Physico-chemical Studies on the Complex of Metals. I. Thermometric Studies on the Composition of Manganese Arsenate Complexes

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The composition of so-called manganese arsenate has been studied by the thermometric method involving the thermometric titrations between $MnCl_2 \cdot 4H_2O$ and disodium hydrogen arsenate in aqueous and alcoholic medium. The direct titration curves suggest the formation of $MnHAsO_4$, $MnNa_2(HAsO_4)_2$, and in reverse titrations the formation of $MnHAsO_4$ (ratio of Mn : As is 1 : 1) is indicated. The results of this investigation support the formation of $MnHAsO_4$.

Referance in literature about the elaborate study of the composition of manganese arsenate is scarcely available. Coloriano[1] prepared chestnut brown needles of manganese ortho-arsenate $Mn_3(AsO_4)_2 \cdot H_2O$ by heating sodium ortho-arsenate with an excess of manganese sulfate in a sealed tube at 175°C. Scheele[2] treated manganese salt with alkali-hydro-arsenate and obtained a white gelatinous precipitate, which according to J. H. Debray became crystals when digested for a long time in the mother liquor. Rose[3] said that the precipitate was a mixture of sodium-manganese-ortho-arsenate and manganese-hydro-arsenate $MnHAsO_4 \cdot H_2O$. The monohydrate of the hydro-arsenate, $MnHAsO_4 \cdot H_2O$ was obtained from solutions containing MnO and As_2O_5 in the ratio of 3 : 1 by precipitation with alcoholic solution of arseneous acid. The salt is stable in water at 25°C. Schiefer[4] reported that $Mn(H_2AsO_4)_2$ was obtained from a solution of $MnCO_3$ in theoretical quantity of arseneous acid. Amadori[5] found that $Mn(H_2AsO_4)_2 \cdot H_2O$ was deposited from a solution containing excess of arseneous acid. The composition of manganese arsenate should correspond to the formula $MnHAsO_4$ when manganese chloride is added to disodium hydrogen arsenate. Apart from the above study a number of variable and more complex formula have been reported in literature, e.g., $Mn(H_2AsO_4)_2H_3AsO_4$, $Mn_2As_2O_7$ (Otto), $Mn_5 \cdot As_4O_7 \cdot 2H_2O$ or $Mn_5H_2(AsO_4)_4 \cdot H_2O$ (Coloriano), $MnAsO_4 \cdot H_2O$ (Christensen[6]).

Takahasi and Sasaki[7] during the course of phase rule study of MnO-As_2O_5-H_2O system and heat of formation of $MnHAsO_4$ showed the existence of $Mn_3(AsO_4)_2 \cdot H_2O$, $MnHAsO_4 \cdot H_2O$, $Mn(H_2AsO_4)_2$ and $Mn(H_2AsO_4) \cdot 2H_3AsO_4$. Reference in literature about the study of these complexes by applying other physico-chemical methods i. e., conductometric, potentiometric and thermometric, etc. is scarcely available. In view of the difficulties associated with the analytical work and in the absence of any decisive views on the composition of manganese-arsenate complexes, it was considered worthwhile to undertake the study of these complexes by physico-chemical methods.

With the results of potentiometric, conductometric and amperometric measurements in progress, the results of thermometric titrations are incorporated and discussed in this paper.

Experimental

A.R.E.D.H reagents were used. Solutions of $MnCl_2 \cdot 4H_2O$ and Na_2HAsO_4 were prepared by weighing and the strength of $MnCl_2 \cdot 4H_2O$ was further cheked by estimating manganese as manganese pyrophosphate, Na_2HAsO_4 solution was standardized against sodium thiosulfate of known strength.

The arrangements for the thermometric titrations were the same described by Haldar[9]. Using different concentrations of the two salts in solution, the direct and reverse titrations (i. e., when manganese chloride solution from micro-burette was added to Na_2HAsO_4 solution in the thermos flask and vice versa) were done. Titrations were also carried out in presence of alcohol upto the total concentration of 20% by volume. The conditions for the experiments for the various titrations were maintained the same. The total rise in temperature was then plotted against the titre in cc.

Discussion

The possible reaction between manganese chloride and sodium hydrogen arsenate in reverse titrations i. e., when disodium hydrogen

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TABLE I. SUMMARY OF THERMOMETRIC TITRATIONS-OBSERVATIONS

Curve No.	$MnCl_2$ Concn.	Na_2HAsO_3 Concn.	Points showing breaks			Formula supported	Ratio
			Medium	Calcd.	Obs.		
Direct titrations (Fig. 1)							
1	M/5	M/20	Aq.	5.0	5.0	$MnHAsO_4$	1 : 1
1	M/5	20 cc.		2.5	2.5	$MnNa_2(HAsO_4)_2$	(1 : 2)
2	M/5	18 cc.	Alc. 10%	4.5	4.5	$MnHAsO_4$	1 : 1
2	M/5	18 cc.	Alc. 10%	2.25	2.2	$MnNa_2(HAsO_4)_2$	1 : 2
3	M/5	16 cc.	Alc. 20%	4.0	4.0	$MnHAsO_4$	1 : 1
3	M/5	16 cc.	Alc. 20%	2.0	2.0	$MnNa_2(HAsO_4)_2$	1 : 2
4	M/5	M/40	Aq.	2.5	2.6	$MnHAsO_4$	1 : 1
4	M/5	20 cc.	Aq.	1.25	1.1	$MnNa_2(HAsO_4)_2$	1 : 2
5	M/5	18 cc.	Alc. 10%	2.25	2.1	$MnHAsO_4$	1 : 1
5	M/5	18 cc.	Alc. 10%	1.125	1.1	$MnNa_2(HAsO_4)_2$	1 : 2
6	M/5	16 cc.	Alc. 20%	2.0	1.0	$MnHAsO_4$	1 : 1
6	M/5	16 cc.	Alc. 20%	1.0	0.95	$MnNa_2(HAsO_4)_2$	1 : 2
Reverse titrations (Fig. 2)							
1	M/40 20 cc.	M/5	Aq.	2.5	2.3	$MnHAsO_4$	1 : 1
2	18 cc.	M/5	Alc. 10%	2.25	2.2	$MnHAsO_4$	1 : 1
3	16 cc.	M/5	Alc. 20%	2.0	2.0	$MnHAsO_4$	1 : 1
4	M/20 20 cc.	M/5	Aq.	5.0	5.2	$MnHAsO_4$	1 : 1
5	18 cc.	M/5	Alc. 10%	4.5	4.4	$MnHAsO_4$	1 : 1
6	16 cc.	M/5	Alc. 20%	4.0	4.0	$MnHAsO_4$	1 : 1

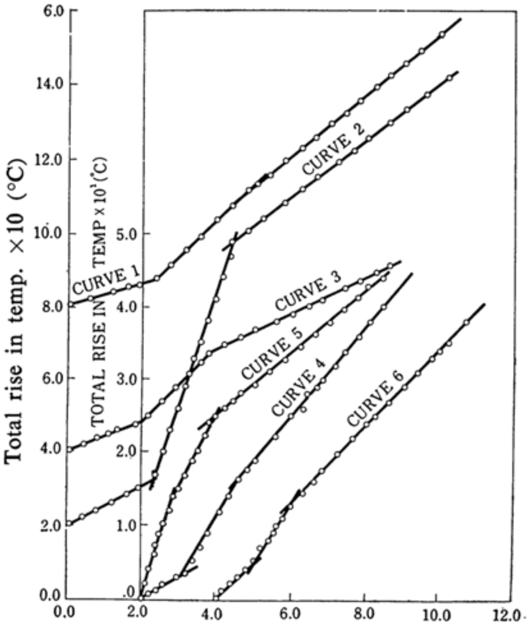

Fig. 1. Direct-thermometric-titrations. Curves 1, 2 and 3; M/5 $MnCl_2$ and M/20 Na_2HAsO_4. Curves 4, 5 and 6; M/5 $MnCl_2$ and M/40 Na_2HAsO_4.

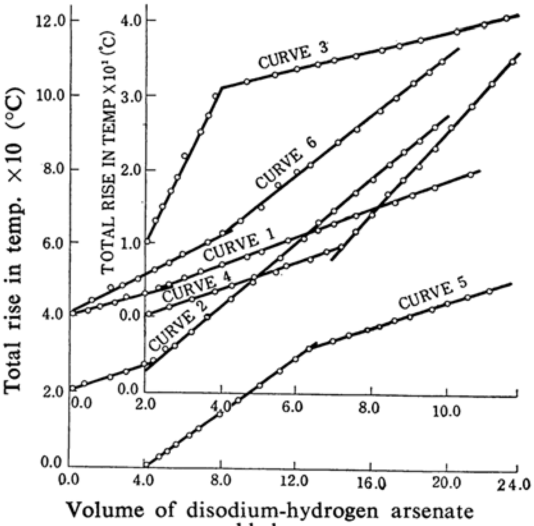

Fig. 2. Reverse thermometric-titrations. Curves 1, 2 and 3; M/5 Na_2HAsO_4 and M/40 $MnCl_2$. Curves 4, 5 and 3; M/5 Na_2HAO_4 and M/20 $MnCl_2$.

arsenate was added from microburette to manganese chloride contained in thermos flask, can be represented as follows:—

$$Na_2HAsO_4 + MnCl_2 = 2\,NaCl + MnHAsO_4$$

In case of direct titrations the mechanism may be explained as follows:—

$$MnCl_2 + 2\,Na_2HAsO_4 = 2NaCl + MnNa_2(HAsO_4)_2 \quad (1)$$

$$MnCl_2 + Na_2HAsO_4 = 2NaCl + MnHAsO_4 \quad (2)$$

Considering the strength of the solutions of manganese chloride (M/5) and disodium hydrogen arsenate (M/20 and M/40), the theoretical calculated titre values for 20, 18 and 16 cc. of disodium hydrogen arsenate solution for the direct thermometric titrations are 5.0, 2.5, 4.5, 2.25, 4.0, 2.0, 2.5, 1.25, 2.25, 1.125, 2.0 and 1.0 cc. respectively, which are in fair agreement with the observed values in each case respectively, for the formation of the compounds: $MnHAsO_4$ and $MnNa_2(HAsO_4)_2$ (in direct titrations). The formation of only $MnHAsO_4$ is supported in reverse titrations. The theoretical titre values required for the formation of $MnHAsO_4$ (ratio 1 : 1) in reverse titrations can be calculated accordingly. It is observed that the formation of $MnNa_2(HAsO_4)_2$ in the ratio of Mn : AsO_4 as 2 : 1 is not proved in the reverse titrations. It is observed from the curves obtained in direct titrations that only two breaks are observed corresponding to the formation of $MnHAsO_4$ and $MnNa_2 \cdot (HAsO_4)_2$ in the ratio of Mn : AsO_4 as 1 : 1 and 1 : 2. The reverse titration curves show only one break at the point of equivalence (the ratio of Mn : AsO_4 as 1 : 1).

Potentiometric and conductometric studies on the complexes are in progress and the results will shortly follow.

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