[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Phase Behavior of Dodecyl Sulfonic Acid and of its Alkali Salts with Water

BY MARJORIE J. VOLD

This study of the phase behavior of dodecyl sulfonic acid with water was undertaken in order to compare it with that of typical sodium soaps[1] which differ chemically only in having the sulfonate group replaced by carboxylate. It has been possible to determine the phase diagram fairly completely, chiefly through a systematic application to the binary system of the dilatometric technique[2] developed for the study of transitions in dry soaps. Exploratory experiments sufficient to show some of the qualitative features of the phase behavior have been made on the lithium, sodium and potassium salts of the acid.

The results provide material for further discussion of the hypothesis[3,4,5] that the existence of liquid crystalline phases requires, in addition to geometrical anisometry, a nice balance in polar character between the constituent groups of the molecules involved.

Experimental.—The dodecyl sulfonic acid (lauryl sulfonic acid, abbreviated LSO_3H), was prepared by Dr. M. Synerholm by the method of Noller and Gordon[6] and is the same preparation used by McBain, Dye and Johnston.[7] The alkali salts were prepared by neutralization of a warm aqueous solution of the acid with the appropriate alkali hydroxide, recrystallization from water at about 10°, and dehydration under reduced pressure over phosphoric anhydride.

The melting points and transition temperatures of the dry materials were determined using the microscopic and dilatometric techniques described elsewhere.[2,8] In the aqueous systems the phase boundaries were established partly by visual determination of certain of the temperatures at which phase changes occur on heating and cooling, in the manner described elsewhere.[1,9] These are the temperatures, T_i, at which liquid crystalline material first separates from isotropic liquid on cooling, and can be made to disappear on heating; the temperatures, T_0, at which the last trace of liquid disappears on cooling and reappears on heating; and the temperatures, T_c, at which a solid crystalline phase dissolved or melted to form either isotropic liquid or liquid crystal.

About thirty samples of dodecyl sulfonic acid and water were studied dilatometrically. Samples of the desired composition, made up and thoroughly mixed by agitation in the liquid state, were sealed to carefully selected Pyrex capillary tubes calibrated by weighing the mercury contained per unit length (one mm. corresponded usually to about 2×10^{-4} cc.). The remainder of the bulb and the stem of the dilatometer were filled with mercury, which can be conveniently introduced in the following manner. The stem of the dilatometer is inserted through a rubber stopper into a glass bulb half filled with mercury, with a second outlet connected to a Cenco Hyvac oil pump. Air is removed by pumping with the dilatometer stem projecting into the air space in the bulb. The bulb is then rotated slightly so that the mercury covers the dilatometer stem, and air is readmitted forcing mercury into the dilatometer. The bulb of the dilatometer was immersed in a freezing mixture during the process to minimize loss of water vapor. The dilatometers were suspended with the bulb about 6 cm. below the surface of a mechanically stirred liquid-bath whose temperature was raised only about 0.2° per minute. The level of the mercury in the stem above an arbitrary zero level was determined as a function of temperature. Discontinuous changes in level or in the slope of the curve are taken as evidence of phase change in the sample.

All observations, visual, microscopic and dilatometric, were made at least in triplicate. Values reported for temperatures of phase change (except in a few instances as specified later) are reproducible within 1 to 2°. The compositions may be in error by up to 1%, owing to the highly deliquescent nature of dodecyl sulfonic acid, which makes it difficult to transfer and weigh accurately. Attainment of equilibrium was assured in most instances by approaching a given boundary both from higher and lower temperatures, and in all cases the rate of temperature change during observations was very small. The reproducibility of the results and their ready representation on a completely self-consistent phase rule diagram may be taken as further evidence for the attainment of equilibrium.

Experimental Results

Equilibria Involving Crystalline Dodecyl Sulfonic Acid.—This substance melts[10] directly from crystal to isotropic liquid at 74°. No transitions were found between −25° and the melting point. Addition of water up to 4.6 wt. % lowers the temperature of melting to isotropic liquid from 74° to a eutectic temperature of 41.5° at which the dry acid, isotropic solution and a third phase, crystalline dodecyl sulfonic acid monohydrate, can be in equilibrium. This behavior was established dilatometrically, curve E of Fig. 1 being

---

(1) J. W. McBain, R. D. Vold and M. Frick, *J. Phys. Chem.*, **44**, 1013 (1940).

(2) R. D. Vold and M. J. Vold, THIS JOURNAL, **61**, 808 (1939).

(3) J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.*, **29**, 1032 (1933).

(4) R. D. Vold, C. W. Leggett and J. W. McBain, *J. Phys. Chem.*, **44**, 1058 (1940).

(5) M. J. Vold, M. Macomber and R. D. Vold, THIS JOURNAL, **63**, 168 (1941).

(6) Noller and Gordon, *ibid.*, **55**, 1090 (1933).

(7) McBain, Dye and Johnston, *ibid.*, **61**, 3210 (1939).

(8) M. J. Vold, *ibid.*, **63**, 160 (1941).

(9) R. D. Vold, *J. Phys. Chem.*, **43**, 1213 (1939).

(10) The value 52° reported by Noller and Gordon[6] apparently corresponds to a sample containing 2% water.

typical of the four obtained on samples in this range of composition. The rate of expansion is uniform up to 41.5°, the two solid phases being present in unchanging proportion. At 41.5° a "flat" occurs showing that some of the solid melts. Above 41.5° the rate of expansion is larger as the proportion of liquid increases. When all has melted (52°) the expansion curve is again almost linear. The change in slope of the dilatometer curve occurs at the same temperature (52°) at which the last trace of solid is observed to disappear.

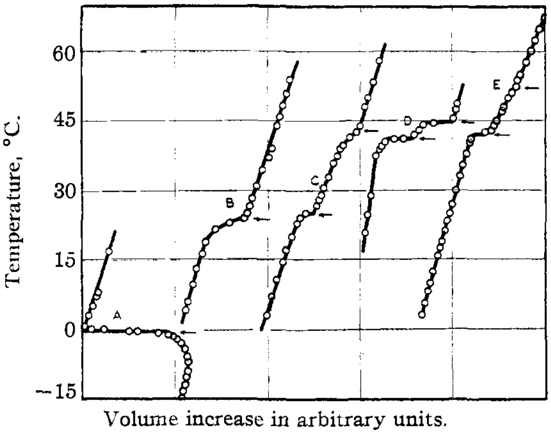

Fig. 1.—Typical dilatometer curves for dodecyl sulfonic acid and water: Curve A, 30.6% LSO_3H; B, 88.9% LSO_3H; C, 91.2% LSO_3H; D, 95.0% LSO_3H; E, 98.3% LSO_3H.

The Existence of Two Liquid Crystalline Phases.—Addition of more than 5% of water raises the temperature at which complete melting occurs. Values of T_i and T_0 are given in Table I and plotted in Fig. 2. The T_i curve exhibits two maxima, showing that there are two separate liquid crystalline phases. Both are of variable composition (solutions, not compounds); they appear to correspond closely to the "superneat" and "middle" forms of aqueous soap systems.[1]

Evidence for the Existence of a Monohydrate.—The crystalline solid which forms on cooling samples containing more than 5.5% water appears to be the compound dodecyl sulfonic acid monohydrate. The evidence for the existence of this compound is principally the dilatometric behavior of samples containing between 95.0 and 91.8% acid. The crystalline material disappears at the same temperature (44.5° to 45.5° for six different samples), marked by a horizontal "flat" in the dilatometer curves. The phases formed are liquid and liquid crystal in proportions varying with the composition from wholly liquid at 95% acid to wholly liquid crystal at 91.8% acid. 45° is thus established as the temperature of the three-phase equilibrium involving isotropic liquid containing 95.0% acid, liquid crystal containing 91.8% acid, and a crystalline solid containing an amount of water lying between these two extremes. A sample containing 95.0% acid shows two flats in its dilatometer curve (curve D of Fig. 1), one at 41.5° where two crystalline phases are in equilibrium with liquid, and one at 45°. The flat at 41.5° is absent from a sample con-

TABLE I

VISUAL OBSERVATIONS OF TEMPERATURES OF PHASE CHANGE, T_i AND T_0, FOR SOLUTIONS CONTAINING VARIOUS PERCENTAGES OF DODECYL SULFONIC ACID

Wt. %	T_i	T_0	Wt. %	T_i	T_0
93.9	49	45	58.6	203	198
94.1	50		56.2	195	172
93.1	58		53.3	174	146
92.1	80	65	52.2	170	144
91.8	84		50.9	156	147
89.5	117		50.1	154	145
88.9	124		47.6	160	155
89.0	133	128	43.0	164	
86.2	153		36.9	153	148
78.1	192		36.0		141[a]
76.3	—	197[a]	33.5	136	130
75.4	192		30.8	111	100
70.2	213	211	30.6	110	
67.6	214	213	28.1	71	
65.0	210		26.0	50	27
63.9	212		22.2	*ca.* 2	
61.7	209	204			

[a] Values determined microscopically.

TABLE II

VISUAL AND DILATOMETRIC VALUES FOR THE TEMPERATURES AT WHICH VARIOUS CRYSTALLINE PHASES DISAPPEAR IN CONCENTRATED SYSTEMS OF DODECYL SULFONIC ACID AND WATER[a]

Wt. %	T_c	Wt. %	T_c
100	74	88.9	24
99.2	59	85.4	23.5
98.3	53	75.4	22
97.9	51	73.9	20.5
95.8	43	65.2	18
94.8	44.5	65.0	19.5
94.1	45.5	61.4	15.5
93.9	45.5	59.9	15.5
93.1	45.5	53.3	9.5
92.6	45.5	52.2	8.5
91.1	45.5	50.9	5.5
91.2	43.5	47.6	4.0
89.8	39	36.9	− 0.5
89.0	37		

[a] From 100 to 94.8% LSO_3H isotropic liquid is formed; from 94.1 to 91.1% isotropic liquid and liquid crystal are formed; from 91.2 to 36.9% liquid crystal is formed.

taining 94.2% acid. Thus the crystalline hydrate contains between 95.0% and 94.2% acid.[11] It has been arbitrarily placed at 94.5% in the phase rule diagram. (Fig. 2, note insert.)

The temperatures, T_c, at which the crystalline monohydrate dissolves to form liquid crystal are given in Table II, and plotted in Fig. 2. These were determined both dilatometrically and visually. Curve B of Fig. 1 is typical of the dilatometer curves obtained. Above T_c (24°) the expansion is nearly linear. Well below T_c it is also linear, but the expansion rate becomes larger as T_c is approached, giving the rounded portion between 19 and 24° where the amount of liquid crystal is increasing rapidly.

Equilibrium between Liquid Crystalline Phases.—From about 87–71% acid the temperature at which the last trace of solid hydrate dissolves remains nearly constant. Further, drier samples, containing nevertheless more than enough water to form the monohydrate, separate some liquid crystal at this same temperature (about 24°), as shown by the existence of flats in the dilatometer curve well below T_c. Curve C of Fig. 1 is a typical example. Thus 24° is the temperature at which three phases, two liquid crystalline solutions containing 87 and 71% acid, respectively, and crystalline monohydrate can exist together in equilibrium. Again, T_0 is constant at about 145° from 54 to 49% acid. Here the three phases are isotropic solution (51% acid) and the two liquid crystalline solutions, provisionally named superneat (54% acid) and middle soap (49% acid).

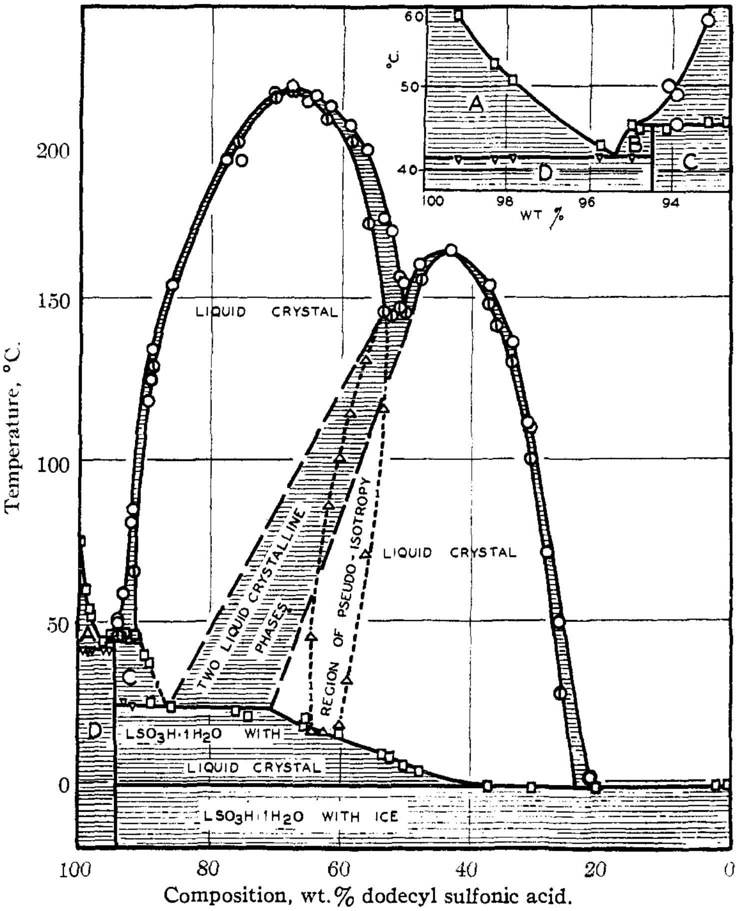

Fig. 2.—The phase diagram of dodecyl sulfonic acid and water: ○, T_i; ⦶, T_o; □, T_c; ▽, eutectic temperatures determined dilatometrically; △, points defining the region of pseudo-isotropic appearance; A, LSO_3H with isotropic solution; B, $LSO_3H \cdot 1H_2O$ with isotropic solution; C, $LSO_3H \cdot 1H_2O$ with liquid crystal; D, LSO_3H with $LSO_3H \cdot 1H_2O$.

During a study of the microscopic appearance of samples in the central portion of the diagram (Fig. 2) a definite region was discovered in which the material develops a partly isotropic appearance without separating isotropic liquid and without any change in consistency or specific volume or any other indication of change of phase. The range of temperature within which this curious

Table III

Data Defining a Region of Pseudo-isotropy in Systems Containing a High Percentage of Dodecyl Sulfonic Acid[a]

Composition, wt. %	T_1	T_2
63.9	15.5	45
61.7	15.5	83
61.4	15.5	85
59.8	18	100
58.6	32	114
56.3	70	130.5
53.3	115	145

[a] T_1 is the temperature at which pseudo-isotropy appears on heating. T_2 is the temperature at which pseudo-isotropy disappears on further heating or appears on cooling.

---

(11) The monohydrate should contain 93.3% acid. The author was never able to obtain a sample of acid which was entirely dry, judged by dilatometric behavior, and considers that this discrepancy of about 1% is due to water present in the original material. Similarly, the relative volume changes at the two flats in curve D of Fig. 1 show that the composition of this sample must have been about half way between 95.0 and 94.5% LSO_3H rather than exactly 95.0% as weighed out.

optical effect occurs is given in Table III and also on Fig. 2.

Between 24 and 145° there is a region of composition in which the two liquid crystalline phases coexist. The exact boundaries of this region, except at its upper and lower temperatures, have not been determined and are given only approximately by the dashed lines shown in Fig. 2.

Equilibria Involving Ice.—Isotropic solutions containing less than 21.5% acid separate ice directly on cooling. (Accurate freezing points are available for very dilute solutions from the work of McBain, Dye and Johnston.[7]) Middle soap containing up to about 36.5% acid also separates ice on cooling, but more concentrated samples separate the crystalline monohydrate, as shown by the T_c curve. Thus four phases occur in the narrow temperature interval between −1 and 0° (ice, isotropic solution, liquid crystalline middle soap and crystalline monohydrate). It seems likely that there are two temperatures of three phase equilibria, one for ice, solution and middle soap (23.5% acid), and just below it one for ice, middle soap (36.5% acid) and monohydrate, rather than a true quaternary point. This result, however, is based only on the observation that samples containing 30–25% acid, after freezing, always appeared on reheating to form only middle soap, and not any liquid solution or crystalline solid.

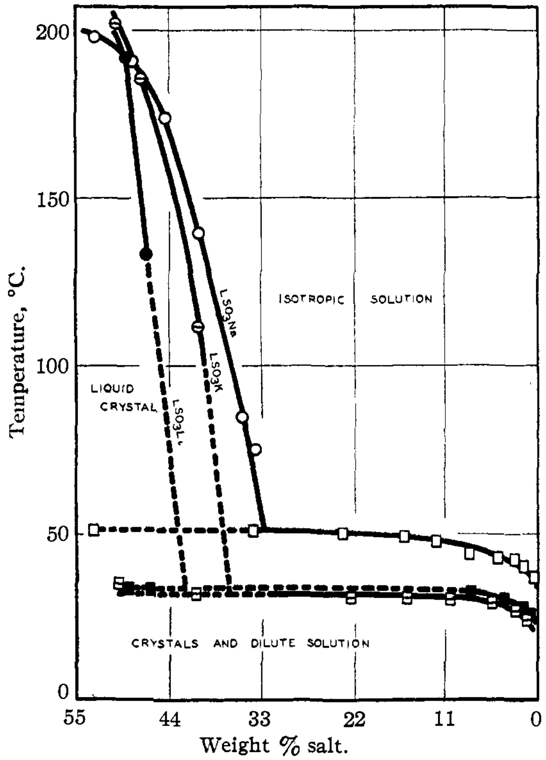

Fig. 3.—Part of the phase diagrams for three alkali dodecyl sulfonates with water: ○, □, T_i and T_c for LSO$_3$Na; ⊖, ⊟, T_i and T_c for LSO$_3$K; ●, ■, T_i and T_c for LSO$_3$Li.

Dilatometric Experiments Involving Ice.—Five samples varying in composition from 61.5 to 20.5% acid were investigated from −25° to well above T_c. Curve A of Fig. 1 is typical of the results obtained. Ice begins to melt at a very low temperature, and melts continuously as the temperature is raised, finally disappearing at a temperature which is practically the −0.5° predicted by the phase diagram in dilute solutions, but rapidly decreases to lower values in more concentrated systems. This behavior has its origin in the structure of the solid.[12,13] Even though the solid contains enmeshed solution whose freezing point in bulk is higher than −1°, no ice will form until a considerably lower temperature is reached because the activity of the water in the solution is further lowered by being confined in spaces of small diameter. These interstices are probably of continuously variable diameter and can be filled with solution to different levels so that the initial freezing point and the amount of ice at each temperature depend on the concentration of water in the sample, as found.

Transitions of the Alkali Sulfonates

The lithium, sodium and potassium salts of dodecyl sulfonic acid decompose above 360° without melting. All exhibit a transition from crystal to a mesomorphic form resembling under the microscope the subneat phase of sodium soaps. The temperatures, determined dilatometrically and microscopically, are 214 ± 2° for the lithium salt, 204 ± 2° for the potassium salt, and 192 ± 7° for the sodium salt.

Phase Behavior of the Alkali Sulfonates with Water.—Only a small part of the phase diagrams for the alkali dodecyl sulfonates has been established, owing to the tendency of concentrated samples to decompose on heating, before becoming fluid enough to permit adequate mixing to ensure subsequent attainment of equilibrium. The boundaries obtained are shown in Fig. 3, which was plotted from the data of Table IV.

---

[12] J. W. McBain, M. J. Vold and S. A. Johnston, THIS JOURNAL, 63, 1000 (1941).

[13] W. A. Patrick and W. A. Kemper, *J. Phys. Chem.*, **42**, 381 (1938).

The curves for the equilibrium between the crystalline salts and isotropic solution are very similar to those obtained for sodium soaps. The solubility is small at room temperature but increases rapidly at higher temperatures, the curve finally becoming nearly horizontal. This behavior for the sodium salt also has been studied by Wright and Tartar[14] whose curve, while very similar to ours, lies about 6° lower. A liquid crystalline solution corresponding in appearance and composition to middle soap is formed by all three alkali salts.

TABLE IV

PHASE DATA FOR ALKALI DODECYL SULFONATES WITH WATER. VISUALLY DETERMINED TEMPERATURES OF PHASE CHANGE

Wt. % salt	T_i	T_c	Wt. % salt	T_c
		A. Sodium salt		
52.7	198	*ca.* 51	15.8	49
48.2	191		12.1	48
44.2	174		8.12	44
40.5	140		4.69	42.5
35.4	85		2.86	42
33.6	65	51?	1.65	40
32.8	(45?)		1.17	38.5
23.3		50	0.36	37
		B. Potassium Salt		
50.2	202	35	10.5	30
47.2	186		5.58	29
40.6	112	32	2.59	27
22.2		31.5	1.29	24
15.7		31.0	0.65	23
		C. Lithium Salt		
49	192	33	4.07	30
46.6	134	33	1.93	27
8.08		32	1.11	25

T_0 values: for LSO_3Na, 44.2% 158°, 40.5% 106°; for LSO_3K 47.2% 177°; for LSO_3Li, 46.6% 117°.

Discussion

Dodecyl sulfonic acid as can be seen from Fig. 2 provides an example of a substance which, though incapable of exhibiting stable mesomorphic forms in the pure state, interacts with water to form two different liquid crystalline solutions. For such mesomorphic forms to exist[3] the molecule must contain groups of contrasting intermolecular forces so that a temperature range exists within which the violence of thermal agitation is large enough to overcome some but not all of the mutual attractions and repulsions which at a lower temperature lead to the arrangement of the molecules in a regular crystal lattice. Further, these groups must be so located that such a partial melting permits a random distribution in some directions without disturbing the regular periodic spacing in other directions. Apparently interaction with a solvent is required in the case of dodecyl sulfonic acid before these conditions are fulfilled.

The fundamental role played by the solvent in the formation of these structures is further emphasized by the similarity between the phase behavior of dodecyl sulfonic acid and a typical sodium soap.[1] The two dry solids are fundamentally different, one melting at a single temperature, and the other exhibiting numerous liquid crystalline forms. Yet in water both form at least two new liquid crystalline solutions not continuous on the phase diagram with any phase of the dry material. Each of these forms for both substances exhibits a maximum solution temperature, and the amounts of water present at these points are similar; for $C_{12}H_{25}SO_3H$, they occur at 13.3 and 5.3 mole % acid, for $C_{11}H_{23}COONa$ at 21.7 and 6.5 mole % soap, for $C_{15}H_{31}COONa$ at 18.2 and 4.7 mole % soap. The relative thermal stability of the two anisotropic solutions is the same for the soaps and dodecyl sulfonic acid, the more concentrated phase persisting to a higher temperature. The forms are also similar in microscopic appearance and in consistency.

In the alkali salts of dodecyl sulfonic acid, in contrast to the acid itself, the conditions necessary for step-wise melting are apparently satisfied, just as they are for the sodium and potassium salts of the *n*-fatty acids but not for the acids. However, only one liquid crystalline form of the sulfonates has been detected, in contrast to the series found for the soaps.[2,5] It most nearly resembles subneat soap in optical properties.

In so far as the behavior could be determined the alkali dodecyl sulfonates interact with water, in the same way as do either the soaps or dodecyl sulfonic acid. This type of behavior of an amphipathic[15] molecule with water thus appears to be of a very general nature. It is not shared by such a bile salt as sodium deoxycholate which is also a good solubilizing detergent, but in which the distribution of polar groups is very different.[16]

Acknowledgment.—The author wishes to thank Dr. J. W. McBain for many valuable discussions during the course of this investigation.

---

[14] THIS JOURNAL, **61**, 539 (1939).

[15] G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann and Co., Paris, 1936, p. 44.

[16] R. D. Vold and J. W. McBain, THIS JOURNAL, **63**, 1296 (1941).

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

RECEIVED FEBRUARY 14, 1941

[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

---

[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 pH range during the titration (Fales, "Inorganic Quantitative Analysis," The Century Co., New York, N. Y., p. 352).