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EFFECT OF SOLVENT COMPOSITION ON ELECTROCHEMICAL SPECTRAL SENSITIZATION AT THE SnO_2/RHODAMINE B INTERFACE

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The anodic sensitized photocurrent at a SnO_2 electrode in contact with a dye-containing acetonitrile-water mixed electrolyte solution depends remarkably on the solvent composition, due to a change in the adsorption behavior of the dye.

Spectral sensitization of semiconductors has been studied by many workers not only in relation to photographic,$^{1)}$ photosynthetic,$^{2)}$ and photocatalytic$^{3)}$ processes but also as a model system for studying interfacial charge separation in general. On an n-type semiconductor, the initial event is an electron transfer from an excited dye molecule to the conduction band of the substrate. In most cases where the electron transfer is supposed to occur from a short-lived singlet excited state of the dye, it is generally assumed that only the dyes in direct contact with the substrate are involved in spectral sensitization.$^{4)}$ However, except for a work by Spitler and Calvin,$^{5)}$ who noticed a fairly good correlation between the sensitized photocurrent (i_p) and the interfacial absorbance, no direct evidence for the participation of the adsorbed dye has been reported. In the present work we found that the solvent composition in the acetonitrile (AN) - water binary system greatly affects the adsorption of a sensitizer, rhodamine B (RhB), on SnO_2. This phenomenon was utilized to correlate i_p with the adsorbed amount of RhB.

Photocurrents were measured by a standard technique.$^{2)}$ A 3 x 3 cm^2 glass plate carrying a SnO_2 layer (200 nm thick), a Ag wire, and a Pt wire were used as the working, reference, and counter electrode, respectively. The supporting electrolyte was 0.1 M (1 M = 1 mol dm^{-3}) $NaClO_4$. The water concentration $[H_2O]$ in AN was determined by the Karl-Fischer titration. The adsorption measurement was conducted as follows. Six sheets of SnO_2 plates pretreated with concentrated H_2SO_4 were made into three pairs by sticking the sides opposite to the SnO_2 face. The plates were immersed in a dye solution, having the same composition as that for i_p measurements, in a thermostated beaker (20 °C). After 15 min the plates were emersed, then soaked for a few seconds in benzene to remove the dye solution adhering on the surface. Finally the amount of adsorbed RhB was determined spectrophotometrically after washing them out with 10 ml of methanol.

A significant influence of the solvent composition on the magnitude of the RhB-sensitized i_p is shown in Fig. 1, curve a. With increasing $[H_2O]$ in AN, i_p remains fairly constant up to $[H_2O]$ = 1 M, where it starts to decrease to reach a 1/20-fold lower level at $[H_2O]$ = 3-20 M, and then abruptly increases to a maximum value in a pure aqueous solution. Such a behavior is, at least qualitatively, correlated with the behavior of adsorbed amount of RhB on SnO_2 given by curve b. The adsorption isotherm of RhB, measured at 20 °C and $[H_2O] < 1$ M, was found to be of the Langmuir type. The lower adsorptivity in the 2-20 M region of $[H_2O]$ arises most probably from higher solubility of RhB. This has been checked by measuring the latter at several $[H_2O]$'s. As expected, the solubility limit of RhB was clearly detected at $[H_2O] < 1$ M and in pure aqueous solution, but was hardly attainable at $[H_2O] = 5$-10 M. Such appears to be a general phenomenon observed at intermediate compositional ranges of polar mixed solvents.$^{6)}$ The adsorbed amount of the coexisting reducing agent (hydroquinone, H_2Q) was nearly constant throughout the composition range studied. Further, the presence of H_2Q did not affect the adsorption behavior of RhB, as indicated by full circles in Fig. 1. These findings provide evidence that i_p results mainly from the photoresponse of adsorbed sensitizer molecules.

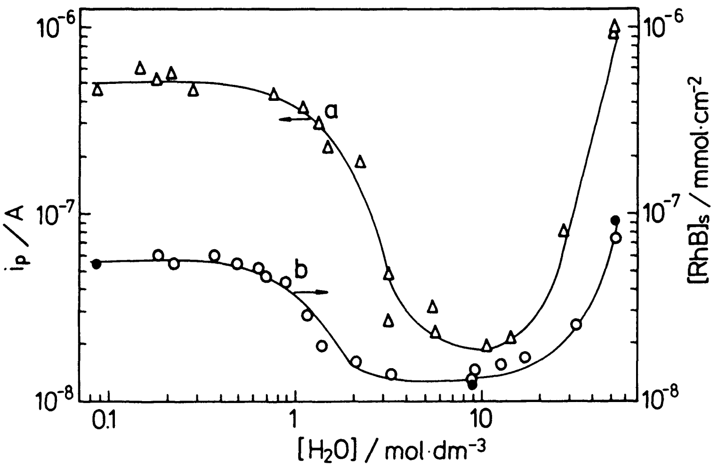

Fig. 1. (a) Dependence of the RhB-sensitized i_p on solvent composition. E, +0.3 V vs. Ag; wavelength of illumination, 555 nm; $[RhB] = 10^{-5}$ M; $[H_2Q] = 10^{-2}$ M. (b) Dependence of the adsorbed amount $[RhB]_s$ on solvent composition. Points o and ● are in the absence and presence of H_2Q (10^{-2} M), respectively.

From Fig. 1 the quantum yield (QY) of i_p generation is evaluated to be 2.1, 0.5, and 2.9% at $[H_2O] = 0.2$, 2.0, and 55.6 M, respectively. This is in contrast to the general tendency of increasing QY with a decrease in surface coverage.$^{7)}$ As a cause for this discrepancy, it is probable that trace amounts of residual dye-containing solution have interfered with the measurement of very low levels of adsorption in the intermediate composition range. Another possibility is that the adsorption behavior of RhB on a polarized SnO_2 surface is slightly different from that on SnO_2 with no applied voltage. Though a number of points still remain to be clarified, the present result demonstrates that the measurement of sensitized i_p, conversely, provides useful information on the adsorption behavior of organic molecules.

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