

The change in concentration of surfactant as water evaporates from the "isolated film" has been neglected. This is justified because the film-forming solutions are almost saturated in surfactant to begin with^{4,5}.

The eight-fold increase in concentration within the film as its aqueous core shrinks from some 100 Å to 12 Å has also been neglected because by itself it would probably make only a minor contribution to the lowering of p_s .

KAROL J. MYSELS

Research Department,
R. J. Reynolds Tobacco Company,
Winston-Salem, North Carolina.

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Metallized Membrane Electrode : Atmospheric Oxygen Monitoring and other Applications

POLAROGRAPHIC measurement of the partial pressure of oxygen in air is usually carried out with the cell devised by Clark¹ or with a similar device. In the Clark device, the cathode is embedded in a block of glass, ceramic or some other suitable electrical insulator, in such a way that it is flush with one face of the block. A membrane, usually between 5 and 50 μm thick, of rubber or of a polymer such as polythene or polytetrafluorethylene (PTFE) is stretched over this face, and a thin layer of electrolyte is held between the membrane and cathode block either in the surface roughness or in paper tissue. An appropriate potential is applied to the cell and the magnitude of the electrical current depends on the rate at which oxygen diffuses through the membrane to accept electrons from the polarized cathode. This rate in turn is dependent on the partial pressure of oxygen in the atmosphere.

The layer of electrolyte between the membrane and the cathode is one of the drawbacks of the Clark device. The layer must be quite thin, otherwise the device would be slow to respond to changes in the partial pressure of oxygen. If it is too thin, however, the evaporation of electrolyte through the membrane will tend to dry up the layer. Unfortunately, the thickness of the layer cannot be fully controlled because changes in atmospheric pressure or in the dimensions of parts of the device can alter the thickness. Furthermore, such a device is often sensitive to shock, because relative movement between the membrane and cathode may bring oxygen-rich electrolyte to the cathode.

A new form of electrode has now been developed consisting of a metallized membrane in which the thin layer of electrolyte between the membrane and the cathode is eliminated (British Patent Application No. 46675/66).

The metallized membrane used at present consists of a film of PTFE 3–12 μm thick, coated on one side with a thin porous film of gold and silver by a process of vacuum evaporation. Although the materials and the method of metal deposition are not critical, two factors must be satisfied. First, the plastic film must be non-porous but have high permeability to oxygen by activated diffusion. Second, the metal layer must be deposited in such a way that there is ample metal/electrolyte interface spread evenly very close to the plastic film.

The metallized membrane is clamped into an electrode assembly in such a way that electrical contact is made to the metal layer, an area of the layer is exposed to the electrolyte and a defined part of this area on the opposite side of the membrane is exposed to the atmosphere. The

defined area is given mechanical support by incorporation into a sandwich of suitable materials. On the electrolyte side a material such as a dialysis membrane adds to the mechanical strength, is smooth enough not to distort the metal layer, and minimizes the interference caused by oxygen diffusing through the electrolyte. On the gas side a thin, smooth membrane filter backed by a porous polythene plug provides support while leaving the speed of response of the electrode unimpaired.

A membrane electrode formed with a metal in the platinum group can be used as a hydrogen electrode. The advantages over a conventional type are: the interface between the electrolyte and gaseous hydrogen is constant for no bubbling is necessary, ultra-high purity metal can be used because so little is needed, and the thin electrode layer absorbs less hydrogen and is thus less sluggish than the conventional type.

The metallized membrane electrode can also be used to detect the presence of basic or acidic gases. For example, a solution containing quinhydrone and bicarbonate will act as a $p\text{CO}_2$ electrode in conjunction with a platinum group metal. The effect of gases on the film of electrolyte contained in the metal layer will be rapid and large when it is backed by a dialysis membrane or other layer which restricts diffusion.

Metallized membrane electrodes can be used in fuel cells; they do not suffer from the disadvantage of flooding, but give only low current densities with the materials currently available.

I. BERGMAN

Safety in Mines Research Establishment,
Ministry of Power,
Central Laboratories,
Sheffield.

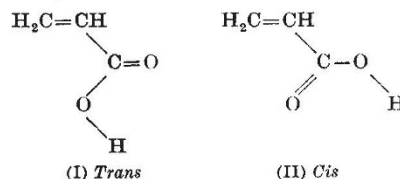
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MOLECULAR STRUCTURE

Microwave Spectra of Rotational Isomers of Acrylic Acid

EVIDENCE for *cis-trans* isomerism of the conjugated systems of molecules with bond-structures analogous to that of butadiene has frequently been sought (refs. 1 and 2 summarize earlier work), but it is often difficult to establish its occurrence. The possibility of such isomerism obviously exists in the case of acrylic acid, but electron diffraction³ and vibrational spectroscopy⁴ have given no clear evidence. We have found that the microwave spectrum of acrylic acid shows it to contain comparable proportions of isomers with the planar structures I and II in the gas phase



About eighty lines in the spectra of $\text{H}_2\text{C}:\text{CHCO}_2\text{H}$ and $\text{H}_2\text{C}:\text{CHCO}_2\text{D}$ were assigned to transitions involving J values between 1 and 10. The rotational constants for the four species concerned are shown in Table 1. Each species shows absorptions of both a and b types. The inertial defects, Δ , also tabulated, have very small negative values, strongly supporting planar molecular geometry for all the species. A similar inertial defect has been found for nitro ethylene⁵, which is also planar, and for acrylyl fluoride, in which the existence of planar *cis* and *trans* isomers has recently been demonstrated by