THE HYDROGEN-ION CONCENTRATION OF OINTMENT OF ROSE WATER.

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INTRODUCTION.

The Ointment of Rose Water in various modifications has been used in American pharmacy for more than a half century. The original Unna (1) formula contained no borax. It was observed by Vomacka (2) that borax facilitated the mixing of the fatty substances with the aqueous fluid. Many modifications of these earlier formulas have been suggested, but the original formula of Vomacka is essentially the official ointment in the present edition of the Pharmacopœia. The official Ointment of Rose Water has not been adequately discussed by any of the leading textbooks on pharmacy. Pharmaceutical authors are of the opinion that the presence of borax in the ointment is necessary to impart the desirable "whiteness." On the other hand, however, they point out that its presence makes the ointment incompatible with alkaloidal salts, mercurous chloride and other substances.

In 1930 Scoville (3) engaged in a preliminary study of the purpose of borax in this ointment. In his communication to THIS JOURNAL, Scoville pointed out that the problem needed further study. His reasons were twofold; *first*, the possibility of eliminating borax from the ointment would be of practical importance, *second*, the solution of the problem may elucidate our knowledge of pharmaceutical emulsions in general. With these purposes in mind this investigation was begun.

EXPERIMENTAL.

1. Surface Tension Measurements.—Various substitutes for borax were chosen, and their surface tensions measured by means of the Du Noüy tensiometer (4). The molar concentration of borax in Rose Water as employed in the ointment is 0.069.

The results of these measurements are given in Table I.

TABLE I.—SURFACE TENSION MEASUREMENTS 24° C.

No.	Compound.	Concentration.	Surface Tension Dynes per Cm.
1	$Na_2B_4O_7.10H_2O$	0.069 M.	63.7
2	$Na_2CO_3.H_2O$	0.069 M.	69.5
3	$NaHCO_3$	0.069 M.	71.3
4	$Na_4P_2O_7.10H_2O$	0.069 M.	62.7
5	NaOH	0.100 M.	67.7
6	NaOH	0.010 M.	70.7
7	Sodium ricinoleate	0.031 M.	42.7
8	Hexylresorcinol	Sat. aqueous sol.	38.0

2. Hydrogen-Ion Concentration Measurements.—The p_H of certain of the solutions which were employed in the preparation of Ointment of Rose Water was measured electrometrically. The hydrogen electrode Wilson (5) type was employed for all solutions with the exception of sodium bicarbonate. The p_H of this solution was calculated from the dissociation constants of carbonic acid.

The results of these measurements are given in Table II.

TABLE II.—HYDROGEN-ION CONCENTRATION MEASUREMENTS.

No.	Compound.	Concentration.	p_H.
1	$Na_2B_4O_7.10H_2O$	0.069 M.	9.17
2	$Na_2CO_3.H_2O$	0.069 M.	11.30
3	$NaHCO_3$	0.069 M.	8.37
4	$Na_4P_2O_7.10H_2O$	0.069 M.	9.92
5	NaOH	0.100 M.	12.76
6	NaOH	0.010 M.	11.71
7	Sodium ricinoleate	0.031 M.	7.70

3. *Preparation of the Ointment.*—Using these various solutions in place of borax, ointments were prepared according to the official process. Electrical stirring was employed and all of the conditions and manipulations involved in the manufacture were kept as uniform as possible.

4. *Evaluation of the Ointments Obtained.*—Various plasticity experiments were attempted to evaluate the consistency of the ointments. Not any of these was considered to be satisfactory and the simple manipulation test observing which ointments separated water was employed.

The ointments are graded in Table III according to their capacity to retain water under the influence of manipulation.

TABLE III.—CHARACTER OF OINTMENTS.

No.	Compound.	Retention of Water.	Color.	p .
1	$Na_2B_4O_7.10H_2O$	Excellent	White	8.9
2	$Na_2CO_3.H_2O$	Excellent	White	9.5
3	NaOH 0.1 M.	Excellent	White	8.8
4	Magnesium oleate	Excellent	White	7.6
5	$Na_4P_2O_7.10H_2O$	Excellent	White	8.3
6	Water	Poor	Cream	...
7	Hexylresorcinol	Poor	Cream	...
8	NaOH 0.01 M.	Poor	Cream	...
9	Sodium ricinoleate	Fair	Cream	...
10	NaCl	Poor	Cream	...
11	$NaHCO_3$	Poor	Cream	...

DISCUSSION OF RESULTS.

In addition to the ingredients mentioned in the foregoing paragraphs an attempt was made to prepare an ointment using all unsaponifiable (paraffin and petrolatum) fat-like substances. No satisfactory ointment could be prepared. However, upon the addition of a small amount of soap, emulsification did take place. In this connection it is interesting to relate that in 1895 Rouillion (6) recommended the addition of a saturated solution of soap in benzin to this ointment which was prepared without borax. This immediately raised the question as to whether or not the preparation of the ointment depended upon a surface tension reductant like soap or an alkaline substance of the nature of borax. Scoville used quinic acid, a surface tension reductant, in place of borax. His results were not satisfactory. To answer this question the present authors employed a practically neutral saturated solution of hexylresorcinol in water. This is a very powerful surface tension reductant as shown by Leonard and Frier (7). This substance produced a very unsatisfactory ointment.

From this experiment the authors concluded that an alkaline substance which produced a partial saponification of the fats present was necessary. Accordingly, various salts were employed which imparted an alkalinity to the aqueous fluid. All of these substances produced a satisfactory ointment with the exception of sodium bicarbonate and 0.01 molar sodium hydroxide solution. In the case of the former the alkalinity of p_H 8.37 is thought not to be adequate to produce sufficient saponification of the fats. With the latter substance, although the p_H is quite high the molar concentration of the salt is approximately one-seventh of that of sodium borate. The validity of this view is shown by the fact that by increasing the concentration of sodium hydroxide tenfold, a satisfactory product can be obtained.

Ointment of Rose Water is evidently an emulsion of the water-in-oil type. Newman (8) working in Bancroft's laboratory in 1914 observed that univalent salts of oleic acid emulsified benzene in water, whereas divalent salts of oleic acid produced water-in-oil emulsions. This work was extended by one of us (J. K.) with Gordon (9) in 1928. Hence it occurred to the authors to employ magnesium oleate in the preparation of the ointment. This compound used in the same concentration as borax yields an excellent ointment that retains water more efficiently than the ointment made with borax. It appears to be a typical water-in-oil emulsion. Besides it is practically neutral, whereas Table III indicates that the ointments made with alkaline substances retain a considerable degree of their alkalinity depending upon the proportion of the fatty substances saponified.

In the preparation of the ointment magnesium oleate is dissolved in the fatty substances and the product is prepared in the usual manner.

SUMMARY.

1. In the preparation of Ointment of Rose Water, the reduction of the surface tension of the aqueous fluid is not an essential criterion in the formation of the emulsion.

2. Salts producing a hydroxyl-ion concentration represented by p_H 9.17 or greater, as well as free alkalies in sufficient concentration, produce a satisfactory ointment.

3. Magnesium Oleate produces a neutral, stable, water-in-oil emulsion of Rose Water and owing to its compatibility with medicaments in general the authors recommend its use in the official Ointment of Rose Water.

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