

## The Critical Micelle Concentration of Anionic Soap Mixtures

H. B. Klevens

Citation: [The Journal of Chemical Physics](#) **14**, 742 (1946); doi: 10.1063/1.1724097

View online: <http://dx.doi.org/10.1063/1.1724097>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/14/12?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Confinement induced critical micelle concentration shift](#)

J. Chem. Phys. **127**, 034506 (2007); 10.1063/1.2749521

[Critical concentration of micelle solutions](#)

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

[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 Effect of Solvents on the Critical Concentration for Micelle Formation of Cationic Soaps](#)

J. Chem. Phys. **14**, 640 (1946); 10.1063/1.1724076

[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

---



## Letters to the Editor

**T**HIS 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 Critical Micelle Concentration of Anionic Soap Mixtures

H. B. KLEVENS\*

Department of Chemistry, University of Chicago,  
Chicago, Illinois

September 5, 1946

**M**ANY technical papers have dealt with the increase in solubilization, wetting, detergency, etc., of soap mixtures as compared with pure soaps, but except for some ultramicroscopic studies there have been no data reported on the properties of soap mixtures in the region of the critical micelle concentration (*cmc*). The changes occurring in dye spectra upon the addition of varying amounts of soaps<sup>1</sup> have been used in this work.

The change in *cmc* (the sum of the concentration of the two soaps) of soap mixtures (potassium myristate plus potassium laurate, potassium caprate, potassium caprylate, and sodium lauryl sulfate) as determined with the dye, pinacyanol chloride, is plotted in Fig. 1. The *cmc* of potassium caprylate and potassium caprate have not been

reported previously by means of the dye method, but the values of  $3.94 \times 10^{-1}$  and  $9.9 \times 10^{-2} M$  observed here agree with those of  $3.6-3.8 \times 10^{-1}$  and  $9.5-10.0 \times 10^{-2}$  reported by Ekwall,<sup>2</sup> and  $3.7-4.0 \times 10^{-1}$  and  $10.0-10.2 \times 10^{-2}$  as determined by refraction.<sup>3</sup> Other unreported data which will be discussed in a following report include mixtures of alkyl sulfonates as well as potassium laurate plus potassium caprate and potassium caprylate, and potassium caprate plus potassium caprylate. Similar results have been observed for mixtures of cationic soaps using indophenol<sup>4</sup> as the dye indicator.

It can be seen from the curves in Fig. 1 that the greatest change in *cmc* of the soap mixtures is observed when there is the largest difference in the *cmc* of the pure soaps. It is also evident that there are no *cmc* values which do not fall within the range of values of the pure soaps. These results over certain mole fraction ranges are similar to the effects of salts on the *cmc* of pure soaps.<sup>5</sup> In this connection, however, it is necessary to consider not the sum of the concentration in the soap mixture at the appearance of micelles, but the concentration of one of the soaps at this point as affected by the other. When this is done, it is found, for example, that potassium caprate acts like a salt, say potassium chloride or sodium chloride, depressing the necessary concentration of potassium laurate. This value, which is equal to the mole fraction times the total *cmc*, is found to be similar to a salt effect for mole fractions of the laurate as low as 0.50.

This treatment was found to be valid in various other mixtures only in the region of higher mole fractions of the less soluble soap. In the portion of the curves in Fig. 1 where the greatest change in the total *cmc* occurs, the salt effect phenomena were not observed. Thus, a much greater change in the total *cmc* can be obtained by adding a small amount of a less soluble soap than by adding an equivalent amount of a salt. The tendency of the less soluble soap to aggregate seems to have a much greater effect on the total aggregation associated with micelle formation than a salt.

When two soaps of approximately the same *cmc* are mixed, there is no observable change in the *cmc* of the mixture and no region of a salt effect is observed. A mixture of this type, potassium myristate plus sodium lauryl sulfate, is seen in Fig. 1.

In the consideration of soap mixtures, it seems that the difference in the tendency of single soaps to form micelles controls the micelle formation in their mixtures; the greater the difference (for example in solubility), the greater will be the initial effect of the more soluble soap. If this tendency to aggregate is different in two soaps, then in a limited concentration range of mixtures, the soap having the lower tendency to aggregate will act as a salt towards the other. Soaps having about the same tendency to aggregate will have little effect on each other as far as salt effect and change in total *cmc* are concerned.

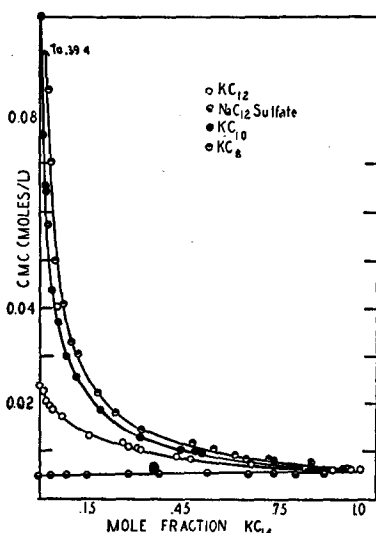


FIG. 1. The critical micelle concentrations in moles per liter (the sum of the concentrations at the appearance of micelles) of various soap mixtures.

\* Present address: Chemical & Physical Research Laboratories Firestone Tire & Rubber Company, Akron, Ohio.

<sup>1</sup> M. L. Corrin, H. B. Klevens, and W. D. Harkins, *J. Chem. Phys.* **14**, 480 (1946).

<sup>2</sup> P. Ekwall, *Kolloid Zeits.* **101**, 135 (1942).

<sup>3</sup> H. B. Klevens, *J. Chem. Phys.* **14**, 567 (1946).

<sup>4</sup> H. B. Klevens, *J. Am. Chem. Soc.* to be published.

<sup>5</sup> M. L. Corrin and W. D. Harkins, in preparation.