# COMMUNICATIONS TO THE EDITOR

## STUDY OF SOAP MICELLES IN NON-AQUEOUS SOLVENTS USING A FLUORESCENT DYE[1]

*Sir:*

A number of dyes may serve as indicators for the presence of soap micelles in aqueous systems.[2] We have found rhodamine B peculiarly suited to a similar detection of soap micelles in non-aqueous solvents such as benzene, cyclohexane, cetane, and di-(2-ethylhexyl)-sebacate. This dye is slightly soluble but almost non-absorbing and non-fluorescent in benzene but fluoresces strongly upon the addition of as little as $10^{-5}$ mole per liter of an oil-dispersible metal soap such as the calcium or sodium salt of an arylstearic acid, a petroleum sulfonic or naphthenic acid or of an alkyl sulfonic acid.

That adsorption of the dye on the soap micelle is essential to the fluorescence observed is confirmed by this fact; the light emitted when a dilute solution containing dye and soap is illuminated with plane polarized green light is 28% polarized, whereas that from a similar concentration of the dye in methyl alcohol (with a comparable viscosity) is only 2.3% polarized. This difference is to be expected from Perrin's[3] relation for the depolarization resulting from Brownian rotation during the excited period

$$1/p = 1/p_0 + (1/p_0 - 1/3)\tau\, RT/V\eta$$

if instead of taking $V$ equal to the hydrodynamic volume of the dye molecule one takes $V$ to be the volume of the micelle to which the former is adsorbed. $V$ is estimated from osmotic pressure measurements to be 14,000 cc. per "mole" in this case.[4] Taking for $\tau$ the maximum and minimum values of the average life of the excited rhodamine B molecule reported by Szymanowski[5] we calculate polarizations, $p$, of 20 and 26%, respectively. *These observations furnish an obvious basis for a new method of determining the average volume of soap micelles or other suitable colloids.*

If the concentration of dye in benzene is held constant while that of the soap is varied from $10^{-4}$ to 0 mole/liter and the fluorescence is measured under constant illumination it is found that the emission becomes undetectable at a very low but finite soap concentration, as appears in Fig. 1.

The plot of intensity against the square root of the soap concentration approximates linearity at low concentrations and permits extrapolation to determine the soap concentration at zero intensity, which we take as the critical concentration for micelle formation. For calcium xylylstearate this concentration is $1 \times 10^{-6}$ mole/liter and for calcium xenylstearate it is $8 \times 10^{-6}$ mole/liter.

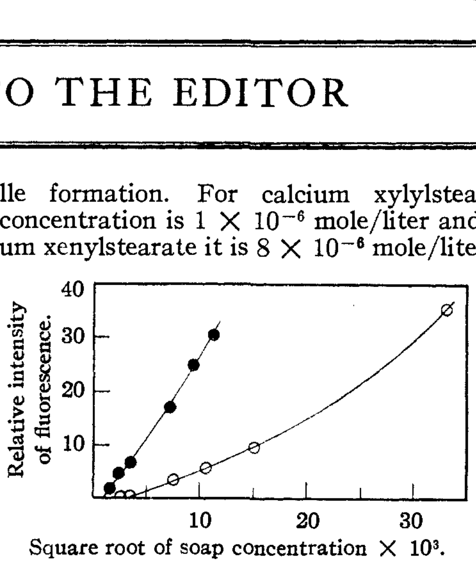

Fig. 1.—Fluorescence intensity of $2 \times 10^{-6}$ molar rhodamine B in benzene as a function of soap concentration: ○, calcium xenylstearate; ●, calcium xylylstearate.

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(1) The opinions or assertions contained in this communication are the authors' and are not to be construed as official or reflecting the views of the Navy Department. Not copyrighted.

(2) Corrin and Harkins, This Journal, **69**, 679 (1947).

(3) Perrin, *J. de Physique*, [VI] **7**, 390 (1926).

(4) Unpublished measurements in this Laboratory.

(5) Szymanowski, *Z. Physik*, **95**, 460 (1935).

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## HYDROCARBON OXIDATION INITIATED BY ATOMIC HYDROGEN[1]

*Sir:*

Mechanisms for the gas-phase oxidation of hydrocarbons have been proposed by many investigators. The most widely accepted of these have postulated attack on a primary C–H bond with resultant degradation to formaldehyde. Many have been based on the observation that aldehydes other than formaldehyde are absent in the products. Walsh[2] has recently reviewed these schemes and concluded that they were all unsatisfactory and has postulated that initial attack of an oxygen-containing radical should occur at tertiary in preference to secondary and secondary in preference to primary C–H bonds. Although this is to be expected, experimental evidence is largely missing, since aldehydes and ketones occurring in early stages of the oxidation are conceivably degraded to formaldehyde.

This communication reports some results of experiments in which oxidation of $C_4$-hydrocarbons has been initiated by atomic hydrogen. This method of oxidation, which has only been briefly previously reported for methane and acetylene by Geib and Harteck[3] supplies evidence regarding the

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(2) A. D. Walsh, *Trans. Faraday Soc.*, **42**, 269 (1946).

(3) K. H. Geib and P. Harteck, *Z. Physik. Chem.*, **A170**, 1 (1934).