CCC.—*The Action of Sodium Hydroxide on Stannic Oxide Sol. Part II.*

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IN the preceding paper measurements of membrane equilibria and osmotic pressure of stannic oxide sols, containing various proportions of sodium hydroxide, have been recorded, and the results are now added of measurements of hydroxyl-ion concentration, freezing-point lowering, and conductivity of five sols in which the ratio $Na_2O : SnO_2$ varied from 2 : 1 to 1 : 4.

Determination of the Hydroxyl-ion Concentration.

To form an idea of the composition of the colloidal complex present in a sol, it is necessary to determine what fraction of the total amount of sodium hydroxide added to it exists in the free state. This can be done from a determination of its hydrogen-ion concentration. The first four sols, in which the ratio $Na_2O : SnO_2$ varied from 2 : 1 to 1 : 3, were prepared from a stock sol, containing 16·6 g. of SnO_2 per litre, by adding the requisite amount of pure sodium hydroxide; the fifth, in which the ratio was 1 : 4, was prepared from another stock sol, containing 34 g. of SnO_2 per litre. These solutions were stored as before for 4 days after preparation. The hydrogen-ion concentration was determined by the *E.M.F.* method, a normal calomel electrode being used as the half element. Saturated potassium chloride solution was used as a bridge to eliminate the junction potential. The hydrogen was purified by passage through a series of wash-bottles containing solutions of caustic potash, mercuric chloride, potassium permanganate, and lead acetate. The measurements were conducted in a thermostat maintained at 25°. Whenever a platinum electrode showed signs of poisoning, which occurred somewhat frequently, it was electrolysed in concentrated hydrochloric acid to remove the deposit of platinum, then washed carefully and replatinised. The hydrogen-ion concentration C_H was calculated from the *E.M.F.* data by means of the formula $-\log_{10} C_H = (E_0 + E_1 - 0{\cdot}283)/0{\cdot}0591$, where E_0 represents the observed *E.M.F.*, and E_1 the correction for the variation of barometric height. The concentration of the hydroxyl ions C_{OH} was then calculated from the equation $C_{OH} = K_w/C_H = 1{\cdot}1 \times 10^{-14}/C_H$.

Some of the results were checked by a colorimetric method with Tropæolin O : 0·8 c.c. of the indicator solution was added to 20 c.c. of the sol and of each of a number of solutions containing known quantities of sodium hydroxide, until a match was obtained in a colorimeter. The data for pure sodium hydroxide solutions given in Table I were used in plotting a graph, from which, the activity of hydroxyl ions in a sol being known, the concentration of free sodium hydroxide in it could be calculated : these values are recorded in the third column.

TABLE I.

E.M.F. method.

Conc. of NaOH, *N* ...	0·10	0·075	0·050	0·035	0·020	0·0100
Activity of OH′	0·090	0·067	0·046	0·032	0·019	0·0096

Conc. of total NaOH.	Activity of OH′.	Free NaOH.	$\frac{\text{Free NaOH}}{\text{Total NaOH}}$.	Conc. of $NaHSnO_3$.	Composition of colloid.
		$Na_2O : SnO_2 = 2 : 1.$			
0·1	0·076	0·084	0·84	0·0045	$Na_2O,3{\cdot}6SnO_2$
0·065	0·051	0·056	0·86	0·0029	$Na_2O,4{\cdot}4SnO_2$
0·033	0·027	0·029	0·88	—	—
0·0165	0·014	0·0145	0·88	—	—
		$Na_2O : SnO_2 = 1 : 1.$			
0·1	0·065	0·072	0·72	0·0074	$Na_2O,4{\cdot}1SnO_2$
0·065	0·046	0·050	0·77	0·0048	$Na_2O,5{\cdot}4SnO_2$
0·033	0·025	0·026	0·79	—	—
0·0165	0·013	0·0135	0·82	—	—
		$Na_2O : SnO_2 = 1 : 2.$			
0·1	0·046	0·050	0·50	0·014	$Na_2O,4{\cdot}8SnO_2$
0·0605	0·032	0·034	0·57	0·009	$Na_2O,5{\cdot}9SnO_2$
0·0305	0·017	0·018	0·59	—	—
0·0152	0·009	0·009	0·60	—	—
		$Na_2O : SnO_2 = 1 : 3.$			
0·067	0·026	0·028	0·42	0·012	$Na_2O,6{\cdot}5SnO_2$
0·043	0·019	0·020	0·47	0·0077	—
0·023	0·011	0·0113	0·50	—	—
		$Na_2O : SnO_2 = 1 : 4.$			
0·1	0·026	0·028	0·28	0·0164	$Na_2O,6{\cdot}6SnO_2$
0·0605	0·019	0·020	0·33	0·0099	$Na_2O,7{\cdot}3SnO_2$
0·032	0·011	0·0113	0·35	—	—

Colorimetric method.

$Na_2O : SnO_2 = 1 : 3.$		$Na_2O : SnO_2 = 1 : 4.$	
Conc. of total NaOH.	Free NaOH.	Conc. of total NaOH.	Free NaOH.
0·067	0·026	0·1	0·026
0·043	0·019	0·0605	0·018
0·023	0·010	0·032	0·011

It will be seen from the above data that the agreement between the concentrations of free sodium hydroxide determined by the two methods is fairly satisfactory. The results show that at higher ratios of $Na_2O : SnO_2$ the major portion of the alkali is free, whereas its concentration steadily diminishes as the ratio is decreased : for the ratio 2 : 1, 84% of the total alkali added remains uncombined, but at 1 : 4 this has fallen to 28%. The difference between the free and the total sodium hydroxide added gives the amount which has combined with stannic oxide. A part of it, however, goes to form the diffusible matter, which is probably a mixture of Na_2SnO_3, $NaHSnO_3$, and a small proportion of more highly stannated complexes. The total amount of diffusible stannic oxide at any given ratio of $Na_2O : SnO_2$ can be obtained from the results of the investigations on membrane equilibria. The acid H_2SnO_3 is very weak, and therefore its normal salts in dilute solution should be largely hydrolysed and exist mainly in the form of the acid salt $NaHSnO_3$. Hence, assuming that the whole of the diffusible matter consists of this salt, the figures so calculated will not be very far from the actual ones. These are given in col. 5 of the table. Now, knowing the total sodium hydroxide which has combined with the stannic oxide, and the fraction of it which has been used in forming $NaHSnO_3$, it is possible to calculate roughly the average compositions of the colloidal complexes. These are given in the last column of Table I, and it will be seen that for the ratio 2 : 1, on an average 3·6 g.-mols. of stannic oxide combine with 1 g.-mol. of sodium oxide. With increasing dilution the hydrolysis of the sol increases and the composition of the colloid also changes. For the same total alkali content, as the ratio $Na_2O : SnO_2$ decreases from 2 : 1 to 1 : 4, the number of g.-mols. of SnO_2 combined with 1 g.-mol. of Na_2O steadily increases. In the previous paper it has been shown that the osmotic pressure of the colloid is very small. The average molecular weight of the colloidal particles should therefore be very high. Hence the actual composition of the micelle is a multiple of the simple composition given above.

The Determination of the Lowering of Freezing Point.

The measurement of the depression of freezing-point of a sol gives a measure of the total number of molecules present in it. The concentrations of hydroxyl ion in the different sols have already been determined, and the amount of diffusible matter which each of them contains is roughly known. Assuming that the latter consists wholly of $NaHSnO_3$, it is of interest to compare the sum of the concentrations of free NaOH and $NaHSnO_3$ with the values derived from the freezing-point data.

The experiments were done in the ordinary Beckmann apparatus, and in Table II, Δt is the observed lowering of freezing point, $[NaHSnO_3]$ and [NaOH] represent the concentrations of the respective molecular species in a sol, and [BA], which stands for that concentration of a binary electrolyte of the type NaOH which would account completely for the observed value of Δt, is derived

TABLE II.

Pure sodium hydroxide.

Conc., *N*	0·20	0·10	0·05	0·02
Δt	0·681°	0·341°	0·173°	0·069°

Stannic oxide sol.

Conc. of total NaOH.	Δt.	[BA].	[NaOH].	[$NaHSnO_3$].	Degree of dissociation of colloid.
		$Na_2O : SnO_2 = 2 : 1$.			
0·1	0·316°	0·0925	0·084	0·0045	70%
0·065	0·208	0·0610	0·056	0·0029	69
0·033	0·108	0·0315	0·029	—	—
		$Na_2O : SnO_2 = 1 : 1$.			
0·1	0·296	0·0856	0·072	0·0074	60
0·065	0·198	0·0580	0·050	0·0048	63
0·033	0·100	0·0293	0·026	—	—
		$Na_2O : SnO_2 = 1 : 2$.			
0·1	0·246	0·072	0·050	0·014	44
0·0605	0·163	0·047	0·034	0·009	46
0·0305	0·088	0·0255	0·018	—	—
		$Na_2O : SnO_2 = 1 : 3$.			
0·067	0·150	0·044	0·028	0·012	30
0·043	0·106	0·031	0·020	0·0077	43
		$Na_2O : SnO_2 = 1 : 4$.			
0·1	0·162	0·047	0·028	0·0164	9
0·0605	0·116	0·034	0·020	0·010	26
0·032	0·064	0·019	0·0113	—	—

from a graph based on the data for pure sodium hydroxide solutions as given in Landolt and Börnstein's tables (4th edition), this choice being guided by the consideration that the major portion of the observed lowering of freezing point of a sol is produced by the free sodium hydroxide it contains. It will be noticed that the sum of [NaOH] and [$NaHSnO_3$] is slightly less than [BA], and in view of the results given in the preceding paper, which show that the osmotic pressure of the colloidal particles is very small and hence that their concentration must necessarily be very small, this difference is attributed to the presence of sodium ions resulting from the dissociation of the colloidal micelles which behave like huge multivalent anions. Knowing the total amount of sodium hydroxide combined with the micelles and the amount of free sodium ions resulting from their dissociation, it is possible to calculate the average degrees of dissociation. These are given in col. 6 of the above table. It must be emphasised that these values are intended only to give a rough idea, since the assumption involved in their calculation, *viz.*, that the whole of the diffusible stannic oxide goes to form $NaHSnO_3$, can only be approximately correct.

The following conclusions can be drawn from the above results. (i) The depression of freezing point of any one of the five sols is mainly due to the free sodium hydroxide it contains : even at the ratio 1 : 4 about two-thirds of it is due to this source. (ii) As the ratio $Na_2O : SnO_2$ diminishes, the depression of freezing point also diminishes, showing that an increasing proportion of sodium hydroxide is entering into combination with stannic oxide to form the colloidal complex. (iii) The degree of dissociation of the colloid diminishes rapidly as the proportion of stannic oxide in a sol is increased; thus, in the 2 : 1 sol the degree of dissociation is about 70%, whereas in the 1 : 4 sol it is only 9%.

Conductivity Measurements.

The conductivity measurements were undertaken with a view to obtain some information as to what fraction of the total conductivity is contributed by the colloidal micelles and the diffusible stannates. The sols were the same as those used in the previous experiments, and their conductivity was measured 4 days after their preparation. The measurements were carried out at 25° in a thermostat. The conductivity cell had a capacity of about 25 c.c. and was provided with a ground-glass stopper to protect its contents from atmospheric carbon dioxide. In the course of the experiments the cell constant was frequently checked. In Table III, N is the normality of the total sodium hydroxide contained in the sol, a represents the specific conductivity of the sol, b that of the free sodium hydroxide, $c = (a - b)$ that of the mixture consisting of sodium stannates and the colloidal micelles, $d = [BA]$ (see p. **2300**), e is the concentration of sodium hydroxide (determined by the *E.M.F.* method), and $f = (d - e)$ is a measure of the concentrations giving rise to the specific conductivity c.

In the above table the data for sodium hydroxide solution are used for plotting a graph from which, the concentration of free sodium hydroxide in a sol being known, its specific conductivity can be calculated. The results show that the major portion of the conductivity of a sol is due to its free sodium hydroxide : at the highest ratio of $Na_2O : SnO_2$, 90% of the total conductivity is due to this and the remaining 10% to the stannates and colloidal micelles. The conductivity diminishes as the proportion of stannic oxide is increased, evidently owing to the diminution of free alkali, as shown by the *E.M.F.* data.

It will be noticed that c/f increases as the ratio $Na_2O : SnO_2$ is raised from 1 : 4 to 2 : 1. This is probably to be attributed to an increase in the migration velocity of the colloidal particles with an increase in their electrical charge due to the further adsorption of

TABLE III.

Sodium hydroxide solution.

Conc. of NaOH	0·100	0·075	0·050	0·035	0·020	0·010
Spec. cond.	0·0214	0·0162	0·0110	0·0077	0·0045	0·0028

Stannic oxide sols.

N.	$a \times 10^4$.	$b \times 10^4$.	$c \times 10^4$.	$d \times 10^3$.	$e \times 10^3$.	$f \times 10^3$.	100*c*/*f*.
			$Na_2O : SnO_2 = 2 : 1$.				
0·1	199	181	18	92·5	84	8·5	21·1
0·065	134	124	10	61·0	56	5·0	20·0
0·033	70·0	64·5	5·5	31·5	29	2·5	22·0
			$Na_2O : SnO_2 = 1 : 1$.				
0·1	176	156	20	85·6	72	13·6	14·7
0·065	120	110	10	58·0	50	8·0	12·5
0·033	62·4	58	4·4	29·3	26	3·3	13·3
			$Na_2O : SnO_2 = 1 : 2$.				
0·1	128	110	18	72·0	50	22	8·2
0·0605	84·1	75·0	9·1	47·0	34	13	7·0
0·0305	44·5	40·0	4·5	25·5	18	7·5	6·0
			$Na_2O : SnO_2 = 1 : 3$.				
0·067	74·0	62	12	44	28	16	7·5
0·043	51·2	45	6·2	31	20	11	5·6
0·023	28·4	26	2·4	—	11·3	—	—
			$Na_2O : SnO_2 = 1 : 4$.				
0·1	75·2	62	13·2	47	28	19	7·0
0·0605	51·9	45	6·9	34	20	14	5·0
0·032	30·3	26	4·3	19	11·3	7·7	5·6

hydroxyl ions. In Table II it has been shown that the degree of dissociation of the colloidal particles increases as the ratio $Na_2O : SnO_2$ increases; now each of these particles must possess a certain amount of electrical charge for its stability, and hence an increase in the degree of dissociation means an increase in the number of units of charge carried by each of them.

The measurements of conductivity of the sols were carried to much higher dilutions than those given in the above table, and in Fig. 1 the equivalent conductivity μ is plotted against $\log_{10} C$. The points for the ratios 1 : 3 and 1 : 4 lie in straight lines and those for higher ratios in curved lines. The extrapolation of the curves to give μ_∞ is only possible for the ratios 2 : 1 and 1 : 1, which give about 225 and 199.

Summary.

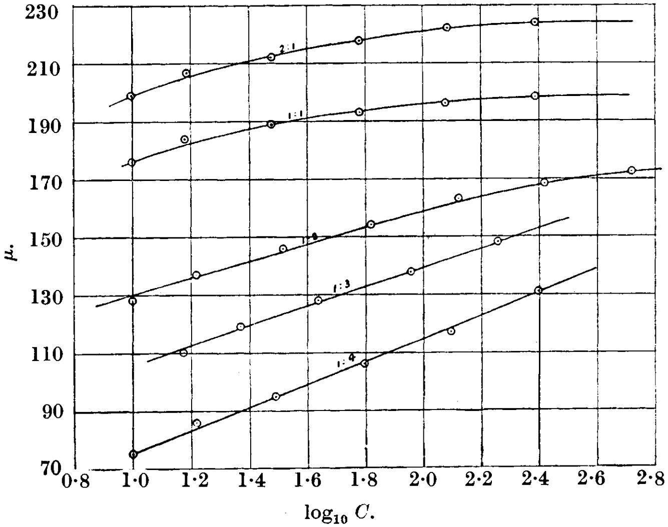
1. The hydroxyl-ion concentration, depression of freezing point, and conductivity of five stannic oxide sols, in which the ratio $Na_2O : SnO_2$ varied from 2 : 1 to 1 : 4, have been measured.

2. The results of the determination of hydroxyl-ion concentration

lead to the conclusion that a considerable portion of the alkali added to a sol remains uncombined, but this diminishes as the proportion of stannic oxide increases. The average composition of the micelle has been roughly indicated.

3. The depression of freezing point of a sol is mainly due to the free alkali it contains. As the ratio $Na_2O : SnO_2$ diminishes, the value of Δt also diminishes. Combining the results of measurements of membrane equilibria, hydroxyl-ion concentration, and freezing-point lowering, an attempt has been made to calculate the degree of dissociation of the colloid. The dissociation increases with the ratio $Na_2O : SnO_2$.

FIG. 1.



4. The conductivity measurements show that the fraction of the total conductivity contributed by the colloidal particles and the stannates is very small. The micellar conductivity seems to increase with an increase in the ratio $Na_2O : SnO_2$.

My best thanks are due to Prof. F. G. Donnan, C.B.E., F.R.S., for his advice and encouragement.

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