

The Effect of Solvents on the Critical Concentration for Micelle Formation of Cationic Soaps

M. L. Corrin and William D. Harkins

Citation: *The Journal of Chemical Physics* **14**, 640 (1946); doi: 10.1063/1.1724076

View online: <http://dx.doi.org/10.1063/1.1724076>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/14/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Critical concentration of micelle solutions](#)

J. Chem. Phys. **61**, 430 (1974); 10.1063/1.1681661

[The Critical Micelle Concentration of Anionic Soap Mixtures](#)

J. Chem. Phys. **14**, 742 (1946); 10.1063/1.1724097

[Determination of Critical Concentrations for Micelle Formation in Solutions of Cationic Soaps by Changes in the Color and Fluorescence of Dyes](#)

J. Chem. Phys. **14**, 641 (1946); 10.1063/1.1724077

[The Determination of Critical Concentrations for the Formation of Soap Micelles by the Spectral Behavior of Pinacyanol Chloride](#)

J. Chem. Phys. **14**, 480 (1946); 10.1063/1.1724177

[The Critical Concentration for the Formation of Micelles as Indicated by the Absorption Spectrum of a Cyanine Dye](#)

J. Chem. Phys. **14**, 216 (1946); 10.1063/1.1724122



Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

The Effect of Solvents on the Critical Concentration for Micelle Formation of Cationic Soaps*

M. L. CORRIN AND WILLIAM D. HARKINS
The University of Chicago, Chicago, Illinois
August 21, 1946

THE effect of various solvents upon the critical concentration for micelle formation has been discussed by Ward¹ and by Ralston and Hoerr.² The development of titrametric methods for the determination of critical concentrations has made it practical to extend such studies.³ With the titration technique it is possible to measure a number of critical concentrations under varying conditions far more easily than if a conductometric method is used; by this latter procedure a large number of accurate measurements are required for a single determination. The work of Ward is restricted to sodium dodecyl sulfate, while Ralston and Hoerr consider only dodecylammonium chloride; the latter workers, however, do not report any values for the critical concentration. The work herein reported is restricted to cationic soaps since no indicator is available which gives a sharp end point with anionic materials in solutions containing organic solvents.

Data for the critical concentration of dodecylammonium chloride in various solvent-water mixtures are plotted in

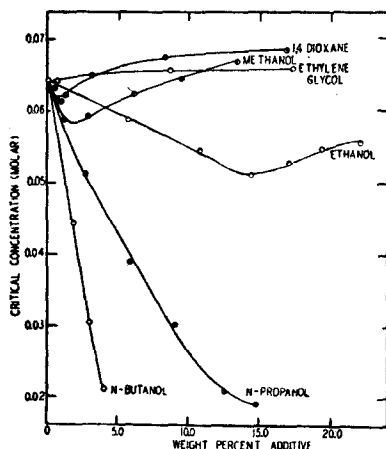


FIG. 1. The critical concentration for micelle formation in solutions of dodecylammonium chloride in various solvent-water mixtures.

Fig. 1; the indicator was dichlorofluorescein. With decyl trimethyl ammonium bromide the measurements were extended in the region of low solvent concentration. These data are plotted in Fig. 2; the indicator employed was Sky Blue FF.

With decyl trimethyl ammonium bromide the decrease in critical concentration becomes more pronounced as the chain length of monohydric alcohol used as the solvent is increased. Dioxane also produces a slight initial decrease in critical concentration while no decrease was observed with ethylene glycol even at low solvent concentrations. A similar behavior was observed with dodecylammonium chloride. Isopropanol is but slightly different in its effect from *n*-propanol. At higher solvent concentrations the critical concentration of the detergent increases with dioxane, ethylene glycol, glycerol, and ethanol. At the highest concentrations of isopropanol, *n*-propanol, and *n*-butanol employed, the critical concentration was still decreasing.

On the basis of the above results it seems probable that Ward's hypothesis, which attributes the initial drop in critical concentration to adsorption of solvent molecules on the "surface of the micelle" is untenable.

It is, at present, difficult to correlate experimental observations with any dielectric constant data for the various solvent pairs. This is not unexpected since Ward has pointed out that a significant term in micelle formation is the dielectric environment about the polar head groups of the detergent molecules in the micelle; this quantity cannot, at the present time, be measured or even approximately calculated.

The term "interfacial energy" applied by many authors to the energy arising from an interaction of amphipathic molecules with surrounding solvent molecules is misleading and tends to obscure the actual processes involved in such systems. Interfacial energy is both defined and measured as the energy difference between the surface and bulk of a substance; there is no reason to consider that the interfacial energy represents the interaction energy of a

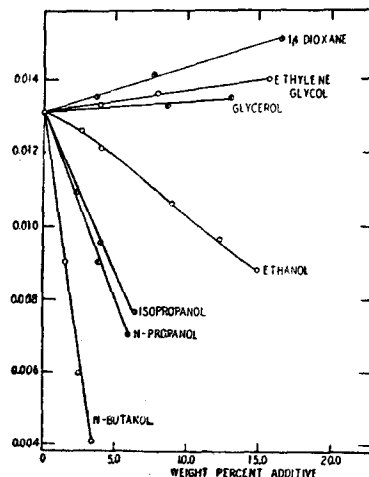


FIG. 2. The critical concentration for micelle formation in solutions of decyl trimethyl ammonium bromide in various solvent-water mixtures.

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).