

relative amounts of the components in the mixture. In the case of mixtures of alcohol and water, the Murphree efficiency appears to be substantially independent of the rate of distillation; with mixtures of benzene and toluene the increased splashing incident to increase in the rate of flow appears to cause a slight increase in the Murphree efficiency.

With mixtures of benzene and toluene the liquids containing about 60 to 70 per cent benzene show the maximum over-all efficiencies. When the percentage of benzene is very high or very low, the entrainment increases and the over-all efficiency decreases. With aqueous alcohol the entrainment is relatively high when the concentration of alcohol is low; increase of the alcohol content above about 30 per cent results in little further change in the amount of entrainment or in the over-all efficiency.

In the intelligent design of a distilling column for any specific purpose, due attention should be paid to the component factors that determine the over-all fractionating efficiencies of the plates and to the variation of these separate factors with

the composition of the liquid, the rate of flow of the vapor, and other conditions. For example, these results indicate that, in the design of an alcohol still, entrainment may be particularly serious on those plates carrying low concentrations of alcohol and that such plates should be widely spaced and designed to operate with low vapor velocities, whereas the upper plates of the column may be more closely spaced and operated at higher vapor velocities.

Attempts to measure the amount of entrainment in a column by blowing air or gas through water or oil on the plates and to apply the data thus obtained to the prediction of the performance of the column under actual operating conditions are probably of little value. The entrainment varies so widely with the nature and concentration of the liquid that significant results can be obtained only by measurements made under conditions that approach, as closely as possible, those under which the column is to operate.

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Effect of Salts on Detergent Action of Soap

F. H. RHODES AND C. S. WYNN
Cornell University, Ithaca, N. Y.

THE detergent power of a specific soap solution varies with the alkalinity (6, 7), and the addition of an alkaline builder at first increases and then decreases the detergent efficiency (4). With sodium hydroxide, sodium carbonate, and trisodium phosphate the maximum effectiveness is exhibited when the solution has a pH of about 10.73 at room temperature (4). The maximum detergent power obtained, at optimum alkalinity, with solutions of the same concentration of the same soap varies considerably with the nature of the added builder. These results indicate that the effect of the builder is not due solely to its action in altering the alkalinity of the solution but is to be attributed, in part at least, to the specific effects of the added anions or cations, or both. In this investigation an attempt was made to determine the specific effects of certain anions on the detergent power of soap at the optimum alkalinity.

Experimental Methods

The effectiveness of the added builder was measured as follows:

Samples of cotton cloth were soiled to a standard darkness by a standard soiling solution, and were then subjected to four successive washings with a washing solution of standard alkalinity and soap concentration and of known concentration of builder. The whiteness of the final sample was measured. The effect of the builder was expressed in terms of the percentage ratio of the increase in brightness in four washes with the soap solution containing the builder, to the increase in brightness in four washes with soap solution, without builder, of the same concentration and alkalinity.

In washing tests made with artificially soiled cloth at 60° C., the detergent action of a 0.25 per cent soap solution is at a maximum when the alkalinity of the solution is adjusted to a pH of about 9.66. The addition of sodium chloride, sulfate, or phosphate to soap solutions at the optimum pH at first increases and then decreases the detergent effect. The effectiveness of the added salt at the optimum concentration is approximately proportional to the valence of the anion of the added salt. Sodium borate and acetate do not enhance the detergent action of the soap.

The laboratory washing machine was similar to that described by Rhodes and Brainard (5). The soiling solution was prepared by grinding together 2 parts by weight of carbon black (Dar brand, Standard Carbon Company), 3 parts of Crisco, and 5 parts of medium-viscosity paraffin-base petroleum lubricating oil, and diluting 10 grams of the resulting paste with 2 liters of carbon tetrachloride. The cloth used was Utica cotton sheeting (68 to 70 thread count), freed from starch and filler by treatment with diastase solution, followed by thorough washing with soap solution, rinsing, drying, and ironing. The ironed cloth took the soil much more evenly than did unironed cloth. A strip of the cleaned cloth 14 cm. wide and 100 cm. long was passed three times through 200 cc. of the soiling solution in a shallow dish. After each pass the cloth was allowed to dry in the air. After the last pass the cloth was dried for an hour at 80° C. and was then aged for 11 hours at room temperature before washing. The prepared cloth was made into bags 10 cm. square, and the brightness was measured. Into each bag were placed 100 grams of 5-mm. glass beads, and two of the filled bags were washed simultaneously in the machine. The washing temperature was 60° C., the time for each wash was 7.5 minutes, the speed of the machine was 80 r. p. m., and the volume of washing solution was 500 cc. The washed bags were rinsed by dipping five times in each of the following solutions: (a) detergent solution of the same composition as that used in washing, (b) and (c) distilled water, (d) 0.05 N acetic acid, and (e) distilled water. The beads were removed, the bags were pressed flat between filter paper and dried at 80° C., and the brightness was measured. A reflectometer similar to that described by Rhodes and Brainard (5) was used to measure the brightness. Instead of using a photometer of the Lummer-Brodhun type for measuring the intensity of the reflected light, a photoelectric tube (General Electric No. PJ-22) was employed. The tube was connected

with a 45-volt B battery and a swinging coil galvanometer (Leeds & Northrup No. 2500F) with a sensitivity of 0.0001 microampere per mm. scale division at one meter. The lighting tube for the reflectometer was provided with a 50-candle-power incandescent bulb, backed by a chromium-plated reflector and carrying 4.70 ± 0.02 amperes from a storage battery circuit. The light was rendered parallel by an achromatic doublet lens. A water-cooled copper tube was wrapped around the end of the lighting tube to prevent overheating from the bulb.

This reflectometer was calibrated by comparison with a reflectometer provided with a photometer of the Lummer-Brodhun type. Samples of cloth ranging in brightness from about 75 to 25 per cent were measured on both instruments; from the results, a calibration curve was drawn that permitted the translation of the readings from the light-sensitive cell into terms of true brightness. The calibration was checked at frequent intervals.

The standard soap used in these experiments was a commercial white soap flake of the following analytical characteristics:

Moisture, %	1.5	Glycerol, %	0.40
Free alkali	0.00	Total alkali (as Na ₂ O), %	10.91
Free fatty acid	0.00	Titer of fatty acids, °C.	34.3
Sodium chloride, %	0.82		

Other chemical materials were of standard C. P. grade unless otherwise specified.

Measurement of pH of Soap Solutions

The alkalinities of the various detergent solutions used in these experiments were computed from the results of measurements of the electromotive force developed between a hydrogen electrode immersed in the solution and a standard 0.1 *N* calomel electrode.¹ The measurements were made by the general method described by McBain and Martin (2). The temperature of the washing solution containing the hydrogen electrode was 60° C. The solution was connected by a salt bridge of saturated potassium chloride (also at 60° C.) with a calomel electrode at room temperature. The mercury used in the calomel electrode was prepared by the electrolysis of a solution of purified mercuric perchlorate, following the procedure described by Newbery (3). The mercurous chloride was prepared by dissolving some of the pure metal in redistilled nitric acid, precipitating the chloride with purified and redistilled hydrochloric acid, and washing the precipitate thoroughly with distilled water. The hydrogen electrode consisted of a sheet of platinized platinum, supplied with purified hydrogen. The hydrogen was humidified by passage through water at 60° C. before being admitted to the electrode. The usual corrections were applied to correct for the deviations from standard atmospheric pressure, for the partial pressure of the water vapor in the hydrogen, and for the difference in temperature between the hydrogen electrode and the calomel electrode. With the apparatus used, a value of 0.7798 volt was obtained for the difference between the electromotive force of the calomel electrode and the hydrogen electrode immersed in 0.1 *N* sodium hydroxide at 90° C. This value agrees well with that of 0.7797 reported by McBain and Martin (2). Solutions prepared by mixing

¹ The measured difference in electromotive force was corrected for the deviation of the pressure of the hydrogen from the standard value of 760 mm. of mercury and for the partial pressure of the water vapor in the hydrogen. The correction was computed as follows:

$$\text{Correction (volts)} = 0.0591/2 \log 760/(B - P_w)$$

where *B* = barometric pressure, mm. Hg

P_w = vapor pressure of water at 60° C.

The value for the electromotive force of the calomel electrode at 25° C. was taken as 0.3376 volt. The temperature coefficient was 0.00079 volt per degree, so that the electromotive force at 60° C. was computed as $0.3376 - (60 - 25) \times 0.00079 = 0.3376 - 0.0277$ volt. The difference in potential between the hypothetical normal hydrogen electrode and the 0.1 *N* calomel electrode at 25° C. is 0.3376 volt at 25° C. and 0.3317 volt at 60° C. The change in this difference with temperature is 0.0059 volt. The corrected equation by which the pH was computed from the measured difference in potential was:

$$\text{pH} = \frac{\text{Corrected e. m. f.} - (0.3376 - 0.0277 + 0.0059)}{0.000198 (273 + 60)}$$

together equal volumes of Sorensen's standard borate buffer solution (1) and a 0.1 *N* solution of sodium hydroxide gave, for the value of the pH at 60° C., an average value (in five measurements) of 10.13, with an arithmetical mean deviation of 0.02. This compares with a published value (1) of 10.19.

The pH of a 0.25 per cent solution of the soap used in the washing experiment was 10.19 at 22° C. and 9.30 at 60° C. The value of the pH at the higher temperature is the average of five individual measurements, with a mean deviation of 0.03.

To a solution containing 0.25 per cent of the soap, different known amounts of a standardized solution of sodium hydroxide were added. The pH of each mixture at 60° C. was then determined. The results were as follows:

NaOH Equivalent Mg./l.	pH	NaOH Equivalent Mg./l.	pH
0.00	9.30	0.8	9.66
0.4	9.36	1.0	9.74
0.6	9.48	1.2	9.83

Results of Washing Tests

Four pairs of soiled samples were washed with a 0.25 per cent soap solution, according to the procedure described. In each case the two individual samples of soiled fabric that constituted a pair were washed together through four washes. The brightness of each sample of washed, rinsed, and dried cloth was measured. At least four measurements of the brightness of each sample were made; the individual measurements were made at different points on the two sides of the bag. The following values are the averages of the several individual results obtained with each sample; the individual measurements on a single sample agreed within a maximum variation of one per cent in brightness:

Pair No.	% Increase in Brightness Sample 1	% Increase in Brightness Sample 2
1	21.6	21.6
2	20.5	20.4
3	21.3	20.9
4	21.6	21.9
Average ^a	21.2 ± 0.5	

^a The indicated limit of error is the arithmetical mean of the observed variations from the average value.

Samples of soiled cloth were washed with 0.25 per cent solutions of the soap containing different amounts of free sodium hydroxide. In all cases two samples of the soiled fabric were washed together through four washes, rinsed, and dried; and measurements of brightness were made at four or more points on the surface of each bag. In a few cases duplicate washing experiments were also made. The measurements on two individual bags washed together through four washes agreed within a maximum deviation of 0.6 per cent in brightness and an average deviation of ± 0.3 per cent. The results obtained when two bags were washed separately through four washes showed practically the same consistency as did the results obtained when the two bags were washed together through four washes. The following results were obtained:

NaOH Equivalent Mg./l.	pH	Increase in Brightness %	NaOH Equivalent Mg./l.	pH	Increase in Brightness %
0.00	9.30	21.2	0.8	9.66	22.45
0.4	9.36	21.0	1.0	9.74	20.55
0.6	9.48	21.6	1.2	9.83	20.0

These results agree with those of Rhodes and Bascom (4): (1) The addition of sodium hydroxide to a soap solution at first increases and then decreases the detergent effect; (2) the optimum concentration of sodium hydroxide, with the particular soap used, is about 0.8 mg. equivalent per liter; and (3) the effect of the sodium hydroxide is not very pronounced. The present results indicate that the maximum washing effect is obtained when the pH of the soap solution

TABLE I. EFFECT OF SALTS ON WASHING EFFICIENCY

Salt Equivalent Mg./l.	pH	Increase in Brightness %	E ^a	pH	Increase in Brightness %	E ^a
NaCl Added						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.66	21.5	96	9.69	21.3	95
1	9.65	22.8	102	9.69	21.5	96
2	9.65	23.3	104	9.67	22.95	102
5	9.68	23.5	105	9.72	23.3	104
10	9.68	22.8	102	9.70	23.7	107
20	9.71	18.7	83	9.64	24.3	108
50	9.69	16.8	75	9.69	20.9	93
K₂HPO₄ Added						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.66	23.55	105	9.63	20.7	92
1	9.65	24.3	108	9.62	20.8	93
2	9.67	25.0	111	9.69	21.0	94
5	9.65	25.85	115	9.67	21.2	95
10	9.66	25.75	115	9.63	21.6	95
20	9.67	20.5	91	9.66	20.4	91
50	9.68	19.1	85	9.69	19.8	88
Na₂SO₄ Added						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.65	24.9	111	9.71	18.5	82
1	9.66	25.2	112	9.64	19.1	85
2	9.67	25.7	114.5	9.66	19.4	86
5	9.65	27.6	123	9.66	19.3	86
10	9.66	25.9	115.5	9.67	21.2	94
20	9.62	20.4	91	9.66	21.2	94
50	9.67	18.8	84	9.66	20.1	90
Na₂B₄O₇ Added						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.65	24.9	111	9.71	18.5	82
1	9.66	25.2	112	9.64	19.1	85
2	9.67	25.7	114.5	9.66	19.4	86
5	9.65	27.6	123	9.66	19.3	86
10	9.66	25.9	115.5	9.67	21.2	94
20	9.62	20.4	91	9.66	21.2	94
50	9.67	18.8	84	9.66	20.1	90

^a E = ratio of increase in brightness in four washes with the salt solution to the increase in brightness in four washes with a 0.25 per cent soap solution, adjusted to pH 9.66 at 60° C.

is 9.66 at 60° C.; Rhodes and Bascom found that a solution with a pH of 10.7 at room temperature showed the greatest efficiency.

To solutions containing 0.25 per cent of the soap were added known amounts of the following salts: disodium phosphate, dipotassium phosphate, sodium sulfate, sodium tetraborate, sodium chloride, and sodium acetate. To each mixed solution a dilute solution of sodium hydroxide was added until the adjusted pH of the final solution, at 60° C., was at the optimum value. With each solution, washing tests were made. In each case two samples of soiled fabric were washed together through four washes, and measurements were made as described. In some instances completely independent duplicate washing experiments were made. Since the results of such completely independent experiments agreed as closely as did the results obtained when the duplicate samples were washed together, the completely independent washing experiments were not made in every instance. The average deviation between the results of the duplicate experiments was usually not greater than ± 0.5 per cent; in the series of washings made with sodium sulfate the arithmetical average deviation was ± 1.0 per cent.

The addition of the simple inorganic salts of sodium (chloride, sulfate, and phosphate) causes first an increase and then a decrease in the detergent power of the soap solution. With all three of these salts the optimum concentration is about 5 milligram equivalents per liter. The effect of the added salt appears to be about proportional to the valence of the anion. Potassium phosphate in very low concentrations appears to decrease the effectiveness of the soap; larger concentrations decrease the detergent power. The optimum concentration of potassium phosphate is much higher than that of sodium phosphate; at this optimum

concentration the potassium salt is less effective than is the sodium salt at its optimum concentration.

Some of these observed facts are in agreement with the generally accepted theories of the structure and behavior of soap solutions; some can be explained only by hypotheses that have little or no independent substantiation. It is generally assumed that the detergent action of soap is due primarily to the adsorption of micellar aggregates of the anions of the soap or of un-ionized molecules of the acid soap on the particles of dirt. The addition of the simple inorganic salts of sodium in relatively small concentrations, by increasing the agglomeration of the ions into micellar aggregates, should increase the activity of the soap and enhance its detergent action. This effect may be ascribed primarily to the anions of the added salt; as is to be expected, it increases with increase in the valence of the anion. The action of larger concentrations in decreasing the detergent action may be due to the effect of the added sodium salt in depressing the ionization of the soap; it may also be due in part to the excessive agglomeration of the colloidal soap particles in very large micelles that are less effective in peptizing the dirt.

The results appear to indicate that the potassium cations have a specific effect in decreasing the detergent action of the soap. Conceivably the potassium ion may decrease the tendency toward the formation of active micelles; more probably, perhaps, the potassium ions may diminish the effective adsorption on the particles of soil. That the final decrease in the detergent power with increasing salt concentration appears at a higher concentration with potassium phosphate than with sodium phosphate suggests, but does not prove, that in both cases the decrease is due to the decrease in the solubility of the soap rather than to a specific effect of the added anion.

It is conceivable that the action of acetates and borates in decreasing the washing effect may be due to the adsorption of acetate and borate ions on the particles of dirt, with consequent decrease in the adsorption of the more effective anions of the soap. There is no independent proof of this hypothesis.

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