Some Applications of Ultraviolet Spectrophotometry in Drying Oil Research[1]

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DURING the last few years greatly improved developments in spectrophotometric methods and equipment have resulted in an expanded use of ultraviolet spectrophotometry in the study of many chemical problems. This technique has been applied to investigations on unsaturated fats and oils through the medium of the chromophore groups or double bonds which occur in natural unsaturated fatty acids. These chromophore groups absorb radiant energy in a characteristic manner depending upon whether they possess natural conjugation or the conjugation was produced synthetically through some process or prior treatment.

The principal impetus behind the utilization of ultraviolet spectrophotometry in the study of drying oils was furnished by early observations (16, 10, 13, 15) on the shifting of the double bonds of a hydrocarbon chain to a conjugated system upon exposure to alkali and heat. Another invaluable aid has been the publication of reference values for highly purified, conjugated acids. Kass (10) and Miller (13) adapted this technique to the quantitative determination of the amount of linoleic acid in vegetable oils. Mitchell (15) devised reference standards for linoleic and linolenic acid and published a complete fat analysis method based on spectrophotometric data and iodine values. Beadle and Kraybill (2) later published reference values for arachidonic, linoleic, and linolenic acids.

More recently the ultraviolet spectrophotometer has been widely adopted in theoretical studies on the oxidation and polymerization of unsaturated fatty oils, monohydric fatty esters, or fatty acids.

Working mainly with linoleic acid and its simple esters, a large group of workers have in recent years accumulated valuable information on the autoxidation of unsaturated fatty products. Farmer and his associates (5, 6, 7) studied a series of olefinic compounds and concluded the primary products of autoxidation of unsaturated fatty acids are hydroperoxides whose formation can cause a shift of double bonds, making possible the production of a conjugated system in compounds such as linoleic acid. Bolland and Koch (4) found the monohydroperoxides to be at least 70% conjugated by spectrographic analysis. Bergstrom (3) independently concluded the development of conjugated diene hydroperoxides. Lundberg (12) recently reported that most of the oxygen absorbed by autoxidized methyl linoleate was in the form of relatively stable linoleate peroxides in which a constant fraction of the total peroxides was present as conjugated dienes. Holman, Burr, and co-workers have published a series of investigations (9) on the possibilities of spectrophotometric research on vegetable oils and an interesting feature of their work was the utilization of alkali to produce enolization of alpha-keto groups resulting in conjugated systems having absorption maxima at characteristic wave lengths.

Hilditch (8) summarizes the question of the polymerization of autoxidized oils by stating that positive experimental evidence on this problem clarifies only a few points; that is, "the oils pass through a phase involving the production of conjugated di- or triethenoid systems adjacent to a hydroperoxide group; compounds of a cyclic mono- or dimeric type are formed to some extent; and the peroxidic properties disappear as polymerization proceeds." Until this rudimentary knowledge of the autoxidation reaction is extended, any hypothesis as to the mechanisms of polymerization is little more than speculation.

Long (11) found that a remarkable correlation existed between the area under the absorption curve in the ultraviolet and the durability or weather resistance of a dried oil film. This technique has also been applied to plasticizers incorporated in nitrocellulose films (1).

The present paper describes further application of the spectrophotometric method in studies dealing with the ultraviolet absorption of dried oil films in both alkaline and neutral solvents.

Experimental

This method of spectrophotometric analysis of oil films was based upon obtaining a true solution of the aged infusible film through the medium of alkali. A 10% alcoholic KOH solution has been the only reagent found which will completely and readily dissolve a dried oil film to a clear solution suitable for spectroscopic examination at the lower wave lengths. For similar type studies on oils, Holman and coworkers (9) have used a 10% solution of KOH in a 50% water-ethanol medium but the saponification of the oil film by this reagent was a slow process. Lundberg (12) suggested the use of a very dilute solution of KOH in ethanol but this technique was also time-consuming for dried films in that 48 hours were required for equilibrium. Tests in our laboratory with the 10% methanolic KOH show maximum absorption in 30 minutes with little change in absorption from 1-4 hours.

Preparation of Alkali Reagent. The 10% alkaline reagent was prepared by adding 10% of analytical grade KOH to synthetic methanol purified by distillation over NaOH and Zn dust. The alkali was dissolved by stirring, and the solution was allowed to stand overnight. The clear solution was decanted from the precipitated carbonates to give a solution approximately 1.65 N. This solution, if properly purified, permitted readings as low as 232 mμ with fairly narrow slit widths.

Preparation of Acid Reagent. The acid reagent was prepared by adding 2.5% by weight of 38% HCl to purified methanol.

Preparation of Film Samples. The oil films were prepared on either Sanderson drying plates by con-

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ventional methods or were doctor bladed on stainless steel panels. These plates or panels were treated in the manner required for the experiments, and the film specimens were readily removable at any time during the drying, aging and/or exposure period. The usual driers used in these studies were 0.2% Pb and 0.25% Co as the naphthenates.

Spectrophotometric Analysis of Film Specimen. Samples for spectral examination were obtained by the removal of an area of film approximately 3″ square, equivalent to a weight of 100-200 mgm. The specimen was accurately weighed into a 50-ml. volumetric flask which was partially filled with the KOH reagent and the film was dissolved by shaking. The solution was made up to volume and allowed to stand for one hour at 25°C. A 5-cc. aliquot of the alkaline solution of the dried film was added to each of two volumetric flasks, to one was added the alkali reagent and to the other the acid reagent. These solutions were allowed to stand until the salt settled from the neutralized sample with about ten minutes being required. The blanks were prepared in an identical manner from the respective reagents.

The optical densities of the diluted samples were then determined in two separate runs using a model DU Beckman Quartz Spectrophotometer. The characteristic absorption of the enolizing portion of the oil film was readily determined by subtracting the density values of the neutralized sample from the corresponding value for the enolized or alkaline solution. The absorption curves were usually plotted in specific absorption units on semilog graph paper.

Results and Discussion

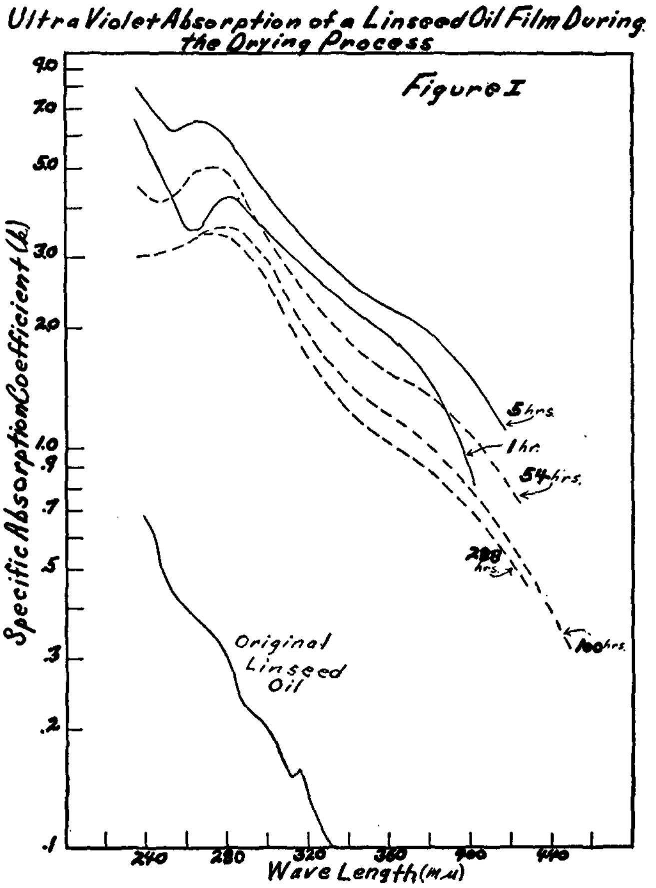
Typical data obtained by spectrophotometric studies on the drying and aging process of an oil film are given in Table I. This film was prepared by previously described methods from a sample of alkali refined linseed oil. The specific absorption coefficients at 240, 270, 320, and 370 mμ corresponding to diene, triene, tetraene, and pentaene conjugation were determined in the alkaline reagent for different periods of time during the drying and aging process.

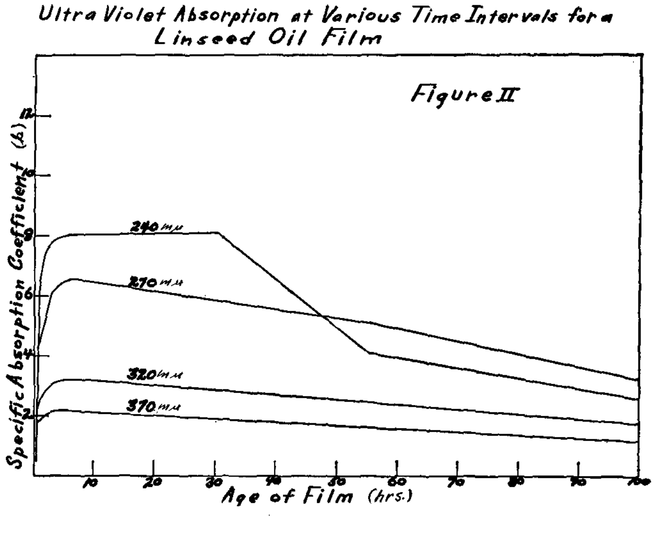
TABLE I

Specific Absorption Coefficients of a Linseed Oil Film During the Drying Process

Film Age (hrs.)	Wave Length (mμ)				Remarks
	240	270	320	370	
0	.65	.35	.13	....	Original oil
1	6.3	4.4	2.6	1.8	....
3	8.0	6.2	3.1	2.1	Film set-up
5	8.0	6.5	3.2	2.1	Film dry to touch
30	8.0	5.8	2.9	1.8	Film hard–no tack
54	4.1	5.1	2.3	1.5	....
100	3.1	3.6	1.8	1.2	....
288	3.0	3.6	1.6	1.0	....

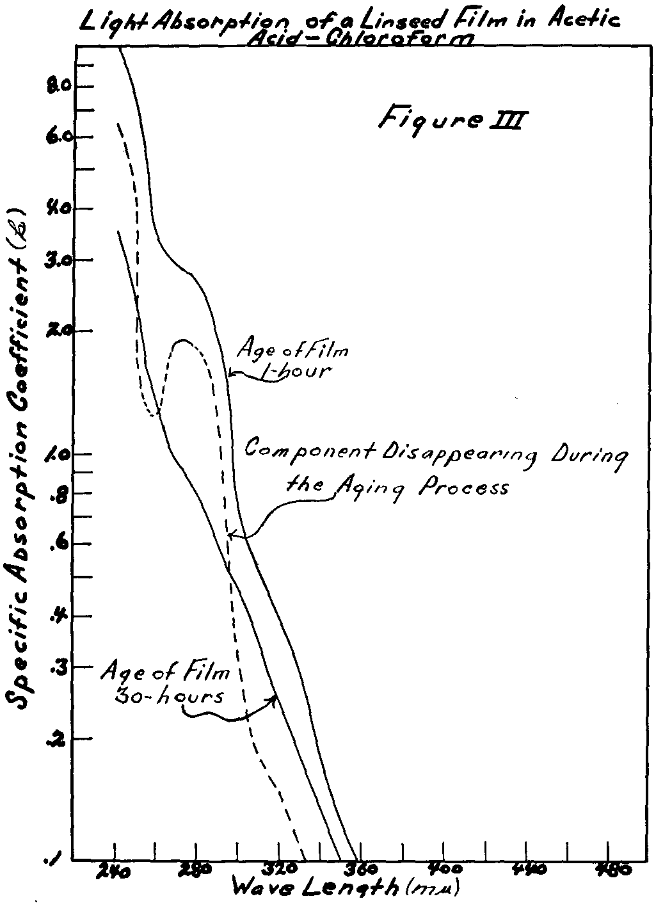
With reference to Table I, the film had started to polymerize in three hours, was set to touch in five hours, and was completely dry in 30 hours. It was interesting to note that the stage of polymerization obtained in five hours was characterized by maximum absorptions at the critical wave lengths corresponding to the various conjugated systems. The conclusion may be drawn that the initial polymerization process does not destroy the equilibrium of the conjugated-absorption systems induced by autoxidation since the film was set before any appreciable drop in absorption was detected. However, the aging of the film which occurred after one to three days resulted in a decline in diene conjugation to approximately half its maximum value. After three days the decline was slow but in time the absorption at all wave lengths became approximately half the maximum values obtained at the time the film became continuous. These changes in ultraviolet absorption are shown graphically in Figure I. The solid line curves show the increase in absorption obtained during the early stage of drying with the maximum absorption being obtained in five hours, while the broken line curves illustrate the decrease in absorption during the inter-





mediate stage of the drying process. The original linseed oil gave minor absorption at the critical wave lengths.

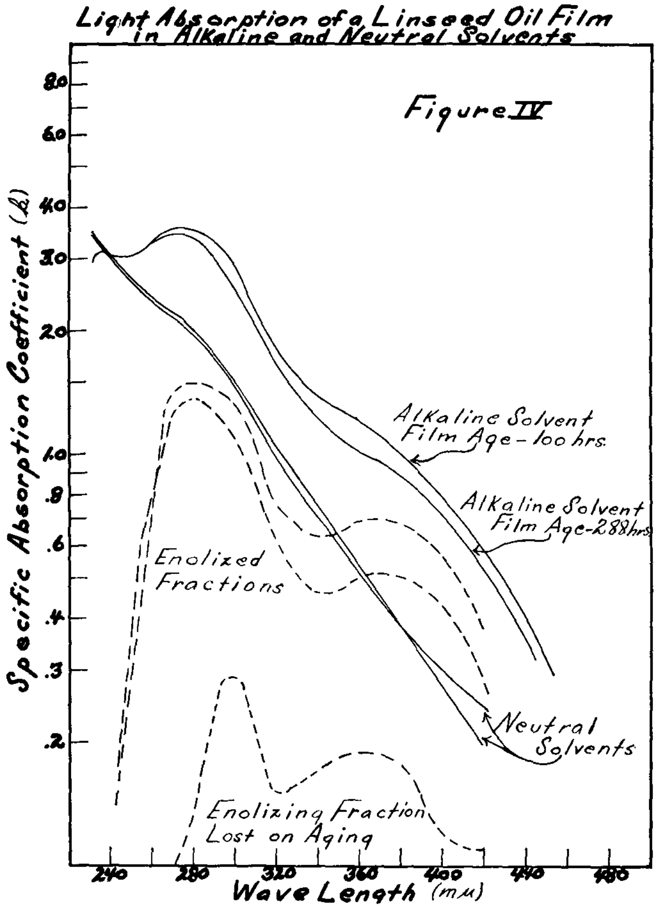
The above relationships are shown in a different manner in Figure II where the specific absorption coefficients are plotted against the age of the film. As illustrated in Figure II, the absorption coefficient at 240 mμ increased to 8.0 in five hours, exhibited the same value after 30 hours, and then decreased to a level of 3.0 in 100 hours. Similarly, the absorption at 270 mμ increased to 6.5 in five hours and then showed a slow decrease to 3.6 at 100 hours. The same generalizations apply to the absorption measured at 320 and 370 mμ.



It should be remembered that the conjugation values discussed above were obtained in alcoholic KOH and represent the sum of at least three components. One component is the carbon to carbon conjugation which appears in non-polar or neutral solvents; the second component would include conjugated-oxygen compounds which also absorb in neutral solvents; and the third component is the enolized form of carbon to oxygen conjugated systems.

In Figure III are two curves of an alkali-refined linseed oil film obtained from a solution of the film in 2% glacial acetic acid-chloroform.[3] The upper curve was from a film sample aged for one hour and the lower solid curve was from the same film after aging for 30 hours. The difference between the two curves was plotted on the broken line curve to show the absorption characteristics of the compounds disappearing during the aging of the film. As seen in Figure III these compounds had distinct peaks at 240 and 270 mμ corresponding to diene and triene conjugation. From these curves it can be seen that the drop in conjugation upon aging of the film (noted in Figures I and II) was largely due to a decrease in the carbon to carbon conjugation or conjugated oxygen compounds which absorb in the absence of alkali rather than in the enolizable component. Unfortunately, the chloroform-acetic acid cannot be applied to films which have thoroughly hardened; however, data obtained by neutralization of alkaline solutions of films indicate that after 30 hours the films show practically identical diene absorption in alkali and neutral solvents.

Upon neutralizing the alkali reagent after methanolysis has occurred, absorption curves were obtained which represent the concentration of all chromophores not produced by enolization. The corresponding sets of curves for a linseed oil film aged for 100 and 288 hours are shown in Figure IV. These curves illustrate the fact that the maxima at 270 and 370 mμ were suppressed upon neutralization and the neutralized curves for the different periods of aging were practically identical. The broken line curves show the enolizable fraction for the two samples. They had absorption maxima at 270 and 370 mμ which presumably would represent ketonic derivatives of carbon to carbon conjugated systems. The small amount of enolizable substance disappearing between 100 and



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[3] 2:1 glacial acetic acid-chloroform cannot be used as glacial acetic acid has too high absorption at the lower wave lengths.

288 hours is shown graphically in the bottom line curve with absorption maxima at 300 and 360 mμ.

Numerous studies on films of blown, heat bodied, and modified soybean or linseed oils along the principles discussed above in some detail for alkali refined linseed oil have led to an interesting observation. The drying time of the oils as measured by set-to-touch was directly related to the absorption maxima in the diene conjugated region. In other words, the set-up time coincided with the development of maximum diene conjugation regardless of whether or not this conjugation was produced through autoxidation or previous treatment of the oil.

The alkaline solvent used in these experiments for obtaining a true solution of a completely dry oil film does not produce conjugation of isolated double bond systems and should not be confused with the prolonged saponification treatment of Moore (16) or high temperature treatment used by Burr, Mitchell, Kraybill, which induces carbon to carbon conjugation of linoleic, linolenic, and other highly unsaturated fatty acids. Undoubtedly, our alkali treatment induces certain minor changes in oxidized vegetable oils other than saponification and enolization of alpha-carbonyl systems; however, these changes are indeed minor since diene conjugation is always essentially the same in neutral and alkline solutions while absorption in the region of 270-275 mμ is always greater with an oxidized or autoxidized oil. This is an indication of the enolization of an alpha-carbonyl diene system to a triene carbon to carbon system. Furthermore, if the action of the alkali solvent on the U. V. absorption of an oxidized oil is mainly enolization, the reaction should be reversible by neutralization. This is found to be true, and the neutralized curve is quite reproducible. It was also found that the neutralized material can be returned to the alkaline condition giving the original alkali curve.

The alkaline-solution technique on oil films was applied to a series of oils in an attempt to duplicate the studies of Long (11) who concluded that a direct relationship existed between the light absorption and the weather resistance of oil films. A series of 12 oils were used in preparing duplicate films on stainless steel panels which were allowed to dry for 288 hours at constant temperature and humidity.

A film sample was removed from each panel for spectrophotometric analysis in the usual manner. The duplicate panels were then placed in a weatherometer for accelerated weathering tests for 254 hours. After this period wide visual differences in the durability of the films were apparent, ranging from little film remaining on the panels to hard, glossy, intact films. After exposure the various types of oils were arranged in the following order by an experienced and neutral observer with the highest durability first: short oil alkyds, long oil alkyds, heat bodied linseed oils, special blown linseed oils, blown-polymerized linseed oils, heat-bodied soybean oils, and raw linseed oil.

The logarithmic curves for the absorption of the unexposed neutralized samples were straight lines in the region of 320-400 mμ which would include almost all of the highly reactive ultraviolet found in sunlight at the earth's surface. According to the Grotthus-Draper law of photochemistry, it is only the absorbed light that induces photochemical reactions: thus the area under the absorption curves from 320-400 mμ should be an index of the reactivity of the film to sunlight. A factor representing this area was calculated for the above series of oil films. This area factor was based on the actual area under the absorption curves in the wave length range of 320-400 mμ. When arranged with respect to an increasing area factor, as shown in Table II, the different types of oils were, without exception, in the same order as originally rated with the most durable films from the short oil alkyds having an absorption area factor in the region of 320-400 mμ, approximately one-third as great as the least durable film from raw linseed.

TABLE II

Ultraviolet Absorption vs. Accelerated Weathering Resistance of Straight Oil Films

Type of Oil	Visual Stability Rating	Area Factor
Short oil alkyds	1	.21
Long oil alkyds	2	.22
Heat bodied linseed	3	.27
Special blown linseed	4	.38
Blown-polymerized linseed	5	.40
Heat bodied soya	6	.49
Raw linseed oil	7	.57

This work has been expanded to similar studies on pigmented films and varnishes and gives promise of becoming a valuable aid in predicting the gross durability and weather resistance of protective coatings.

Conclusions

An alkaline-solution technique has been developed permitting the study of the drying and aging process of an oil film using the ultraviolet spectrophotometer. This technique has been found to be a valuable tool for investigating some of the chemical changes which occur as a vegetable oil film dries and ages.

The drying or autoxidation of an oil film has been shown to proceed along the general lines of a three-stage reaction with the short initial stage being characterized by an accumulation of conjugated diene and triene structures which reaches a maximum at the time the film has set up or becomes continuous. The second or curing stage was characterized by a slow decrease in the measurable conjugated diene and triene structures. The third or deterioration stage was not investigated; however, this method should be readily adaptable to studies involving film breakdown as represented by phenomena such as after-yellowing since the development of absorption peaks characteristic of linolenic ketones, for example, would permit an early prediction of yellowing long before the concentration of the chromophore groups became great enough for visual observation.

During the initial stage of drying there was also evidence for an increase in the alpha-keto structures capable of enolizing in alkali to give absorption maxima characteristic of triene and tetraene conjugated systems. These enolizable structures also decreased in amount during the film curing period and are not characterizable on the basis of observed absorption maxima and published information.

The method of obtaining a spectral solution of a dry, infusible oil film through the medium of alcoholic KOH was applied to investigations on the relationship existing between the light absorption of the film solution and the durability or weather resistance of the straight oil film. The results obtained verified the principle previously reported that the quantity of light absorbed by an oil film in the region of 320-400 mμ was indicative of the durability of the film upon exposure to accelerated weathering conditions.

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The Hydrolysis of Soap Solutions. III. Values of pH and the Absence of Fatty Acid as Free Liquid or Solid

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SOAPS hydrolyze to form hydroxyl ion and free fatty acid, but the latter is converted into soluble or insoluble undissociated acid soaps. The conversion of free fatty acid into acid soap causes the soaps to hydrolyze far more than the acetates (N/10 sodium acetate hydrolyzes to the extent of 0.007%) though the fatty acids are but slightly weaker than acetic acid. Thus the hydroxyl ion concentration is no longer equal to that of the free fatty acid but is at least an order of magnitude larger, since the corresponding fatty acid is consumed by forming acid soap.

At least three opinions have been expressed as to the presence of fatty acid in soap solutions. McBain has long maintained that, though fatty acid is always formed, there is never sufficient present to saturate the solution. Ekwall (1) holds, however, that there is more than sufficient for saturation only in a narrow range of very dilute solutions, just below the limiting concentration which he describes as the highest concentration in which the free fatty acid can appear before its conversion to acid soap. Powney and Jordan (2), on the contrary, have calculated that, not in the most dilute solutions, but in approximately 0.005 M sodium laurate, 0.001 M sodium myristate, 0.0002 M sodium palmitate, and 0.00003 M sodium stearate at 60°C., the solubility limit of fatty acid is reached and that in a range above these concentrations it is in excess of and may be several hundred times greater than the saturation value.

To confirm one of these views, pH values of potassium and sodium soap solutions were determined, and from them the actual concentration of free fatty acid in solution was calculated. This amount was found to be less than the saturation value, as determined by conductivity measurements, given in the preceding communication.

From the pH values the percentage hydrolysis was also calculated. Estimates of hydrolysis have ranged from negligible to complete hydrolysis, based upon various types of data, including E.M.F. measurements, catalysis, indicators, analysis of ultrafiltrates, extraction with benzene or other solvents, and pH measurements. Much of the earlier work has been done on sodium soaps. Ekwall and Lindblad (3) published pH data obtained by use of the glass electrode for sodium laurate at 20°. Stauff (4) used the hydrogen electrode to measure the pH of sodium soaps at 60°C. and constructed hydroxyl ion activity curves as a function of concentration but did not disclose the pH's. Likewise, Powney and Jordan (2) using the glass electrode determined the pH's of a number of sodium soaps at 25, 40, 60, and 80°C., published hydrolysis-concentration curves but did not give the pH's. Some earlier studies of potassium soaps have involved E.M.F. (5), indicator (6), and extraction (7) methods, but there are but few data on their pH's in the literature. Hence the determination of the pH of sodium and potassium soaps over a range of concentrations is here recorded for 25 and 50°C.

Experimental

Kahlbaum's best acids, and some Lepovsky's purified myristic acid were used in preparing the soap solutions. They were first analyzed by titrating them with alkali in 70-80% aqueous alcohol to determine the equivalent weight. McBain and Van Tuyl (8) showed by the titration curves of lauric and myristic acids in 80% alcohol, using phenolphthalein as indicator, that the equivalence point, the point of inflection, and the color change coincided whereas in aqueous solution the point of inflection required 1.5% excess lauric acid and 6.2% excess myristic acid. In this study titrations were made in aqueous alcoholic solutions using approximately decinormal sodium hydroxide, potassium hydroxide, and sodium hydroxide with a glass electrode; the results of the three titrations agreed closely. Also the results seemed to be independent of the concentration of alcohol, provided that there was sufficient to prevent precipitation.

For the pH determinations stock solutions were prepared by adding the calculated volume of standard alkali to a weighed amount of acid. This was heated on a water bath at approximately 70-90°C. until the acid dissolved, then cooled, and diluted to volume with conductivity water. The sodium hydroxide solutions were made from carbon dioxide-free

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