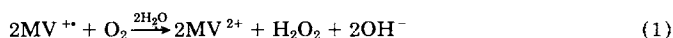


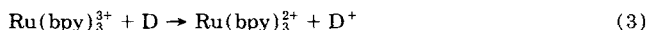
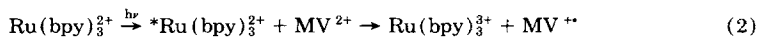
NOTES

Methylviologen Cation Radical as Probe of Oxygen Diffusion Through Polymer

Penetration of oxygen through polymers is an important process. This study reports on a simple method of measuring of the rate of such a process making use of photochemically generated reactive species. It is well known that methylviologen, MV^{2+} /1,1'-dimethyl-4,4'-dipyridinum/ can be easily reduced photochemically.¹ In diluted aqueous solutions the only species primarily formed is a strongly absorbing, blue-colored methylviologen cation radical, MV^{\bullet} .² This radical is capable of reacting with oxygen in the presence of water.^{2,3} The reaction could be written schematically as



The rate constant for this bimolecular oxidation is $7.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.³ Thus, the decrease of absorption of MV^{\bullet} can monitor the diffusion of oxygen into the solution. Typical aqueous solution used in the present experiment had the following composition: $2 \times 10^{-4} \text{ mol dm}^{-3}$ $Ru(bpy)_3^{2+}$ /tris-ruthenium (II) bipyridine/complex as a photosensitizer, $10^{-2} \text{ mol dm}^{-3}$ EDTA or triethanolamine as electron donor and 1 mmol dm^{-3} MV^{2+} as an electron acceptor. The solution was poured into spectrophotometric cell, light path 1 cm, with a plastic-coated bar magnet at the cell bottom. The diameter of the cell opening was $\varnothing = 0.8 \text{ cm}$. The solution was purged with argon for 5 min in order to remove oxygen from the cell. Then the top of the cell was covered with the appropriate polymer (parafilm for laboratory use or polymer hydrogels as: Geliperm or HDR). Closed cell was subsequently illuminated with tungsten lamp for 5–10 min. The solution turned blue, indicating the formation of MV^{\bullet} cation radical. The scheme of the generation of methylviologen cation radical is shown



where D denotes electron donor. The presence of electron donor is necessary in order to prevent fast back reaction between MV^{\bullet} and $Ru(bpy)_3^{3+}$ to restore the substrates. Thus, finally MV^{2+} is reduced on the expense of electron donor.

Absorption at 604 nm is very useful to measure the concentration of MV^{\bullet} , since it does not overlap with the other species present in the solution.² Extinction coefficient at this wavelength is $13,700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.² Absorption of the solution was monitored at 604 nm with ACTA-IVM Beckman spectrophotometer. The solution was continuously stirred in the dark by magnetic stirrer. The decrease of the absorption with the time of oxygen penetration is shown in Figure 1.

The main purpose of the present work was to determine the efficiency of penetration of oxygen through hydrogels. This type of polymer was applied as a wound dressing⁴ but can also have other medical applications. It is very important that the skin covered with such gel be in contact with oxygen. I have studied two types of hydrogels: Geliperm⁴ and the version developed at our institute, HDR.⁵ It is seen that both show excellent permeability to oxygen (see Fig. 1). Knowing the extinction coefficient of MV^{\bullet} and the diameter of the cell opening, one may estimate the oxygen flux through permeable gel (see right-hand scale in Fig. 1).

It is also demonstrated that an ordinary Teflon stopcock is not completely air-tight. Slightly better prevention from oxygen is achieved by wrapping the top of the cell in parafilm foil.

The reaction of oxygen with MV^{\bullet} is very fast as compared to the rate of diffusion of oxygen through the polymer layer. Therefore, the partial pressure of oxygen above the surface of the solution is probably very small and constant through the experiment. Hence, the process of discoloration of the solution is apparently zero order (straight lines in Fig. 1).

The method of evaluation of oxygen diffusion as described above has some advantages:

1. The indicator (MV^{\bullet}) is produced photochemically after removing oxygen and closing the cell.

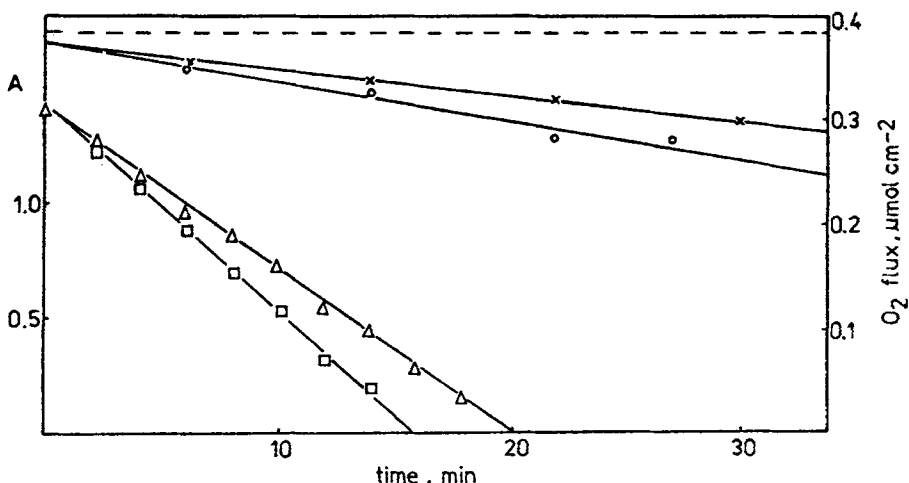


Fig. 1. Absorbance of methylviologen cation radical as measured at 604 nm in a 1 cm cell as a function of time of oxygen penetration through the cover of the cell. (x) Cell covered with parafilm; (O) cell closed with teflon stopcock; (Δ) cell covered with hydrogel HDR; (\square) cell covered with Geliperm. Right-hand scale: amount of oxygen corresponding stoichiometrically to concentration of MV^{++} (reaction 1), normalized to 1 cm^2 of penetration area. Broken line: absorbance monitored in vacuum-tight cell.

2. The concentration of oxygen inside the cell is constant and close to zero throughout the experiment.
3. The method is highly sensitive due to high extinction coefficient of MV^{+} and both slow and fast diffusion can be studied.
4. The same solution can be used repetitively for a series of experiments.
5. The diffusion process is visualized by disappearance of blue color, which can be used for demonstration.

The disadvantage of the method is that H_2O_2 produced in reaction (1), reacts slowly with MV^{++} and it makes very long measurements (lasting several hours) unreliable. Another disadvantage is certainly the cost of chemicals. However, the concentrations of chemicals and used volumes are very small.

This work was supported by the Research Program C.P.B.P.01.19.02.03.

References

1. C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, **10**, 49-102 (1981).
2. M. Wolszczak and Cz. Stradowski, *Rad. Phys. Chem.*, **26**, 625-633 (1985).
3. J. A. Farrington, M. Ebert, and E. J. Land, *J. Chem. Soc.*, **74**, 665-674 (1978).
4. B. Kickhofen, H. Wokalek, D. Scheel, and H. Ruh, *Biomaterials*, **7**, 67-72 (1986).
5. J. Rosiak, A. Rucińska-Rybus, and W. Pękala, Method of production of hydrogel dressing materials, Pol. Pat. Appl. P-263410 (1986).

Received December 17, 1988

Accepted December 13, 1989

CZESŁAW STRADOWSKI
[deceased]

Institute of Applied Radiation Chemistry
Technical University (Politechnika)
Wróblewskiego 15, 93-590 Łódź, Poland