

Determination of Critical Concentrations for Micelle Formation in Solutions of Cationic Soaps by Changes in the Color and Fluorescence of Dyes

M. L. Corrin and William D. Harkins

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single molecule or portion of a molecule with the surrounding solvent molecules.

Since it is impossible at present to evaluate the energy terms involved in micelle formation, the experimental data herein reported can contribute only to the empirical knowledge of the properties of detergent solutions. It is hoped that the accumulation of further experimental information on a wide variety of properties of such solutions may eventually lead to a true understanding of their nature.

* The work reported in this paper was done in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

¹ A. F. H. Ward, Proc. Roy. Soc. A176, 412 (1940).

² A. W. Ralston and C. W. Hoerr, J. Am. Chem. Soc. 68, 851 (1946).

³ M. L. Corrin and W. D. Harkins, following letter.

Determination of Critical Concentrations for Micelle Formation in Solutions of Cationic Soaps by Changes in the Color and Fluorescence of Dyes*

M. L. CORRIN AND WILLIAM D. HARKINS

University of Chicago, Chicago, Illinois

August 26, 1946

IN the first paper¹ on the use of dyes for the determination of the critical concentration for micelle formation, a titration method developed by the authors was mentioned. In this work with anionic soaps a cationic dye, pinacyanol chloride, was used. Attempts to use this same dye with cationic soaps were unsuccessful.

The following dyes, whose spectra in alcohol are visually distinguishable from those in water, were found to be ineffective with either anionic or cationic soaps: Orange G (S189), Azophloxin 2G (S40), Bordeaux B (S123), Congo Brown G (S280), New Methylene Blue (S1043), and Ponceau G (S37).

It was thought desirable to attempt to find dyes, one of whose several molecular forms is preferentially solubilized in soap micelles. This involved an extensive investigation in which it was discovered that the following dyes may be used as indicators with cationic soaps: Sky Blue FF, Eosin, Fluorescein, Dichlorofluorescein, and acidified 2,6-dichlorophenol indophenol. Another dye other than pinacyanol chloride applicable to anionic soaps, Rhodamine 6G, was also found. The values of critical concentrations determined by the use of these dyes are quite self consistent, as shown in Table I.

These results are also in agreement with literature values obtained by other, much more laborious methods. The critical concentration for dodecyl ammonium chloride is 0.0130 molar, as reported by Ralston and Hoerr,² and for decyl trimethyl ammonium bromide 0.065 molar by Scott and Tartar.³

Critical Concentration by Change in Fluorescence.—Cationic soap solutions containing eosin or fluorescein are highly fluorescent when micelles are present. This fluorescence is strongly quenched at concentrations below the critical; hence this property, as well as color, serves to

TABLE I. The titrametric determination of critical concentrations with various dyes.

Dye	Anionic Soaps			Cationic Soaps	
	Potassium laurate	Sodium dodecyl sulfate	Sodium decyl sulfonate	Dodecyl ammonium chloride	Decyl trimethyl ammonium bromide
Pinacyanol chloride	0.0235	0.00602	0.0400		
Rhodamine 6G	0.0234	0.00612	0.0387		
Sky Blue FF				0.0643	0.0127
Eosin				0.0635	0.0136
Fluorescein				0.0610	0.0130
2,6-dichlorophenol-indophenol				0.0602	0.0124

determine the critical concentration. With eosin the color is orange above and red below the critical concentration. Both of these dyes are anionic and are effective with only cationic soaps.

Rhodamine 6G, a cationic dye and effective only with anionic soaps, also yields orange fluorescent solutions in the presence of micelles. When the soap concentration is reduced, the color changes to red and the fluorescence almost entirely disappears at the critical concentration.

* The work reported in this paper was done in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

¹ M. L. Corrin, H. B. Kleven, and W. D. Harkins, J. Chem. Phys. 14 480 (1946).

² A. W. Ralston and C. W. Hoerr, J. Am. Chem. Soc. 64, 772 (1942).

³ A. B. Scott and H. V. Tartar, J. Am. Chem. Soc. 65, 692 (1943).

On the Structure of Ozone

W. H. EBERHARDT

Georgia School of Technology, Atlanta, Georgia

September 9, 1946

USING central-force-field methods, Glockler and Matlack¹ have recently presented a discussion of the bond energies and molecular structure of ozone based on a correlation of bond energy and interatomic distance suggested by other oxygen-oxygen bonds. Since their discussion is limited to acute angle models of the molecule, it is interesting to extend the technique to obtuse angle models.

From electron diffraction results² the ozone molecule has been reported to be an obtuse isosceles triangle with O—O bond length $1.26 \pm 0.02 \text{ \AA}$ and bond angle $127 \pm 3^\circ$. The separation of the base oxygen atoms is thus 2.25 \AA . If one assumes the dependence of bond energy on interatomic distance as suggested by Glockler and Matlack, the energy of the two valence bonds is $2 \times 3.06 = 6.12$ electron volts. The contribution of the base O—O bond to the total binding energy will be small, and indeed may well be negative owing to the repulsion of the electron clouds of the two base oxygen atoms. Hence, it may be considered that adequate agreement with the total binding energy, 6.12 electron volts, may be obtained on the basis of this model as well as acute angle models.

¹ Glockler and Matlack, J. Chem. Phys. 14, 505 (1946).

² Shand and Spurr, J. Am. Chem. Soc. 65, 179 (1943).