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## COMBINATION OF WOOL PROTEIN WITH WEAK ACIDS

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## ABSTRACT

Previous studies of the combination of wool with strong acids have been extended to include 13 weak acids. It is shown that, unlike strong acids, these substances combine with wool in the molecular (undissociated) as well as in the ionic (dissociated) form. The amounts combined as molecules may far exceed the amounts taken up as ions.

Estimates are given of the relative tendencies of these weak acids to combine with wool. They vary over a three-hundredfold range. The negligible effect of temperature on the equilibrium between wool and one of these acids, monochloroacetic, suggests that the combination with undissociated acids is akin to a competitive solvation and involves the displacement of combined water.

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## I. INTRODUCTION

Numerous studies have been made of the combination of wool with acids and bases [1, 2, 3, 4, 5, 6].<sup>2</sup> With the notable exception of some measurements by Speakman and Stott [1], practically all of these studies have been made with strong acids and bases which are totally dissociated into their constituent ions. Thus, little is known of the effect of the presence of undissociated acids on the equilibrium between wool and hydrogen ions, or of the relative affinities for wool of the anions of various weak acids. Such knowledge is of practical interest because wool is often exposed, in processing, to solutions which contain weak acids, such as acetic, formic, or glycolic.

It is the purpose of the present paper to show the extent to which wool combines with a number of weak acids, and to demonstrate that wool combines not only with the ions of these acids but with molecules of the undissociated acid as well. The very large extent of combination with wool of such weak acids as formic acid and monochloroacetic acid, in the undissociated form, acquires particular significance in view of the long-known profound influence of these substances on the dyeing, swelling, and the stress-strain characteristics of wool fibers [1]. Similar combination with undissociated acid by dissolved proteins has recently been reported [7].

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<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

## II. EXPERIMENTAL PROCEDURE

Details of the purification of the wool, of the determination of the acid combined, and of the pH have been described elsewhere [3, 4]. Except where otherwise noted, all the reagents used were of reagent grade, and were used without further purification, except for the removal of traces of strong acids present as impurities. Glycolic acid was treated with barium hydroxide to remove sulfuric acid. Hydrochloric acid was removed from solutions of dichloroacetic acid by silver oxide. The phenolic derivatives and nicotinic acid were recrystallized from hot water from one to four times. With one exception, all the experiments were made at 0° C.

## III. RESULTS AND DISCUSSION

The results obtained with most of the weak acids used are compared in figure 1 with those previously obtained with one strong acid, hydrochloric [3]. This graphic comparison brings out clearly the principal difference between the behavior of strong and weak acids with respect to wool. Over a wide range of low concentrations, many of the acids are combined by wool at a given pH to about the extent that it combines with hydrochloric acid. The presence of undissociated acid at these concentrations is without appreciable effect. At higher concentrations, however, the amounts of weak acids which are combined increase more sharply than the amounts combined of hydrochloric acid, and, unlike the latter, give no indication of approaching a saturation value at about 0.8 millimole per gram. Indeed, determinations have been made of amounts combined which are far beyond the upper limits of figure 1 (up to 4 millimoles/g).

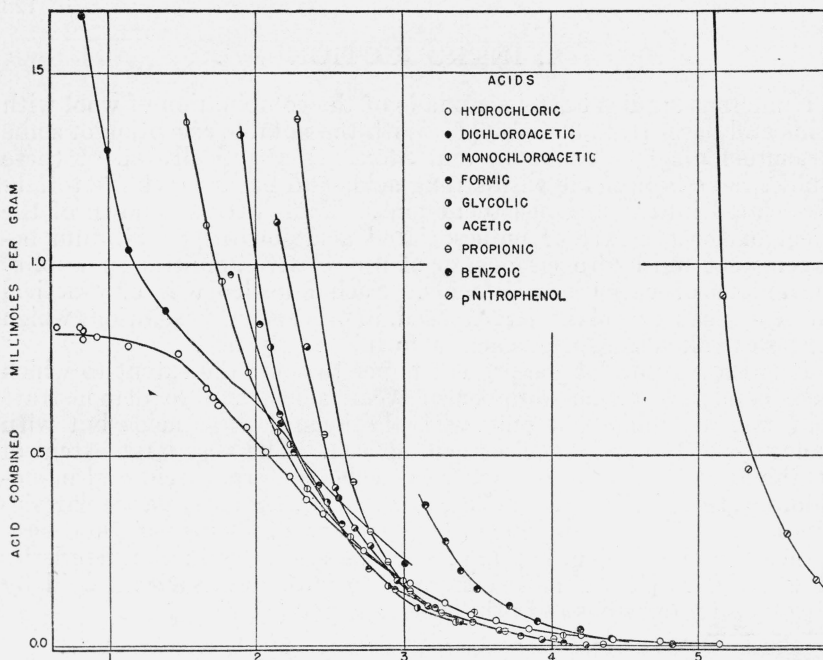


FIGURE 1.—Combination of purified wool with a number of weak acids at 0° C.  
The curve for hydrochloric acid is given for comparison.

It has been shown in earlier papers that different strong acids at the same concentration combine with wool to different extents [5, 6]. Most of the acids shown in figure 1 are organic acids of relatively low molecular weight, and would be expected, if totally dissociated, to give titration curves of wool similar to that obtained with hydrochloric acid [6]. If attention is confined to the lower portion of the curves obtained with acids of molecular weights below 80, it appears that this expectation is well founded. Marked departures from the curve for hydrochloric acid appear only at concentrations at which the amounts of undissociated acid become greater than about 0.01 M.

It may be shown that the increased uptake of weak acids which appears at high concentrations is a rough measure of the amounts of *undissociated acid* that have combined with the wool, possibly by solvating it in competition with water. This demonstration depends on the two experimental results described below: First, this increased uptake of any weak acid is approximately proportional to the concentration of undissociated acid. Second, the increased uptake of any one acid at a given pH value is not fixed, but varies with the concentration of the weak acid.<sup>3</sup>

The first of these generalizations has been tested with the data for all the carboxylic acids studied, with fairly satisfactory results. A representative set of calculations is reproduced in table 1. Monochloroacetic acid has been chosen as an example because the lower part of the curve of this acid coincides most closely with that for hydrochloric acid. Since this coincidence implies that the two acids, when dissociated, have closely similar affinities for wool, this acid should be most suitable for an application of the test. As the table shows, over more than a fiftyfold range of concentration of acid, the proportionality between the extra uptake and the concentration of acid varies by less than half of its mean value, a satisfactory result in view of the assumptions underlying the calculations. The factor of proportionality, which hereafter will be referred to as the partition coefficient, shows a pronounced tendency to fall as the amounts combined increase. This must be expected, whatever view of combination is postulated, since the amounts combined must approach an upper limit unless the fibers swell indefinitely and dissolve. The upper limit indicated by the results, however, must lie far above the highest experimental values shown in the tables. Thus, little purpose would be served by attempting to evaluate it by extrapolation,<sup>4</sup> since the accuracy of the titration data is lower at high concentrations of acid, where only a small fraction combines, and the effects of water absorption by the fibers are greatest [3, 4].<sup>5</sup>

The values of the quotient (column 7, table 1) at the highest dilution should come closest to expressing the inherent tendency of the acid to combine with or to solvate wool. However, it must be recognized that it is these values which are most subject to error. They

<sup>3</sup> The concentration of weak acid may be varied, while the pH is held constant, by adding a strong base in such proportion that the ratio of dissociated acid:undissociated acid remains unchanged.

<sup>4</sup> The upper limit of the amounts combined may be fixed either by a stoichiometric limit, that is, the replacement by acid of all the combined water, or by the development of a definite swelling pressure within an elastic structure due to the difference between the molecular volumes of each acid and water. A decision between these alternatives requires accurate estimates of the maximum amounts of combination of different acids having widely different molecular volumes.

<sup>5</sup> Efforts have been made to estimate the latter effect by comparing the results of the experiments with dry wool fibers with the results obtained with fibers containing 14 percent of moisture. These experiments indicate that the uptake of acid for the first three entries in table 1 may be as much as 10, 6, and 3 percent higher than the values given. The quotients in the last column are correspondingly affected with a resulting improvement in constancy.

TABLE 1.—*Combination of undissociated monochloroacetic acid with wool at 0° C*

pH	Acid combined <sup>1</sup>	HCl combined at same pH	Difference	Total acid	Undissociated acid <sup>2</sup>	Excess combination divided by concentration of undissociated acid
	<i>mmoles/g</i>	<i>mmoles/g</i>	<i>mmoles/g</i>	<i>mmoles/liter</i>	<i>mmoles/liter</i>	
1.36.....	2.08	0.79	1.29	0.971	0.937	1.4
1.52.....	1.39	.77	.62	.477	.455	1.4
1.66.....	1.12	.71	.41	.282	.265	1.5
1.76.....	.97	.66	.31	.184	.070	1.8
1.95.....	.73	.59	.14	.0874	.0769	1.8
2.15.....	.580	.504	.076	.0398	.0332	2.3
2.35.....	.431	.403	.028	.0172	.0132	2.1

<sup>1</sup> No corrections have been applied for the error in calculating the uptake of acid which is introduced by the absorption of water by the fibers. See footnote 6, page

<sup>2</sup> The values in this column are derived from the total acid present by utilizing Wright's value of the dissociation constant [8], and applying the law of mass-action. Since the proportion ionized is small, except in the more dilute solutions, little error is introduced by the neglect of activity coefficients.

depend on the estimation of very small differences between the ordinates of the curves for monochloroacetic acid and for hydrochloric acid, and are also affected most strongly by any failure of the assumption that the anions of these two acids have the same affinity for wool.

The second generalization results from experiments made with monochloroacetic acid over the same range of pH values but at higher concentrations of undissociated acid. This was accomplished by having a constant amount (0.2 *M*) of potassium monochloroacetate in all the solutions. The results of these experiments are shown in table 2. Here the data for hydrochloric acid which are subtracted are not the same as those used in table 1. Instead, values previously reported for the combination of hydrochloric acid in the presence of 0.2 *M* potassium chloride have been used. Again, the quotients entered in column 7 of table 2 are not constant, but show a trend. They agree fairly closely with the values of the quotients shown in the first table for similar concentrations of acid, but the spread is larger because higher concentrations of acid were used.<sup>6</sup> In keeping with the higher concentrations, very much larger

TABLE 2.—*Combination of undissociated monochloroacetic acid with wool, in the presence of 0.2 M potassium monochloroacetate at 0° C*

pH	Acid combined <sup>1</sup>	HCl combined at same pH	Difference	Total acid	Undissociated acid	Partition quotient
	<i>mmoles/g</i>	<i>mmoles/g</i>	<i>mmoles/g</i>	<i>mmoles/g</i>		
1.59.....	3.29	0.79	2.50	2.46	2.43	1.0
1.76.....	2.67	.78	1.89	1.73	1.71	1.1
1.93.....	2.31	.77	1.54	1.21	1.20	1.3
2.07.....	2.04	.75	1.29	0.885	0.876	1.5
2.23.....	1.66	.74	0.92	.594	.588	1.6
2.53.....	1.17	.70	.47	.299	.296	1.6
2.86.....	0.90	.62	.28	.143	.142	2.0
3.20.....	.72	.55	.17	.067	.067	2.5

<sup>1</sup> No corrections have been applied for the error in calculating the uptake of acid which is introduced by the absorption of water by the fibers. See footnote 6. The values in this column are calculated by subtracting the antilogarithm of the pH from the value in the preceding column.

<sup>6</sup> Corrections for the effects of water absorption by the fibers in this experiment would be higher than in the preceding experiment and would serve to reduce the spread.

amounts of acid are here combined, in the same range of pH which was covered in the experiment without potassium chloride. Thus the amounts of monochloroacetic acid taken up in excess of the amounts of hydrochloric acid taken up at the same pH values have been shown in two different kinds of experiments to be proportional to the amounts of undissociated acid. It thus appears very likely that the excess uptake of acid is in the undissociated form.

The experiments just described show clearly that in evaluating the relative tendency of the weak acids represented in figure 1 to combine with wool, little consideration should be given to the pH range at which combination occurs. Thus it appears from the figure that acetic acid is taken up at lower acidities than chloroacetic acid. This depends entirely upon the fact that acetic acid is much the weaker of the two acids, and does not signify, as it would have in the work with strong acids, that acetate has a higher affinity than monochloroacetate. Since the acid taken up is largely in the undissociated form, it is the concentration of acid rather than the hydrogen ion present, which is significant. At equal concentrations of these two acids, considerably more monochloroacetic acid is taken up than acetic acid. It seems reasonable to interpret this combination with *undissociated acids* as a solvation, which depends on the fact that the acids are hydroxylic compounds rather than on their nature as acids.

The inherent tendencies of the acids examined to combine with wool in their undissociated form have been calculated by the method shown in table 1. To avoid inconsistencies which might arise from trends in the quotients, the values corresponding to the same extent of combination, 0.2 to 0.3 millimole of undissociated acid per gram of wool, have been tabulated. The results are summarized in table 3. Approximate values for a few cyclic compounds not represented in figure 1 are also included. The range of the affinities of the undissociated acid for wool, as shown in the table, is approximately 300 to 1.

TABLE 3.—Relative affinities of undissociated acids for wool protein at 0° C.

Acid	Partition quotient
Propionic.....	0.3
Acetic.....	0.4
Glycolic.....	0.6
Formic.....	0.7
Nicotinic.....	* 1.5
Monochloroacetic.....	1.8
Dichloroacetic.....	2
Benzoic.....	11
<i>p</i> -Nitrophenol.....	20
2,4-Dinitrophenol.....	50
2,6-Dinitrophenol.....	60
2,6-Dichloro-4-nitrophenol.....	100
2,4,6-Trichlorophenol.....	100

\* The low value for nicotinic acid is probably due to the use of an incorrect value for the concentration of undissociated acid. It appears probable that a large proportion of the acid is in the zwitterionic form. Due to the high degree of ionization of this acid, the value given is an approximation.

Estimates are available of the heats of combination of a number of strong acids with wool [4, 6]. Values between 2,000 and 12,000 calories have been obtained, the higher values being characteristic of the acids of high affinity. An effort has been made to obtain similar



heat data for the combination of monochloroacetic acid in the undissociated form. This acid has again been selected, partly for the reasons already given and partly because Speakman and Stott [2] have determined by a calorimetric method the heat liberated in its combination with wool. In the present study an estimate of the heat of combination has been made by comparing the partition coefficient at two different temperatures, 0° and 25° C.

Experiments with monochloroacetic acid at 25° C yielded partition coefficients practically the same (within the experimental error) as those given in table 1. If it is assumed that a difference of as much as 10 percent in the partition coefficient would have been detected, it follows from the Van't Hoff equation that the heat absorbed in the combination of the undissociated acid by wool is at most only 300 or 400 calories per mole of acid [4]. This value is so close to zero that it supports the view that the combination with undissociated acid involves the replacement of another hydroxylic compound, presumably water, i. e., a process of selective solvation. The heat of hydration of wool and other proteins is large, but the replacement of 1 solvated molecule by another which is held only slightly more strongly, would probably involve only very small heat changes, such as are found here.<sup>7</sup>

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<sup>7</sup>The heats of combination with wool of monochloroacetic acid, given by Speakman and Stott, are averages of the heats of both the ionic and the nonionic reactions, and are therefore higher than those indicated here. It has already been pointed out [4] that the trends in the values given by these authors indicate a very low heat of reaction for amounts combined in excess of 0.8 millimole per gram.