

Ultraviolet Spectroscopic Studies on Aqueous Polyvinyl Alcohol Solutions.

Part I. Characterization of Chromophores

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In connection with a study of the effects of high energy radiation on aqueous solutions of polyvinyl alcohol made in this laboratory,¹ changes were observed in the ultraviolet spectrum which could not be explained on the basis of published work. In particular, the results suggested that highly conjugated chromophores were present. As a consequence of this, reagents specific to ethylenic and to carbonyl groups have been reacted with polyvinyl alcohol in an attempt to characterize these chromophores. This paper reports the results obtained and confirms the subsequently published and independent results of Yamaguchi et al.,² referred to by Matsumoto, Imai, and Kazusa in a recent note.³

Aqueous solutions of polyvinyl alcohol invariably show the following common features in their U.V. spectra:

- (a) Background absorption, $\lambda > 450 \text{ m}\mu$
- (b) Inflection, $\lambda \sim 330 \text{ m}\mu$
- (c) Maximum, $\lambda \sim 280\text{--}275 \text{ m}\mu$
- (d) Maximum or inflection $\lambda \sim 230 \text{ m}\mu$

Takayama⁴ has shown that the U. V. absorption in polyvinyl alcohol is associated with a low molecular-weight fraction and has suggested that the absorption present between 450 and 330 $\text{m}\mu$ is due to polyene carbonyl conjugation involving from three to seven ethylenic bonds. This selective absorption will be superimposed on the absorption due to light scattered by the polymer molecules themselves.

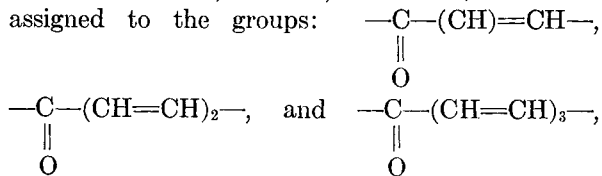
The following chromophores have been suggested as a possible source of the 280–275 $\text{m}\mu$ band: saturated carbonyl,⁴ either as ketone or terminal aldehyde^{5,6}; β hydroxy ketone⁷; β -diketone⁷; α -hydroxy- $\alpha\beta$ -unsaturated ketone.⁶

Most authors attribute the 230- $\text{m}\mu$ band to an α,β -unsaturated ketone and abnormalities observed in the viscometric behavior produced by acid and alkaline hydrolysis to changes in the inner acetals and ketals formed between carbonyl and hydroxyl groups.

Clarke and Blout⁷ were unable to remove all the 280–275 $\text{m}\mu$ band by reduction with hydrogen over metallic catalysts. They also found that the amount of 2,4-dinitrophenylhydrazone formed upon polyvinyl alcohol was approximately one-fifth of that expected if all the 280–275 $\text{m}\mu$ band absorption was due to saturated ketone. Acid hydrolysis of the hydrazone implied that the carbonyl groups were ketonic rather than aldehydic in nature.

The approach used in this paper is based on the fact that alcoholic or aqueous solutions of sodium borohydride reduce ketonic and aldehydic groups to the corresponding hydroxy compounds, but do not react with ethylenic groups. Consequently, when reacted with a polyene ketone, for example, there is a shift in absorption to shorter wavelengths due to the absorption of the polyene alcohol formed. On the other hand, Raney nickel may be used as a catalyst for the hydrogenation of ethylenic unsaturation without affecting carbonyl groups.

After the completion of this paper, our attention was drawn to the work of Yamaguchi et al.,² who have suggested, in view of the difference in molar extinction coefficients between saturated and conjugated carbonyl groups, that the absorption bands at 230, 280–275, and 330 $\text{m}\mu$ should be assigned to the groups:



respectively.

Matsumoto, Imai, and Kazusa³ have shown that the 280–275 $\text{m}\mu$ band is independent of saturated carbonyl content as measured by the dinitrophenylhydrazone derivative and have associated this particular band with the diene-ketone suggested by Yamaguchi et al.

EXPERIMENTAL

The polyvinyl alcohol used was Moviol N 30/98, M.W. = 27,000, Hoechst Chemicals, Ltd. All

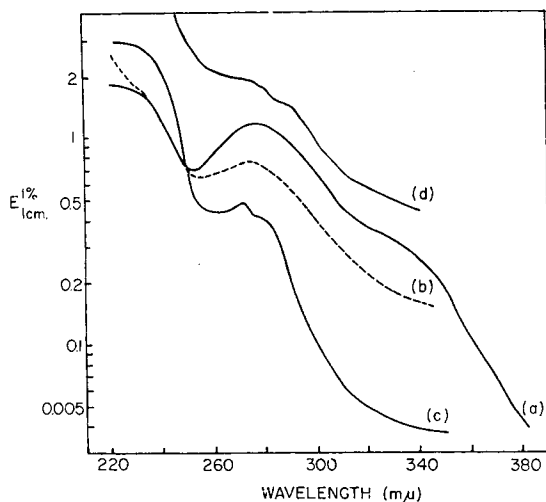


Fig. 1. Changes induced in the ultraviolet spectrum of aqueous polyvinyl alcohol: (a) original solution, (b) following reduction by hydrogen over Raney nickel, (c) after reduction with sodium borohydride, (d) after treatment with sodium hydroxide.

spectra were measured on a Beckman DK2 ratio-recording spectrophotometer. The reaction with sodium borohydride was carried out in the spectroscopic cuvette, and the reduction with hydrogen over Raney nickel, in an all-glass apparatus at room temperature and at a slight positive pressure of hydrogen. Catalyst residues were removed by centrifuging prior to spectroscopic examination.

RESULTS

The ultraviolet spectrum of the stock polyvinyl alcohol solution used, Figure 1a, is typical of that obtained from this polymer and the three bands of interest are well exhibited.

The change observed on reduction with hydrogen over Raney nickel is shown in Figure 1b and could not be reduced further. Due to difficulties in removing the finer catalyst particles, the spectrum should be considered as being qualitative rather than quantitative. This is especially true for the absorption below 250 $m\mu$, where an appreciable contribution from the scatter associated with catalyst fragments is apparent. In spite of this limitation, it is seen that the 330 and 280–275 $m\mu$ bands have been removed, to be replaced by a much weaker absorption band at 270 $m\mu$. It was possible to reduce the absorption of this new band slightly with sodium borohydride.

The spectrum produced following the rapid reaction of sodium borohydride with polyvinyl alcohol is shown in Figure 1c. It is seen that the 330 and 280–275 $m\mu$ bands are removed, being replaced by a much weaker band between 280 and

270 $m\mu$ having some fine structure. There is enhanced absorption below 250 $m\mu$ which is not due to the borohydride or reaction products thereof.

This new absorption spectrum may be further reduced in intensity by hydrogenation or radiolysis (see Part II) and the resulting spectrum, while still retaining some absorption at 270 $m\mu$, is of much weaker intensity.

It has not been found possible, by using a combination of these two techniques, to remove entirely all the selective U.V. absorption found in aqueous solutions of polyvinyl alcohol. The residual absorption may well be due to catalyst fragments attached to the polymer chain during polymerization of the vinyl acetate from which the polyvinyl alcohol is derived.

The profound change produced in the spectrum when sodium hydroxide is added to solutions of polyvinyl alcohol is shown in Figure 1d. In this particular case, the U.V. absorption is enhanced, and there are indications of fine structure below 300 $m\mu$.

DISCUSSION

The fact that the 330 and 280–275 $m\mu$ absorption bands in aqueous solutions of polyvinyl alcohol may be removed independently by sodium borohydride and by hydrogenation over Raney nickel indicates that these bands contain both carbonyl and ethylenic groups.

Since the band remaining after hydrogenation may be further reduced by sodium borohydride, it must, in part at least, be due to saturated carbonyl groups. It is unlikely, in view of the difference in extinction coefficient between saturated and conjugated carbonyl-containing chromophores, that this absorption can arise from products of the reduction, and, therefore, must be due to saturated carbonyl groups present originally but masked by the 280–275 $m\mu$ band.

The fine structure in the 280–270 $m\mu$ region found after reduction of polyvinyl alcohol with the borohydride corresponds to that exhibited by a triene alcohol.^{8,9} Such an absorption spectrum will be formed if the 330 $m\mu$ band originally present is due to carbonyl in conjugation with a triene.

Similarly, enhanced absorption below 250 $m\mu$ will be produced by the reduction of a conjugated diene-carbonyl chromophore (280–275 $m\mu$ band) to the corresponding diene-alcohol.⁸

It is obvious that this enhanced absorption below 250 $m\mu$ would not be produced by the reduction of β -hydroxy ketones, β -diketones, or α -hydroxy- α,β -unsaturated ketones.

The fact that the absorption remaining after the borohydride reduction may be further reduced by hydrogenation or by radiolysis is an added argument for the assignment given above.

When subjected to alkaline hydrolysis, polyvinyl alcohol solutions exhibit spectral changes similar to those undergone by certain fatty acids when isomerized in this medium.¹⁰ Quite apart from an overall enhancement in U.V. absorption, a number of minor inflections have become apparent between 285 and 260 μ . This is consistent with a move into conjugation of isolated double bonds present originally.

Little information is available about the behavior of the 230 μ band from these reactions described, due to interference produced by secondary products. However, the changes observed on radiolysis are consistent with those undergone by $\alpha\beta$ -unsaturated ketones.

It is reasonable, therefore, to consider the U.V. absorption spectrum of aqueous solutions of polyvinyl alcohol as being the sum of contributions from a series of chromophores of empirical formulae $-(CH=CH)_n-CO-$, where n varies from 0 to 3. Values of n greater than 3 may well give rise to the absorption tail which extends into the visible region of the spectrum and which produces the yellow color frequently observed in these solutions.

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Synopsis

The ultraviolet spectra of aqueous solutions of polyvinyl alcohol have been examined with a view to identifying the chromophores present. The spectrum may be modified by reduction with hydrogen over Raney nickel at room temperature, which is specific for ethylenic unsaturation, and by reduction with sodium borohydride, which is specific for carbonyl groups. An analysis of the resulting spectra supports the proposal that the ultraviolet absorption of aqueous polyvinyl alcohol solutions arises from polyene-carbonyl chromophores of empirical formulas: $-(CH=CH)_n-CO-$, where n may vary from 0 to 3.

Résumé

Les spectres ultraviolets de solutions aqueuses d'alcool polyvinylique ont été examinés en vue d'identifier les chromophores présents. Le spectre peut être modifié par réduction avec de l'hydrogène sur nickel Raney à température de chambre réduction spécifique pour l'insaturation éthylénique, et par réduction avec le borohydrure de sodium, spécifique pour les groupes carbonyles. Une analyse des spectres montre que l'absorption ultraviolette de solutions aqueuses d'alcool polyvinylique provient des chromophores polyène-carbonyles de la formule empirique: $-(CH=CH)_n-CO-$, où n peut varier de 0 à 3.

Zusammenfassung

Die Ultraviolettspektren wässriger Lösungen von Polyvinylalkohol wurden untersucht, um die darin vorhandenen chromophoren Gruppen zu identifizieren. Das Spektrum kann durch Reduktion mit Wasserstoff über Raneynickel bei Raumtemperatur modifiziert werden, was für ungesättigte Gruppen vom Äthylentypus spezifisch ist, oder durch Reduktion mit Natriumborhydrid, was für Carbonylgruppen spezifisch ist. Die Analyse der resultierenden Spektren führt zu dem Vorschlag, dass die UltraviolettabSORption wässriger Polyvinylalkohollösungen durch Polyen-carbonylchromophore verursacht wird, denen man folgende empirische Formel zuschreiben kann: $-(CH=CH)_n-C-$, wo n Werte von 0 bis 3 haben kann.

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