in lignin. Experiments on dilution and heating effects are planned which should yield valuable evidence as to the nature of this bond.

An investigation of the spectra of related com-