Summary

The phase behavior of dodecyl sulfonic acid with water has been determined. In addition to crystalline solid and isotropic solution, a crystalline monohydrate and two liquid crystalline solutions are formed in appropriate regions of concentration and temperature. This substance provides an example of a substance which does not itself exhibit liquid crystal formation but which interacts with a solvent (water) in such a way as to make their formation possible.

The lithium, sodium and potassium dodecyl sulfonates each have a transition from crystal to a liquid crystal resembling subneat soap. The phase rule diagram of these salts with water is similar to that of sodium soaps with water as far as investigated. Samples containing more than about 55% salt decompose before becoming isotropic on heating.

STANFORD UNIVERSITY, CALIFORNIA
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[CONTRIBUTION FROM THE RESEARCH LABORATORY, AUTOXYGEN, INC.]

Iodometric Determination of Peroxygen in Organic Compounds

BY V. R. KOKATNUR AND MURRAY JELLING

The use of a modified iodometric method for determining peroxygen in water insoluble organic compounds has been subjected to many variations within the last ten years,[1,2] Liebhafsky and Sharkey recently have pointed out the necessary requirements for a good reaction medium and recommended the use of glacial acetic acid.[1c] During several years of research conducted at this Laboratory on the synthesis of organic peroxygen compounds, it has been found that the use of 99% isopropanol as the reaction medium offers several advantages. A blank is unnecessary as there is no "oxygen error"; the reaction between iodine and thiosulfate seems to be instantaneous in this medium; isopropanol is an excellent solvent for organic substances; the method is widely adaptable, many types of substances, both liquids and solids, having been analyzed directly; the determination is independent of the quantities of isopropanol and reagents used; the determination is precise and accurate; the method is convenient.

The procedure is simple and flexible. Sufficient isopropanol[3] to effect solution (usually 25–50 cc.) is added to the sample, followed by 1 cc. of saturated potassium iodide and 1 cc. of glacial acetic acid.[4] The mixture is heated almost to boiling, kept at *incipient boiling* for two to five minutes with occasional swirling, and, without cooling, titrated with standard sodium thiosulfate to the disappearance of the yellow color. (Starch is an unsatisfactory indicator in this solvent.) It has been found that this procedure results in a homogeneous solution during the titration in practically all cases. The thiosulfate and iodine react rapidly and the danger of overstepping the end-point is slight. The end-point is easily visible to within a drop or two of thiosulfate, it being possible to titrate solutions containing a peroxygen concentration as low as $10^{-4}N$ to within 0.1 cc. using 0.005 N thiosulfate. With slightly colored materials, such as vegetable oils, one can, with practice, titrate to the point where no further disappearance of color is noticed; or a control sample may be used and the color matched at the end-point. By adding an excess of water it is possible to employ starch indicator; but this produces a heterogeneous system and has rarely been found necessary. Saturated potassium iodide (approximately 1 g. per cc.) is convenient to use, some of the salt being precipitated as fine crystals which prevent bumping. The powdered solid may be used, if preferred, as it is sufficiently soluble in isopropanol. The size of the sample and the normality of the thiosulfate will depend on the peroxygen content of the material being analyzed.

Liebhafsky and Sharkey reported that the reaction between iodide and peroxygen was retarded when water was present in the acetic acid medium.[1c] This also occurs in isopropanol and hence the use of the 99% grade. In fact under identical conditions, hydrogen peroxide reacts faster in isopropanol than in water. Therefore, when analyzing materials containing water, or for occasional cases where the liberation of iodine is found to be slow, it is better to heat the analytical solution longer to ensure complete reaction before titration. Reheating may be used as a check on the analysis.

No blank or prior treatment is required in this method. In the absence of peroxygen the solution remains colorless. Thus the "oxygen error" is eliminated. Allowing a blank solution to stand for twenty-four hours in an open flask (not in direct sunlight), resulted in the liberation of a minute amount of iodine. With reasonable precautions, volatility losses should be less than, say, 0.5%. Vigorous

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[1] (a) Wheeler, *Oil and Soap*, **9**, 89 (1932); (b) French, Olcott and Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935); (c) Liebhafsky and Sharkey, THIS JOURNAL, **62**, 190 (1940). Previous literature is referred to in these articles.

[2] Greenbank and Holm, *Ind. Eng. Chem.*, **26**, 243 (1934).

[3] 99% isopropanol is recommended, not the constant-boiling mixture which is 91% isopropanol by volume.

[4] To maintain the correct *p*H range during the titration (Fales, "Inorganic Quantitative Analysis," The Century Co., New York, N. Y., p. 352).

boiling for five minutes may result in appreciable losses. However, longer incipient boiling, beyond that necessary to reduce the peroxygen, has no effect on the consistency of the results. This has been verified experimentally.

This method has been used to analyze various peroxygen compounds, such as water insoluble acyl peroxides in the pure state, in solution and in solid mixtures; peroxygen in aldehydes, ketones, ethers, vegetable and mineral oils, and sterols; and hydrogen peroxide and related peroxygen compounds.

Among several other solvents that have been tried, ethanol (preferably absolute) has also been found suitable.[5] Absolute methanol is unsuitable as it reacts with the reagents. Although acetone is an excellent mutual solvent, produces no blank, and the reaction is rapid even at room temperature, low and inconsistent results are obtained with acyl peroxides.

A comparison of results using the various solvents is given in Table I. Recrystallized benzoyl peroxide was used as a source of peroxygen. In each case 0.1000 g. was added to 25 cc. of solvent (isopropanol, ethanol or acetone) containing 1 cc. of saturated potassium iodide and 1 cc. of glacial acetic acid. The hot solutions were titrated with 0.1 *N* thiosulfate after holding at incipient boiling for two minutes. For glacial acetic acid the method of Liebhafsky and Sharkey, employing sodium bicarbonate to eliminate the "oxygen error," was used.[1c] All results are given in duplicate.

TABLE I

Solvent	% Purity as benzoyl peroxide	
99% Isopropanol	98.4	98.6
95% Ethanol	98.4	98.5
Acetone	67.8	70.5
Acetic Acid[a]	96.5	97.0

[a] The solutions were prepared according to Liebhafsky and Sharkey and immediately boiled for two minutes and titrated while hot.

With the alcohols and with the acetic acid, no further liberation of iodine occurred on reheating.

Summary

A simple iodometric method for determining peroxygen in organic compounds, involving the use of isopropanol as the solvent medium, is described. No blank is required with this solvent. The method is flexible and readily adaptable to various types of peroxygen compounds.

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[5] Although ethanol is the commonest organic solvent, for some reason it has been neglected for this determination in the past.

Particle Size in the Vat Dyeing of Cellulose[1]

BY E. I. VALKO[2]

In vat dyeing, the dye passes through an oxidation–reduction cycle. The original insoluble dye compound (consisting mostly of a quinone) is first converted, by an aqueous reducing solution, into the soluble leuco form (consisting mostly of the alkali salt of a hydroquinone), in which form it is adsorbed by the fiber. The adsorbed leuco compound is then oxidized back to the original compound by air or an aqueous oxidizing solution. The dyeing operation is terminated by an aftertreatment with a hot aqueous soap solution. The three phases of dyeing, reduction, oxidation and aftertreatment, are accompanied by changes of the size of the dye particles. These changes are the subject of the present investigation.

Particle Size of Commercial Vat Dyes.—The tendency of the producers is to make their dyes with the smallest possible particle size in order to secure rapid solution and good yarn penetration, especially when the dye is applied in a printing paste. The dimensions attained are generally below the resolving power of ordinary microscopes. Although gravitational settling is hopelessly slow, a suitable centrifuge gives conveniently measurable rates of sedimentation velocity. In coöperation with Dr. Walter Wolff, an instrument was built, based on the design of Svedberg,[3] which allows the photographic recording of the settling to be carried out during centrifuging. As a much less intense centrifugal field is sufficient, many of the attachments and refinements of Svedberg could be omitted. The results on Indanthrene Brilliant Red FFB powder may be mentioned as an example. Photographs of the suspension were taken at 2000 r. p. m. at intervals of five minutes during one hour. The particle size distribution diagram (weight frequency), calculated on the basis of photometric evaluation

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[1] Original manuscript submitted to the Division of Cellulose Chemistry of the American Chemical Society in July, 1938. Presented at the 97th Meeting of the American Chemical Society, April 3 to 7, 1939, in Baltimore, Md.

[2] Present Address: Onyx Oil and Chemical Co., Jersey City, N. J.

[3] Svedberg, *Ind. Eng. Chem., Anal. Ed.*, **10**, 113 (1938).