# XCVI.—*Sodium Hypochlorite.*

By Malcolm Percival Applebey.

Sodium hypochlorite in a solid form was first obtained by Muspratt and Shrapnell Smith, of the United Alkali Co., Ltd., in the course of investigations directed towards the preparation of very concentrated solutions (*J. Soc. Chem. Ind.*, 1898, **17**, 1096; 1899, **18**, 210; 1903, **22**, 591). Their preparations were obtained by cooling concentrated solutions, and had a composition corresponding approximately with a hexahydrate. The product melted in its water of crystallisation at 20°, and the fusion was unstable. It could be dehydrated slowly by means of a current of dry air under diminished pressure, and had then a melting point of 45°, but the results were deemed to be of no commercial value, and the investigations were accordingly discontinued.

It was suggested by Mr. Muspratt that a complete investigation of the hydration and solubility relationships might furnish information of both scientific and industrial value, and a preliminary survey of the field has accordingly been made. This has already yielded results of some importance, which are the subject of this communication. They are to be regarded as provisional, and will be followed at a later date by a systematic phase-rule treatment.

## *Preparation and Properties of Muspratt's Hydrate.*

The hypochlorite solutions were prepared by treating 35 per cent. sodium hydroxide solution cooled in ice-water with chlorine, removing the precipitated sodium chloride, adding sodium hydroxide equivalent to the sodium chloride separated, and repeating the treatment with chlorine until the solution was about 5*N* when tested with neutral sodium arsenite solution. On a few occasions, preparations were lost owing to spontaneous transformation to chlorate and chloride. Such transformation, when it sets in, takes place with extreme rapidity in concentrated solutions, and is accompanied by the evolution of considerable quantities of gas consisting of both chlorine and oxygen. The transformation to chlorate can, however, be prevented by observing the three conditions laid down by Muspratt and Shrapnell Smith, namely, (1) low temperature; (2) absence of iron or other heavy metals which act as catalysts; (3) presence of excess of free alkali. The solution, which has been freed from precipitated sodium chloride, is now cooled to about −10° in a freezing mixture and induced to crystallise, either by shaking or by impregnating with a crystal from a previous preparation. The hypochlorite then separates as a mass of very fine, hair-like crystals filling the whole liquid, whilst the temperature rises considerably. When the whole has again reached the temperature of the freezing mixture, the crystals are separated from the mother liquor by suction through a Büchner funnel without filter paper or asbestos, the form of the crystals being such as to make their retention easy. The crystals are pressed down to remove adhering mother liquor, and then appear to be colourless at the top, although the mass in the lower part of the funnel is green, owing to the presence of mother liquor, which cannot be entirely removed, being formed anew by deliquescence during filtration. The crystals liquefy at temperatures varying between 18° and 19°, according to their purity. The fusion is not quite transparent, but becomes so at a somewhat higher temperature. This behaviour, in conjunction with the subsequent separation of a lower hydrate on cooling, appears to show that the hydrate does not melt completely, but undergoes a transformation at about 19° to a lower hydrate, formed in very small quantity, and its saturated solution, which has almost the same composition as the original crystals.

Analysis of the crystals gave somewhat unsatisfactory results, since, owing to the low melting point and rapid deliquescence, it was difficult to secure a sample in a sufficiently dry state. After several trials, it was found best to filter off a small quantity in a Gooch crucible without asbestos, and to break up the crystals in the crucible with a spatula while the suction continued. All attempts to dry the crystals with filter paper failed, owing to the rapid oxidising action on the paper, which resulted in the development of heat, and after a time led actually to charring of the paper. For analysis, the substance was weighed out and dissolved in water, and aliquot parts of the solution were titrated against arsenite for active chlorine and against silver nitrate and thiocyanate for total chlorine after reduction of the hypochlorite with the correct amount of arsenite solution. The following analytical data refer to two specimens which gave for total chlorine quantities not greater than would be formed from the hypochlorite present, and were therefore free from chloride:

Sample I, prepared by twice recrystallising after fusion:

1·1147 gave active chlorine 0·4065 = 36·47.
$H_2O$ (by difference) 0·6899 = 62·07.

Sample II, prepared by synthesis from the pentahydrate:

0·5020 gave active chlorine 0·1807 = 35·99.

$H_2O$ (by difference) 0·3123 = 62·21.

$NaOCl,7H_2O$ requires active chlorine = 35·36. $H_2O$ = 62·88 per cent.

$NaOCl,6H_2O$ requires active chlorine = 38·85. $H_2O$ = 59·21 per cent.

From these data, it would appear that Muspratt's hydrate is nearer in composition to a heptahydrate than to a hexahydrate. At the same time, the agreement with the heptahydrate formula is by no means good, and it may be found on further investigation that more than one hydrate is present in the crystals prepared by Muspratt's method.

### *Sodium Hypochlorite Pentahydrate.*

When the cloudy liquid obtained by heating the heptahydrate to 20° is allowed to cool slowly to the ordinary temperature, large and well-formed crystals of a new hydrate are obtained. The crystals are greenish-yellow, and contain a considerable amount of mother liquor; when they are broken up in an agate mortar, a separation of liquid takes place, and the powdered substance must be freed from this liquid by filtration through a Gooch crucible.

When prepared in this way, the substance gave the following analytical results:

| | I. | II. | Calculated for $NaOCl,5H_2O$. |
|---|---|---|---|
| Weight of substance ........ | 0·3482 gram | 0·3786 gram | — |
| Active chlorine .............. | 0·1473 ,, | 0·1615 ,, | — |
| ,, ,, per cent. ... | 42·32 | 42·66 | 43·10 |
| Cl as chloride .............. | 0·0006 | nil | — |
| Water (by difference) ...... | 0·1929 gram | 0·2090 gram | — |
| ,, per cent. .............. | 55·40 | 55·20 | 54·75 |
| Loss on heating .............. | 63·51 | — | 64·47 |

The pentahydrate melts at 27°, and is thus a much more practicable substance than the heptahydrate. The fusion is in this case also somewhat cloudy, but the nature of the suspension cannot yet be definitely stated. Up to the present, a small amount of decomposition has always taken place during melting. The pentahydrate is very deliquescent, but the crystals are not unstable at the ordinary temperature if kept in a well-stoppered bottle; a specimen kept for more than a week in a corked test-tube in a well-lighted laboratory showed no measurable increase in chloride content, although some deliquescence had taken place.

The mother liquor from which the pentahydrate has separated may be made to give a further yield of pentahydrate by freezing out heptahydrate, heating the latter to 20°, and allowing to crystallise as before. By this procedure, there is no difficulty in converting at least 50 per cent. of the heptahydrate into the corresponding amount of pentahydrate.

SIR LEOLINE JENKINS LABORATORY,
JESUS COLLEGE,
OXFORD.

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