It is well known that Phospholipase A₂ hydrolyzes micellar substrates at considerably faster rates than monomeric substrates. The origin of this interfacial activation is a subject of considerable importance in understanding the mechanism of action of lipolytic enzymes. Crotalus adamanteus Phospholipase A₂ exhibits "normal" Michaelis kinetics with monomeric substrates (12) and with micellar substrates at concentrations well above the critical micelle concentration (cmc) (13). However, at concentrations near the cmc anomalous velocity vs substrate concentration plots are observed which are parabolic rather than hyperbolic (11, 13). We have noted this phenomenon for several different substrates and for Phospholipases A₂ from various sources and for cabbage Phospholipase D, and have empirically determined that such anomalous regions give linear plots of $v^{1/2}$ vs substrate concentration. To our knowledge no satisfactory explanation for these anomalous regions have been presented. The purpose of this paper is to explore various explanations for this behavior and to propose a model for substrate micellization which satisfactorily predicts such anomalous kinetics.

The simplest approach would be to apply the phase separation model for micelle formation to the kinetic process allowing both monomer and micelle to be substrates for the enzyme. Such a model can fit the monomer region and high micelle concentration region (Figure 1, solid line), but does not fit the anomalous region, unless one allows $K_m$ and $V_m$ to vary in this region. At the present time there are no physical data which justify such a change in kinetic parameters.
Figure 1. $S/v$ vs $S$ plot for the Phospholipase A$_2$ catalysed hydrolysis of dihexanoylphosphatidylcholine. The solid squares represent experimental data. The line is calculated using the phase separation model and the constants listed in Table 2.