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LETTER TO THE EDITORS

COMMENTS ON THE APPLICATION OF THE REDOX METHOD OF MEASURING MASS TRANSFER COEFFICIENTS IN TWO-PHASE (AIR–LIQUID) SYSTEMS

A RECENT REPORT [1] reported the utilization of the diffusion-controlled ferro-ferricyanide redox couple to measure mass-transfer coefficients between a falling liquid film and a wall. In this paper, no mention was made either of the adverse effects of dissolved oxygen on the redox reaction or of precautions taken to minimize such effects. The purpose of the following comments is to emphasize the need to consider the effects of oxygen when applying the redox-diffusion technique in two-phase (air–liquid) systems.

The electrochemical method to determine mass-transfer coefficients has been used extensively in various geometrical systems by many investigators [2–4, 6, 7, 9–15], but has generally been restricted to oxygen-free systems. In the past, the adverse effects of oxygen on the ferro-ferricyanide reaction have often been mentioned by various investigators [5, 6, 8, 9, 11, 12]. Except for a few studies [6], little has been done to determine the quantitative effect of the presence of dissolved oxygen on the measured mass-transfer coefficients, which is important in situations where the presence of air is unavoidable as in two-phase (air–liquid) flow systems.

As part of a comprehensive study of the mechanics of climbing film flow, a study [16, 17] was recently performed to explore more fully the limitations of the electrochemical technique with respect to the effects of dissolved oxygen in solution. It was found that the redox-diffusion technique is very reliable if all adverse effects are eliminated. Elimination of dissolved oxygen and light, and the proper cleaning of the electrodes are the most important factors in the successful use of the technique. However, absorption of air by any solution and contamination of electrodes are time-dependent, and if suitable precautions are taken accurate electrochemical measurements may be obtained before adverse effects become controlling. It was found that if the test solution was first saturated with nitrogen and if the electrodes were cathodically cleaned beforehand, future exposure of the redox system to air for a short period of time did not greatly affect the accuracy of the mass-transfer data. On the other hand, neglect of such precautions resulted in erroneous data using the redox diffusion technique.

Oxygen contamination of the electrodes and the redox solution can result in chemical polarization effects in which the kinetics at the electrode surface become important. In such situations, the interfacial concentration of the reacting species at the solid–liquid surface is not zero as generally assumed by the redox-diffusion method but must be considered as finite in estimating the mass-transfer coefficient. Since it is extremely difficult to obtain experimentally accurate values of the interfacial concentration, mass-transfer coefficients are most easily obtained when the interfacial concentration is zero. Consequently, it is important that suitable precautions be taken to minimize the effects of oxygen if the redox method of measuring mass-transfer coefficients is applied to two-phase (air–liquid) systems.

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REJOINDER

THE WORK referred to as [1] in the above comments by Sutey and Knudsen *was* conducted in an oxygen-free system; the gas was nitrogen and the electrolyte was saturated with it before use. We considered the deleterious effect of oxygen to be well known, so did not mention it.

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