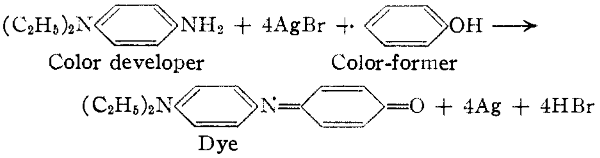
[CONTRIBUTION NO. 295 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Synthetic Color-forming Photographic Colloids[1]

BY DAVID M. MCQUEEN AND DAVID W. WOODWARD

The synthesis of a series of hydrophilic polymers capable of use as photographic colloids with silver halide to form colored photographic images is described. These polymers are formed by acetalization of polyvinyl alcohol both with aldehydes capable of dye-coupling with *p*-phenylenediamine color developers at the site of exposed silver halide and with aldehydes containing water-solubilizing groups. The detailed synthesis of a typical member of the series derived from polyvinyl alcohol, *m*-(1-acetoxy-2-naphthalenesulfonamido)-benzaldehyde and sodium benzaldehyde-*o*-sulfonate, is described together with solution and film properties of this and related polyvinyl acetals.

The technique of color-coupling photographic development originally proposed by Fischer[2] forms the basis for several processes of color photography. In these processes, a substituted *p*-phenylenediamine is used to develop an exposed silver halide image in the presence of selected types of coupling components. At the location of the exposed silver halide image, the color-forming reaction takes place. For example, with phenol as a typical color-former, dye formation occurs as



The metallic silver formed is incidental to this process and is removed from the film to leave a dye image. By suitable selection and positioning of three color-formers, three dye images can be combined in a film to achieve adequate color reproduction.

In multicolor photography, one of the most critical problems is the control of diffusion of the reaction components. Obviously, improper positioning of the color due to diffusion of the dye intermediates will result in falsification of color values. Several methods have been used to control the exact location of the dye, *e.g.*, the production of a single color at a time[3a] and the addition of high molecular weight or slightly soluble color-formers to silver halide–gelatin emulsions.[3b]

This paper describes the synthesis and properties of a class of polymers that has made possible a new solution to the problem of obtaining sharp three-color photographic images. These polymers combine the functions of photographic colloid and diffusion-resistant color-former within a single molecule.

General Plan of Synthesis.—The synthetic color-forming photographic colloids discussed here are based on polyvinyl alcohol, a water-soluble, high polymer with the recurring structural unit $-CH_2CHOH-$.[4] This polymer has been investigated in a limited way as a photographic colloid,[5] and several of its derivatives have been proposed for use in this connection.[6] In the present study, the polyvinyl alcohol was modified by incorporation of a minor proportion of acetal groups through reaction with selected monomeric aldehydes or acetals. The reacting aldehydes or acetals were selected to introduce both groups capable of color formation by the Fischer process of color-coupling development[2] and groups to adjust the colloid properties to those required in a photographic binding agent.[7]

The structures of typical color-formers are well-known and have been described in the journal and patent literature.[8] They include phenols, which yield minus red dyes, acylacetanilides, which form minus blue dyes, and pyrazolones, which give minus green dyes. In the synthesis of the color-forming photographic colloids, typical color-former structures have been introduced into polyvinyl alcohol through the process of acetalization. The selection and synthesis of color-forming aldehydes used in the acetalization have been made on the basis of the spectral characteristics of the resulting color-developed dye.

Besides forming a dye of the correct density and spectral characteristics, the color-forming polymers must have a critical balance of colloid properties to provide the proper environment for dispersion and growth of silver halide crystals in the preparation of photographic emulsions and to ensure adequate permeability to the chemicals used in film processing. In general, the introduction of color-forming acetal groups into polyvinyl alcohol decreases the permeability, solubility and swellability to aqueous solutions below the desired level. Therefore, a means of increasing the hydrophilic properties has been sought. This adjustment has been accomplished by acetalization of polyvinyl alcohol with an aldehyde containing a water-solubilizing group such as $-COONa$ or $-SO_3Na$. The type of control over hydrophilic properties that has been achieved is illustrated in Table I. In these experiments, polyvinyl alcohol has been acetalized with benzaldehyde and with sodium benzaldehyde-*o*-sulfonate. The benzaldehyde acetal groups confer a water-insolubilizing

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(1) This paper was presented before the XII International Congress of Pure and Applied Chemistry.

(2) R. Fischer and H. Siegrist, *Phot. Korr.*, **51**, 18 (1914); Fischer, German Patent 257,160, April 17, 1913; U. S. Patent 1,055,155, March 4, 1913.

(3) (a) J. S. Friedman, "History of Color Photography," The American Photographic Publishing Company, Boston, Mass., 1947, pp. 108–123; (b) pp. 127–132.

(4) W. O. Herrmann and W. Haehnel, *Ber.*, **60**, 1658 (1927).

(5) Lowe, U. S. Patents 2,286,215, June 16, 1942; and 2,311,059, February 16, 1943.

(6) Fordyce, U. S. Patent 2,211,323, August 13, 1940; and Lowe, U. S. Patent 2,253,078, August 19, 1941; see also reference 5.

(7) C. E. K. Mees, "The Theory of the Photographic Process," The Macmillan Company, New York, N. Y., 1945, p. 59, gives a general discussion of properties desirable in a photographic colloid.

(8) Mannes and Gowdowsky, U. S. Patent 2,108,602, February 15, 1938; see also reference 1. Seymour, U. S. Patent 1,969,479, August 7, 1934; K. and L. Schinzel, *Das Lichtbild*, 2, XII, 19 (1936); W. Schneider, *Die Chemie*, **57**, 113 (1944); A. G. Tull, *Brit. J. Phot.*, **85**, 627, 647 (1938).

effect, and the sodium benzaldehyde-*o*-sulfonate acetal groups provide a counteracting water-solubilizing influence.

TABLE I

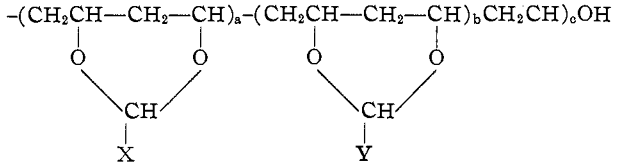
LONGITUDINAL SWELLING OF POLYVINYL ACETAL FILMS

Polyvinyl acetal prepared from		
Benzaldehyde[a]	Sodium benzaldehyde-*o*-sulfonate[a]	Relative swelling[b]
..	..	250
5	..	220
10	..	90
10	5	250
15	..	30
15	5	160
15	10	250
20	..	10
20	5	100
20	10	150
Gelatin		Dissolves

[a] The amounts given are parts by weight of aldehyde reacting with 100 parts polyvinyl alcohol. [b] Per cent. elongation of a strip of film 0.002 inch thick immersed in water at 30°. A strip $1^1/_2 \times {}^1/_4$ in. supporting a weight of 0.35 g. was used in these measurements. Elongations were all measured after 5 min. immersion, beyond which time no appreciable change occurred.

Further increase in the proportion of water-solubilizing acetal substituent yields polymers that are soluble in warm water. Such compositions form films which, like gelatin films, must be processed at temperatures below 25° to avoid excessive softening and film damage. The polymer compositions with the most desirable characteristics for photographic colloids are those containing sufficient solubilizing substitution to make them readily soluble in warm water containing 10–20% of ethanol. Such solutions are satisfactory for emulsion preparation and form films that can be processed safely at temperatures up to 40°. The proportion of water-solubilizing substituent introduced depends on the amount and structure of the color-forming acetal groups but, in general, is in the range of 1–10% of the total weight of the polymer.

The general structure of the synthetic color-forming photographic colloids therefore may be represented as

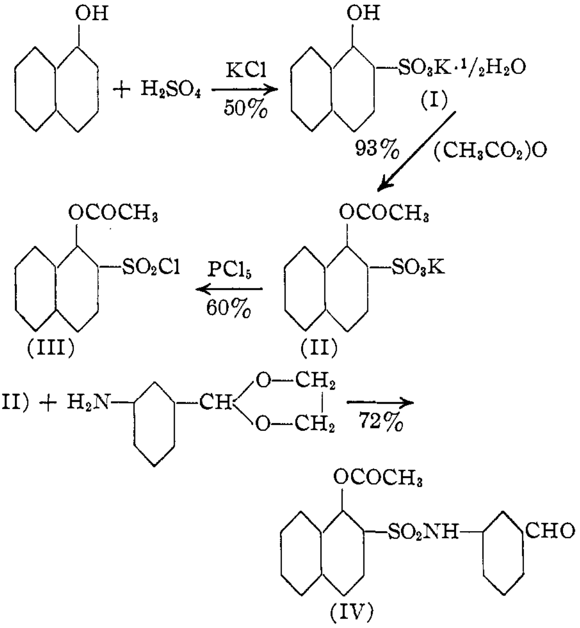


$$-(\mathrm{CH_2}\underset{\mathrm{O}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{O}}{\mathrm{CH}})_a-(\mathrm{CH_2}\underset{\mathrm{O}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{O}}{\mathrm{CH}})_b\mathrm{CH_2CH})_c\mathrm{OH}; \quad \mathrm{O{-}\underset{X}{CH}{-}O}, \quad \mathrm{O{-}\underset{Y}{CH}{-}O}$$

where X is a color-forming group and Y is a group enhancing hydrophilic character, and the numbers *a*, *b* and *c* are selected to contribute the desired degree of colloid properties and to provide the required color density after color-coupling development.

Synthesis of Color-Forming Polyvinyl Acetals.—A wide variety of color-forming polyvinyl acetals have been discussed in the patent literature,[9] and their description need not be repeated here. For purposes of illustration, the synthesis and properties of a typical member of this class of polymers are discussed. This polymer is a cyan (minus red) color-former derived from α-naphthol.

Synthesis of Monomeric Color-Forming Aldehyde.—The synthesis of *m*-(1-acetoxy-2-naphthalenesulfonamido)-benzaldehyde (IV) from α-naphthol is shown schematically.



Yields for preparations on a scale of 500–1000 g. are noted in the diagram. The only step in this synthesis calling for comment is the condensation of the sulfonyl chloride III with *m*-aminobenzaldehyde ethylene glycol acetal.[10] This condensation was carried out[11] at 0 to 5° in an aqueous dioxane (1:1 by wt.) medium containing potassium carbonate to neutralize the hydrogen chloride. The ethylene glycol acetal of the color-forming aldehyde can be isolated from the reaction mixture, but this compound does not crystallize in a form well suited for purification. The crude acetal is therefore stirred at room temperature for one hour with approximately equal weights of acetone and aqueous 10% hydrochloric aid. This results in conversion of the acetal to the free aldehyde but does not cleave the acetoxy group. Two recrystallizations from acetone yield a product, m.p. 171–173°. *Anal.* Calcd. for $C_{19}H_{15}O_5NS$: C, 61.8; H, 4.1; N, 3.8; S, 8.7. Found: C, 62.2; H, 4.1; N, 3.5; S, 8.4.

Synthesis of Hydrophilic Color-Forming Polyvinyl Acetal.—A mixture of 2000 ml. of dioxane, 25 g. of sodium benzaldehyde-*o*-sulfonate monohydrate,[12] 200 g. of *m*-(1-acetoxy-2-naphthalenesulfonamido)-benzaldehyde (IV), 500 g. of polyvinyl alcohol[13] and 25 ml. of 85% phosphoric acid was stirred at 70° for eight hours. The mixture was then filtered, the solid washed well with acetone, and dried. Five hundred grams of colorless polyvinyl acetal containing by weight approximately 10% of color-forming acetal groups and 3% solubilizing acetal groups was obtained.[14]

The rate of acetal formation in this system is a practically linear function of the time of reaction up to a substitution of about 30% by weight, as shown in Fig. 1, and any desired degree of substitution in this range can be obtained by proper

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[9] U. S. Patents: Dorough and McQueen, 2,310,943, February 16, 1943; Martin, 2,476,988, July 26, 1949; Martin 2,472,910, June 14, 1949; Woodward, 2,423,572, July 8, 1947; Jennings, Murray and White, 2,397,864, April 2, 1946.

[10] McQueen and Woodward, U. S. Patent 2,481,434, September 6, 1949.

[11] Woodward, U. S. Patent 2,423,572, July 8, 1947.

[12] This material was obtained by recrystallization from 95% ethanol of technical grade material obtained from the Organic Chemicals Department of E. I. du Pont de Nemours and Company.

[13] The material used was "Elvanol" 90–25 polyvinyl alcohol, a completely hydrolyzed product of medium viscosity, obtained from the Electrochemicals Department of E. I. du Pont de Nemours and Company.

[14] Analysis of the degree of substitution was carried out by comparing the ultraviolet absorption of solutions of the polymer with standard solutions of the monomeric acetals.

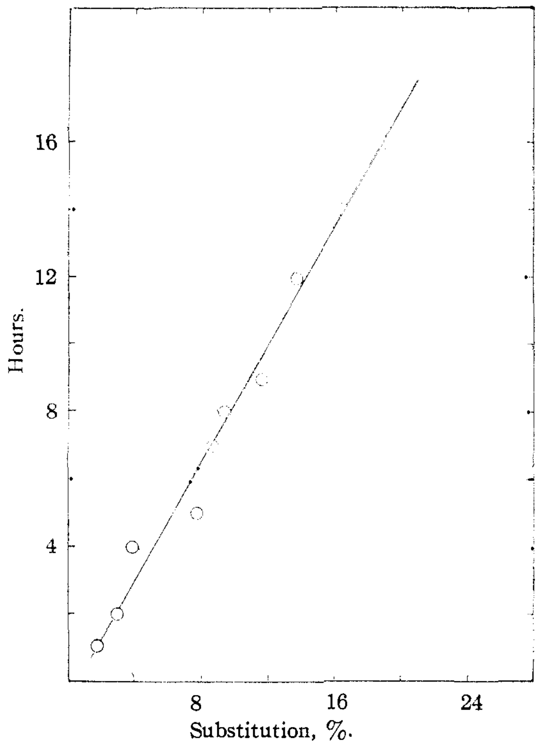
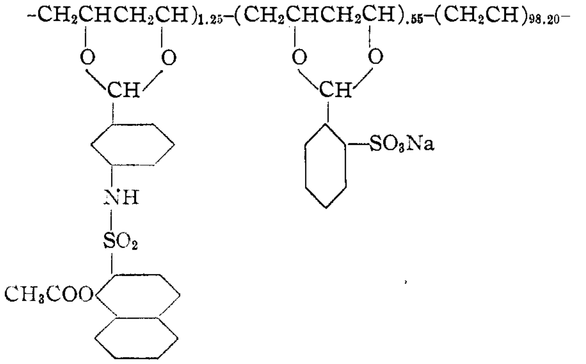


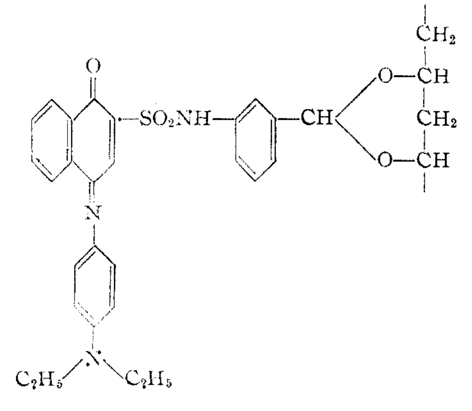
Fig. 1.—Acetalization of polyvinyl alcohol with IV in dioxane at 70°.

adjustment of the reaction time. The structure of the polyvinyl acetal prepared above may be represented as



(V)

This polymer may be used in the preparation of photographic emulsions which, after exposure and color development, yield cyan images. The cyan dye formed on color-coupling development with *p*-aminodiethylaniline contains the following structural units, the acetoxy group being hydrolyzed before or during color-coupling development.



The spectral absorption of a color-developed film of this polymer is given in Fig. 2. Films for color photography have been prepared by combination of cyan color-forming polymer emulsions with similar magenta and yellow systems.[15]

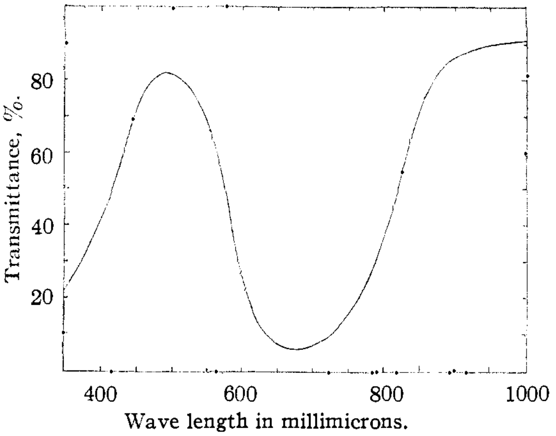


Fig. 2.—Spectral transmittance of film of polyvinyl acetal V color developed with *p*-aminodiethylaniline.

Properties of Hydrophilic Color-Forming Polyvinyl Acetals.—The color-forming polyvinyl acetals are colorless polymers that dissolve readily in warm water containing minor amounts of alcohols. Viscosity relationships of such solutions for the cyan color-forming polymer (V) are shown in Figs. 3, 4 and 5. In Fig. 3, the inflection point at *p*H 7.5 to 8.5 is caused by salt formation of the sulfonamide group. With other polyvinyl acetals, this sharp inflection point may be displaced or absent, depending on the chemical structure of the substituent group.

Solutions of these acetals are excellent dispersing agents for silver halide, as illustrated in Fig. 6.

The permeability of the hydrophilic polyvinyl acetals to typical photographic processing solutions depends to a large extent on the composition of the polymers. However, the ratio of color-forming aldehyde to solubilizing aldehyde may be adjusted to bring any specific polymer into the desired range. This is illustrated in Table II where R, the specific resistance to dialysis,[16] is compared for a series of cyan color-forming polymers of constant total acetal substitution of approximately 20% by weight.

TABLE II

EFFECT OF ACETAL SUBSTITUTION ON PERMEABILITY OF CYAN COLOR-FORMING POLYMER FILMS TO AMMONIUM BROMIDE

Ratio S/CF[a]	$R \times 10^3$[b]
0	320
0.20	245
.23	230
.41	225
.50	200

[a] Ratio of sodium benzaldehyde-*o*-sulfonate to *m*-(1-hydroxy-2-naphthalenesulfonamido)-benzaldehyde. [b] Decreasing values of *R* indicate increasing permeabilities.

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[15] A. B. Jennings, W. A. Stanton and J. P. Weiss, *Journal of the SMPTE*, **55**, 455 (1950).

[16] This quantity was determined by measuring the increase in conductance of distilled water separated from a salt solution of known concentration by a film of polyvinyl acetal. Comparison of the values with calibration curves and substitution in the equation $R = AM/TQ$ where A is the area of the film in square centimeters, M is the concentration of the salt solution in millimoles per liter, T is the thickness of the film in centimeters, and Q is the quantity of salt dialyzed in millimoles per minute, gives values for R, the specific resistance to dialysis. Since the area measured is on the dry film and not on the swollen wet film, the values are not absolute. However, they provide a good comparison of relative permeabilities. In making these determinations, films having a thickness in the range of 0.0025 to 0.004 cm. were used.

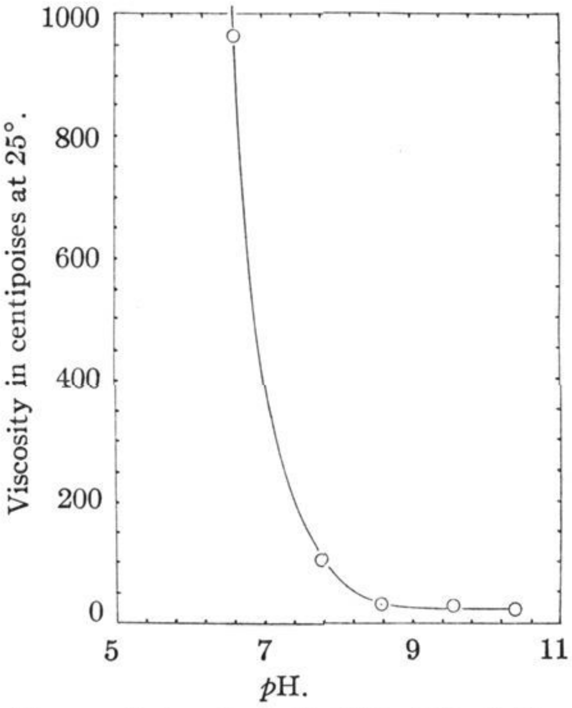

Fig. 3.—Change of viscosity with *p*H in 5% solution of polyvinyl acetal V (solvent 1:2, ethanol:water).

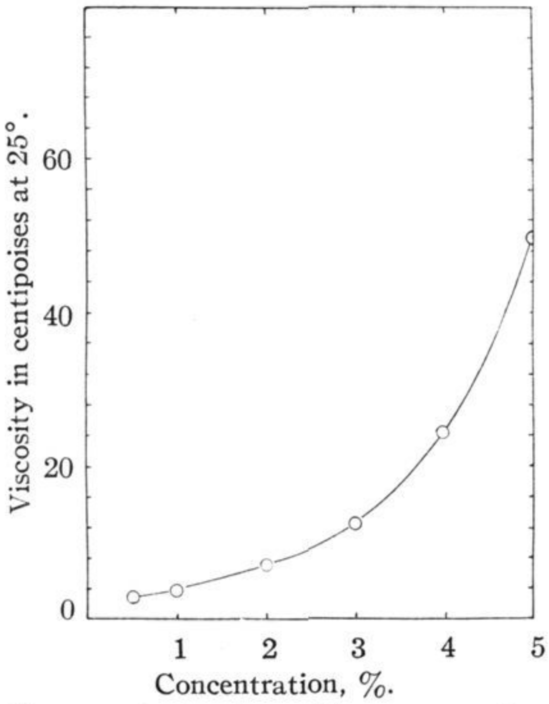

Fig. 4.—Change of viscosity with concentration of polyvinyl acetal V in ethanol:water (1:2).

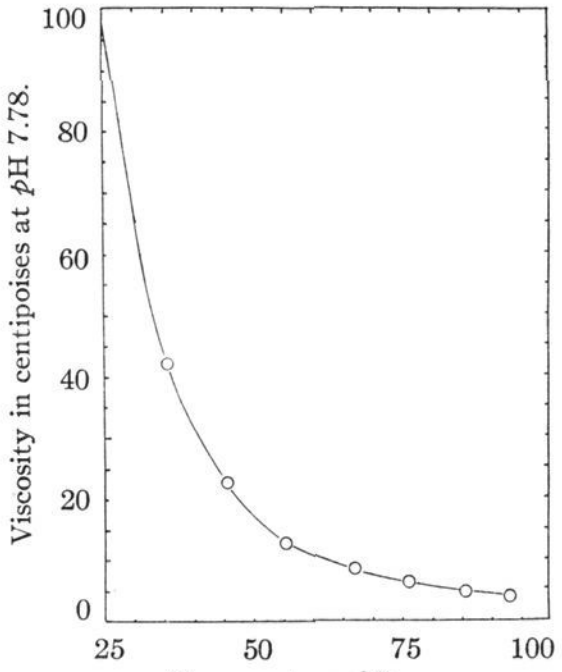

Fig. 5.—Effect of temperature on 5% solution of polyvinyl acetal V in ethanol:water (1:2).

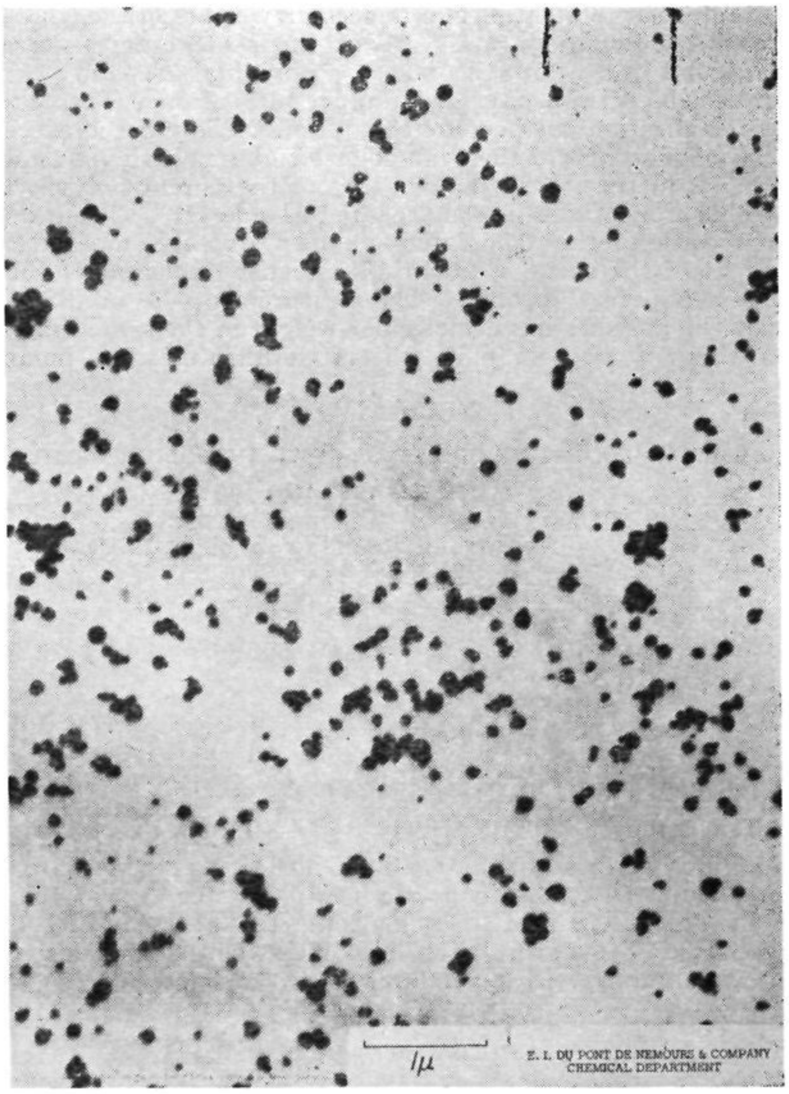

Fig. 6.—Silver iodobromide crystals prepared by simultaneous addition of silver nitrate solution (containing excess ammonia) and ammonium bromide–potassium iodide solution to 5% ethanol:water solution (1:4) of polyvinyl acetal V.

Permeability values obtained on unhardened gelatin films for comparison have not been satisfactorily reproducible but indicate, in general, that the polyvinyl acetal color-formers are fully as permeable as gelatin to typical salt solutions. In equilibrium swelling tests on film discs, it was determined that the ratio of diameter of swollen to dry film was 1.26 for gelatin and 1.44 for a cyan color-forming polyvinyl acetal (V) containing 18.5% color-forming acetal groups and 5% solubilizing acetal groups by weight. This is a further indication of a comparable degree of permeability.

TABLE III

MOLECULAR WEIGHT DETERMINATIONS OF CYAN COLOR-FORMING POLYVINYL ACETAL (V)

Polymer	Temp., °C.	M_n (osmotic)[a] Whole sample	*p*H	Corrected for gel fraction
Synthetic color-forming polyvinyl acetal (V)	25	46,000	8	37,000
Parent polyvinyl alcohol	25	48,000	8	38,000
		37,000	10.7	30,000
Gelatin	37	52,000	8	50,000
		26,200	10.7	25,000

[a] Measurements of osmotic pressure were carried out in a modified Wagner osmometer with gel cellophane membranes that had never been dried. The solutions were buffered with sodium dihydrogen phosphate to swamp ionic charge effects. In the case of polyvinyl alcohol and the color-forming polyvinyl acetal, it was necessary to utilize 25% ethanol and 25% *n*-propanol, respectively, to obtain the desired solubility. The gelatin determinations were carried out at 37° to avoid the possibility of association through gelation.

Molecular Weight.—The molecular weights of the color-forming polyvinyl acetals are of the same order as the molecular weight of the starting polyvinyl alcohol. No appreciable scission or cross-linking resulting from the process of acetalization has been detected, and the number average molecular weight of the cyan color-forming polyvinyl acetal (V) lies in the same range as that of the parent polyvinyl alcohol from which it was prepared (Table III). From its composition, the calculated number average molecular weight of the acetal is about 13% higher than that of the parent polyvinyl alcohol. The measurements also indicate that the polymer has a molecular weight in the same range as that of photographic gelatin. An interesting point brought out by these measurements is the relatively small effect of changing *p*H in the alkaline region on the polyvinyl alcohol as compared with gelatin.

TABLE IV

PHYSICAL PROPERTIES OF FILMS[a] OF CYAN COLOR-FORMING POLYVINYL ACETAL V

Physical property	Polyvinyl acetal V	Gelatin
Tensile strength (lb./sq. in.)[b]		
50% R. H.	9800	13,600
Wet	590	Dissolves
Elongation (%)		
50% R. H.	4.2	6
Wet	60	Dissolves
Flexibility[c] 50% R. H.	1723	190
Tear strength[d] 50% R. H.	9.1	3.0

[a] Films were approximately 0.005 inch thick. [b] Measured on "Tinius-Olson Electromatic Tensile Tester." [c] M.I.T. Fold Test; A.S.T.M. Designation: D643-43 Method B (A.S.T.M. Standards, part 4, p. 907, 1949). [d] Relative values obtained with a pendulum-type tear tester.

Film Properties.—Transparent, colorless films of the color-forming polyvinyl acetals can be cast from aqueous alcohol solutions. These films are strong and relatively flexible and can be handled without a support. A comparison of the physical properties of films of the cyan color-forming polymer (V) with those of gelatin is given in Table IV. Of particular significance is the appreciable strength of the polyvinyl acetal films when wet. This is related to their ability to withstand relatively severe handling in the wet state.

Acknowledgment.—We wish to acknowledge our indebtedness to many of our colleagues without whose creative assistance this work could not have been done. We are particularly indebted to Drs. J. O. Corner, E. L. Martin, M. S. Raasch, and C. Weaver. We also wish to thank Dr. J. B. Nichols and Miss Beverly Price for molecular weight characterizations of the polymer, and members of the Analytical Division of the Chemical Department for analytical determinations and measurements of film properties.

In addition, we wish to acknowledge the continued support of the Photo Products Department in this work as well as the excellent coöperation and assistance of many members of the Photo Products Technical Division.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, COLUMBIA UNIVERSITY AND THE FLORIDA STATE UNIVERSITY]

A Differential Potentiometric Method of Measuring Acid and Base Dissociation Constants[1a]

BY ERNEST GRUNWALD[1b]

A potentiometric method for acid and base dissociation constants and autoprotolysis constants is presented which does not require knowledge of electrode or liquid junction potentials. Acid and base dissociation constants are derived from the rate of change of *p*H with added strong reagent at the equivalence point in the titration of weak bases or weak acids under conditions where the uncertain potentials are constant. A mathematical analysis is given, and the calculation of dissociation constants by rapidly converging successive approximations is discussed. Simple apparatus and experimental procedures are described. The computation of accurate rates of change at the equivalence point from potentiometric data near the equivalence point is outlined. The method has been found practical for the measurement of dissociation constants greater than 10^{-7}. Using the simple apparatus described, dissociation constants have been accurate to 2–3%. Autoprotolysis constants accurate to about 10% have been obtained from the measurement of both acid and base dissociation constants in conjugate acid–base systems.

Thermodynamic acid dissociation constants have been measured by potentiometric methods using cells without liquid junctions,[2a] usually of the type H_2/HA, MA, MX/AgX–Ag, but accurate values of the standard electrode potentials which are required are not generally available, particularly for organic solvents; furthermore, work with the silver–silver halide or hydrogen electrode is difficult in some solvents.[3,4] By using suitable cells with liquid junctions, experimental difficulties may often be overcome,[3] but again either the electrode potentials and junction potentials must be known, or calibration against a standard resorted to.[2b]

A potentiometric method avoiding these limitations measures the rate of change of *p*H with added reagent at the equivalence point of an acid–base titration, under conditions where the uncertain potentials are constant. This derivative is a sensitive function of the dissociation constants of the species present at the equivalence point.[5]

While the measurement of a rate of change of *p*H removes the limitations of the classical potentiometric methods for dissociation constants,[2] it introduces new difficulties. Prominent among these are the solution of the relevant equations, the development of convenient experimental techniques, and the accurate measurement of the derivatives involved.

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(1) (a) Presented at the Meeting of the American Chemical Society in San Francisco, Calif., March, 1949; (b) Frank B. Jewett Fellow, 1948–1949.

(2) (a) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, Chapter 15; (b) *ibid.*, p. 316–325.

(3) (a) Buckley and Hartley, *Phil. Mag.*, [7] **8**, 320 (1929); (b) Goodhue and Hixon, THIS JOURNAL, **56**, 1329 (1934); **57**, 1688 (1935).

(4) Moore and Felsing, *ibid.*, **69**, 1076 (1947).

(5) Kilpi, *Z. physik. Chem.*, **A177**, 116, 427 (1936).