

CIV.—*The Behaviour of Calcium and Magnesium Salts with Soap Solutions and the Determination of Hardness of Water.*

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MANY observers have noted the difference in behaviour of magnesium and calcium salts when titrating waters with soap solutions for the determination of "hardness," and the difficulty of obtaining a satisfactory end-point in the presence of magnesium salts has become well known.

The work described below was undertaken with the object of tracing the cause of this difference and determining more satisfactory conditions.

Buchner (*Chem. Zeit.*, 1892, **16**, 1854) states that temperature exerts a great influence on the appearance of the lather. The thick foam which remains five minutes after the precipitation of calcium and magnesium salts at 15° remains constant for hardly a minute at the higher temperatures reached in midsummer, and scarcely longer with a further addition of soap.

Teed (*J. Soc. Chem. Ind.*, 1889, **8**, 256) states that calcium salts require  $1\frac{1}{2}$  and magnesium salts  $1\frac{1}{2}$  times the equivalent of soap for the production of a permanent lather.

Winkler (*Zeitsch. anal. Chem.*, 1901, **40**, 82) states that magnesium salts require more soap than an equivalent amount of calcium salts, potassium oleate being the soap used.

Jackson (*Chem. News*, 1884, **49**, 149), using Castile soap solution, found that when the hardness due to calcium salts exceeded six degrees, no evidence could be obtained of magnesium salts unless present in amount exceeding 10 per cent. of the calcium salts. He suggested heating to 70° to obtain more accurate results.

The standard soap solutions used in the work here described were made from various soaps, and the results indicate that soaps made from the saturated fatty acids give more accurate results than those

derived from unsaturated acids. As, however, sodium oleate makes a convenient and stable solution, its behaviour was further investigated. The solubility of calcium and magnesium oleates and the nature of the precipitate obtained on titration seemed worth investigating.

Standard solutions of calcium and magnesium salts were titrated with aqueous-alcoholic solutions of sodium oleate, potassium palmitate, Castile soap, and potassium myristate. The soap solutions (with the exception of Castile soap) were prepared by dissolving the acid in alcohol, neutralising with sodium or potassium hydroxides, and diluting with water and alcohol, so that the finished solution contained 50 per cent. of alcohol. They were standardised, so that 100 c.c. water containing 10 milligrams of calcium carbonate required 11 c.c. of soap solution.

The molecular weights of the acids were determined by titration with alkali in alcoholic solution. The iodine absorption was determined by means of Hanus' solution.

The following results were obtained:

Myristic acid, M.W. 228; iodine absorption, 0.5 per cent.; m. p.  $53.3^{\circ}$ .

Palmitic acid, M.W. 257.7; iodine absorption, 0.8 per cent.; m. p.  $61.5-62^{\circ}$ .

Oleic acid, M.W. 283; iodine absorption, 87.4 per cent., corresponding with 97 per cent. of oleic acid; the refractive index was 1.4542 at  $40^{\circ}$ .

The Castile soap gave a clear neutral solution in alcohol. The fatty acids had a mean molecular weight of 280.9, and melted at  $23^{\circ}$ . They absorbed 46.1 per cent. of iodine, corresponding with 52 per cent. of unsaturated acids in terms of oleic acid. Refractive index 1.4493 at  $40^{\circ}$ . As will be seen, a mixture of potassium myristate and sodium oleate standard solutions in equal volumes gives the same results as the solution of Castile soap when used to titrate calcium and magnesium salts.

All the titrations were done on 100 c.c. of water containing calcium or magnesium salts, separately or together, equivalent to 10 milligrams of calcium carbonate.

The figures on p. 994 are the mean of a large number of closely agreeing titrations.

Titration with sodium oleate and magnesium salts were carried out at temperatures ranging from  $15^{\circ}$  to  $60^{\circ}$ , and the following results obtained. At temperatures up to  $30^{\circ}$ , 13 c.c. of sodium oleate were required, whilst above  $40^{\circ}$  only 8 c.c. were necessary. The change between these two temperatures seems somewhat sudden; at  $35^{\circ}$ , 11-12 c.c. were required. The difficulty of keeping the

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temperature constant while titrating and shaking, and of obtaining a sharp end-point, prevented a more accurate determination.

Soap solution used.	Equivalent (in milligrams of $\text{CaCO}_3$ ) of the salts contained in 100 c.c. of solution.		C.c. of soap solution required	
	$\text{CaCl}_2$ .	$\text{MgCl}_2$ .	at $15^\circ$ .	at $60^\circ$ .
Sodium oleate .....	10	—	11·0	12—12·5
Potassium palmitate .....	—	10	13·0	8·0
Potassium palmitate .....	10	—	11·0	10—11
Castile soap .....	—	10	11·0	9·0
Castile soap .....	10	—	11·0	12·0
Myristate and oleate .....	—	10	12·5	8·0
(equal volumes)	10	—	11·0	—
Potassium myristate .....	—	10	12·5	—
Potassium myristate .....	10	—	11·0	10·5—11·0
	—	10	11·0	10·5—11·0

The results in the table given above show the difference in behaviour of soaps made from saturated and unsaturated fatty acids when used for titrating calcium and magnesium salts.

With palmitate and myristate, the end-point, whilst sharp at the ordinary temperature, became unsatisfactory at  $60^\circ$ .

The lather obtained from sodium oleate and calcium chloride was more lasting at  $15^\circ$  than at  $60^\circ$ , whilst with magnesium chloride a white froth was formed early at  $60^\circ$ , which made the true lather difficult to distinguish.

With water and sodium oleate alone, a more profuse lather was obtained at the higher temperature.

The potassium palmitate solution was unsatisfactory, as except in the warmest weather a considerable precipitate formed even after keeping for twenty-four hours and filtering. The precipitate, on analysis, proved to be potassium hydrogen palmitate. Increasing the quantity of alcohol to 75 per cent. prevented this to some extent, but not sufficiently to make it stable.

Potassium myristate gave a clear solution which was quite as stable as that of sodium oleate, and when standardised with calcium chloride gave accurate results with magnesium salts and with mixtures of calcium and magnesium salts in all proportions.

When potassium palmitate was used for titrating magnesium salts, it was noted that after the addition of about half the soap, the magnesium palmitate appeared as a flocculent precipitate suspended in a clear liquid. As the titration was completed this precipitate was rapidly dispersed, and at the end the liquid was uniformly cloudy, and no sedimentation took place until after some minutes. The same kind of separation took place when potassium myristate was used, but it was not so marked. With sodium oleate no such separation was noticed.

This observation is of interest as showing possibly some analogy to the coagulation of colloids by salts of metals of different valency, the magnesium sulphate having a greater effect than the sodium sulphate finally present.

With waters containing both calcium and magnesium salts, accurate results could only be obtained with soaps made from saturated fatty acids. With sodium oleate the end-points were unsatisfactory. When the calcium salts present exceeded 70 per cent. of the total hardness, and the titration was performed rapidly, a lather was obtained when rather more than the equivalent of the calcium alone was added. On keeping, the titration could be continued, but not with much accuracy, and the total amount of soap used was less than required by theory. This was the case at all temperatures with mixtures varying from 10 per cent. of magnesium and 90 per cent. of calcium to 90 per cent. of magnesium and 10 per cent. of calcium.

The equivalent of sodium oleate used in these experiments agrees closely with the figures given by Teed (*loc. cit.*).

One hundred c.c. of sodium oleate solution contained  $\text{Na}_2\text{O}$  equivalent to 25 c.c. of  $N/10$ -hydrochloric acid, giving 0.760 sodium oleate in 100 c.c. of solution.

Ten milligrams of calcium carbonate (equivalent to 60.8 milligrams of sodium oleate) required 83.6 milligrams, or 1.37 times the equivalent of oleate.

An equivalent amount of magnesium salts required 98.8 milligrams of sodium oleate, or 1.62 times the equivalent.

It was noted, however, that at  $60^\circ$  the magnesium salts used up 60 milligrams only or practically the equivalent.

Some of the solutions titrated with sodium oleate were kept for some time. Those containing calcium salts remained translucent, with hardly any formation of precipitate, but on heating to  $60^\circ$  they became opaque, and particles separated. In the case of magnesium salts, an opaque mixture with considerable precipitate formed after a short time at  $15^\circ$ . On heating to  $60^\circ$ , the mixture did not clear, but the particles became suspended, and there was but little sediment. Attempts were made to separate this suspended matter by centrifugalising for fifteen to twenty minutes at 2,000 revolutions per minute. With calcium salts no separation occurred. With magnesium salts a fair separation was effected. Magnesium sulphate equivalent to 10 milligrams of calcium carbonate was used with 6 c.c. to 15 c.c. of sodium oleate solution in a total volume of 100 c.c. With 15 c.c. of oleate, but little separation occurred. In all cases the clearer supernatant liquid contained magnesium, and was alkaline to methyl-orange.

The precipitate from a number of experiments (using 10 c.c. of sodium oleate solution) was collected and dried in a vacuum over sulphuric acid, after pressing on a porous plate. Analysis showed it to be normal magnesium oleate with a small quantity of sodium salt. (Found,  $\text{MgO} = 6.46$ . Calc.,  $\text{MgO} = 6.83$  per cent.)

A few mixtures were placed in the centrifuge at  $60-80^\circ$ , but no separation occurred at this temperature.

In the case of titrations carried out with soaps obtained from saturated fatty acids, separation occurred with both calcium and magnesium salts on keeping.

From the behaviour of sodium oleate with calcium and magnesium salts, it appeared likely that the solubilities of the oleates had some influence on the results. They were determined at  $15^\circ$  and  $60^\circ$ , upward filtration being employed through a layer of filter paper and muslin over the end of a tube  $\frac{3}{8}$  in. in diameter.

The salts were prepared by mixing excess of solutions of the chlorides with sodium oleate. They were purified by washing and drying in a vacuum over sulphuric acid, redissolving in light petroleum (in which they are freely soluble), filtering, and evaporating. Both salts were in a porous, granular condition, and tended to become moist and sticky on exposure to air, particularly the magnesium salt, which softens to a pasty mass in water above  $40^\circ$ .

These salts are not quite pure, some water and light petroleum finally remaining to the extent of about 5 per cent.

On analysis, the magnesium salt gave  $\text{MgO} = 6.4$ , and oleic acid = 91.65 per cent., or 1:14.13 (theory, 1:14.10). The calcium salt contained  $\text{CaO} = 8.87$  (theory, 9.30), corresponding with 95.3 per cent. of calcium oleate.

The quantities dissolving in water are so small that it was only possible to estimate the calcium and magnesium oxides (weighed as pyrophosphate). About 150 grams of solution were taken for the estimation. At the higher temperature,  $60^\circ$ , it was found necessary to redissolve the calcium oxide obtained by ignition, and reprecipitate as oxalate, as an appreciable amount of soluble matter was obtained from the glass vessel. The solutions were slightly turbid even after filtration, and were faintly alkaline to phenolphthalein.

Calcium and magnesium palmitate were prepared by mixing excess of a solution of the chloride with a solution of potassium palmitate. The precipitate was thoroughly washed until, on digestion with water and filtering, the filtrate gave no reaction for chloride.

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The following figures were obtained, 100 grams of solution being used in each case:

Temp- erature.	Calcium oleate.	Magnesium oleate.	Calcium palmitate.	Magnesium palmitate.
15°	0·0041 CaO	0·0015 MgO	0·0030 CaO	0·0009 MgO
60	0·0023 CaO	0·0020 MgO to 0·0025	0·0032 CaO	0·0010 MgO

With both calcium and magnesium palmitate, temperature has no appreciable effect on the solubility, and neither solution gave a pink colour with phenolphthalein.

The solution of magnesium oleate in water at all temperatures gave a lather on shaking, like the false lather always obtained early in the titrations of magnesium salts.

That the separation of particles of magnesium oleate, previously mentioned, is the cause of more soap solution being required is shown by the following experiments. Magnesium oleate was added to 100 c.c. of water containing magnesium sulphate equivalent to 10 milligrams of calcium carbonate, and the mixture then titrated with sodium oleate solution:

MgSO <sub>4</sub> alone .....	13·0 c.c. sodium oleate required
MgSO <sub>4</sub> + 0·1 gram Mg oleate	15·5 c.c. „ „ „
MgSO <sub>4</sub> + 0·2 gram Mg oleate	17·0 c.c. „ „ „

At temperatures above 40°, the addition of magnesium oleate did not increase the amount of soap solution necessary to form a lather, and when the mixture was kept above this temperature for some time before titrating, the amount of soap solution then required to form a lather was slightly less than that required by the magnesium sulphate alone.

Similar experiments with calcium salts gave results in the reverse order, the addition of calcium oleate at 15° affecting the result but little:

CaCl <sub>2</sub> (=10 mg. CaCO <sub>3</sub> ) alone...	11 c.c. sodium oleate required
CaCl <sub>2</sub> + 0·2 gram Ca oleate .....	11·5—12 c.c. sodium oleate required

At 60° the results were more like those obtained with magnesium salts at 15°, thus:

CaCl <sub>2</sub> (=10 mg. CaCO <sub>3</sub> ) .....	12·0 c.c. sodium oleate required
CaCl <sub>2</sub> + 0·1 gram calcium oleate	15·5 c.c. „ „ „
CaCl <sub>2</sub> + 0·2 „ „ „	16·0—16·5 c.c. sodium oleate required

### Conclusions.

It is impossible to obtain accurate measurements of hardness in water containing magnesium salts with a soap solution prepared with sodium oleate standardised with calcium salts.

This seems to be due to the fact that magnesium oleate is less soluble than calcium oleate at  $15^{\circ}$ , and particles of magnesium oleate separate and carry down or adsorb some sodium oleate. With mixtures of calcium and magnesium salts sodium oleate is unsatisfactory, accurate determination being impossible. Heating to higher temperatures up to  $60^{\circ}$  is of no advantage.

Soaps prepared with the saturated fatty acids are more satisfactory. Potassium myristate makes a stable soap solution, and gives accurate results with calcium and magnesium salts occurring alone or together.

Potassium palmitate solution deposits an acid soap, and is therefore unsuitable for use in the concentration necessary for these titrations.

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