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Potentiometric Studies of the Reaction between Mercury(I) Nitrate and Sodium Arsenate

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The reaction between mercury(I) nitrate and sodium arsenate has been studied potentiometrically at various concentrations, by both the direct and reverse methods, employing bright platinum foil as an indicator electrode in conjunction with a saturated calomel electrode. The end-points obtained from the sharp inflections in titration curves and pronounced maxima in dE/dV provide cogent evidence for the formation and precipitation of mercury(I) arsenate, Hg_3AsO_4, in the 8.2—9.4 pH range. The precipitation of the compound is almost quantitative. The reaction can be successfully used for the determination of Hg_2^{2+} or AsO_4^{3-} ions in solutions at suitable concentrations and pH ranges.

The formation of mercury(I) arsenate has been studied earlier analytically. Coloriano1) and Gognet2) obtained mercury(I) arsenate (Hg_3AsO_4) by heating arsenic(V) oxide and mercury in a sealed tube at 230°C for 60 hr., and Haack,3) by treating meraury(I) nitrate with an excess of sodium arsenate, while Simon4) prepared it by adding a solution of mercury(I) nitrate into a concentrated solution of arsenic acid and redissolving the white precipitate so formed in an excess of acid, which had the composition of $HgHAsO_4 \cdot 1/2H_2O$. Recently Guerin and Boulitrop5) studied the arsenic(III) oxide - mercury(I) oxide - water system at 60°C and reported the formation of Hg_3AsO_4. There is, however, no reference in the literature concerning its study by electrometric techniques. The H^+ ion concentration plays an important role in the formation of such compounds.

Because of the complexity of reaction equilibria between alkali metal arsenates as a result of the appreciable tendency for hydrated forms to be concerted into higher aggregated products, which causes the precipitation of heavy metal salts of varying compositions, belonging some times to one type and some times to another,6) the conclusions of the reports on analytical investigations on this reaction seem to be overstrained and require a further approach using recent electrometric methods, which provide more conclusive evidence.7) The present investigation has, therefore, been undertaken with a view to study the reaction between mercury(I) nitrate and alkali arsenate more precisely.

Experimental

Merck's guaranteed extra-pure reagents, mercury(I) nitrate and Na_3AsO_4 were used; their solutions were prepared in air-free conductivity water. The sodium arsenate solution was standardised by the method given by Williams.8) The mercury(I) nitrate solution was prepared in the minimum quantity of nitric acid and was then estimated by titrating it against a standard sodium chloride solution potentiometrically.

The E. M. F. measurements of the cells, which consisted of a bright platinum electrode, acting as an indicator electrode, in conjuction with a saturated calomel electrode dipped into a titre solution, were carried out with a Backmann pH meter. Twenty milliliters of the titre solution was taken in the cell each time, the cell was kept immersed in an electrically-maintained thermostat, and the solution was stirred by an electrical stirrer. The observed values of E. M. F. were plotted against the volume of the titrant added, and the end-points were located graphically; the locations were then checked further by determining the maximum value of dE/dV.

Using different concentrations of the reactants, mercury(I) nitrate and $NaAsO_4$, a series of potentiometric titrations were carried out with each of the reagents, using them alternately as titrants. The reaction was also followed in the presence of 15% and 30% ethanolic media. The results of this study have been tabulated below (Table I); only one figure (Fig. 1) illustrating direct and reverse titrations has been given, in the interests of brevity.

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Table 1. A SUMMARY OF THE RESULTS OF POTENTIOMETRIC TITRATIONS

Molarity of solutions		Equivalence point (ml.)				Formula supported
			Obs. in presence of Alc.			
Na_3AsO_4	$HgNO_3$	Calcd.	0.0%	15.0%	30.0%	
			Direct titrations : Fig. 1, curve I			
M/9	M/10	6.00	5.95	5.96	6.02	Hg_3AsO_4
M/24	M/40	4.00	3.90	3.94	3.98	
M/120	M/160	5.00	4.90	4.94	4.96	
			Reverse titrations : Fig. 1, curve II			
M/180	M/15	5.00	4.94	4.96	4.96	Hg_3AsO_4
M/250	M/25	6.00	5.9	5.92	5.95	
M/750	M/50	4.00	3.9	3.92	3.96	

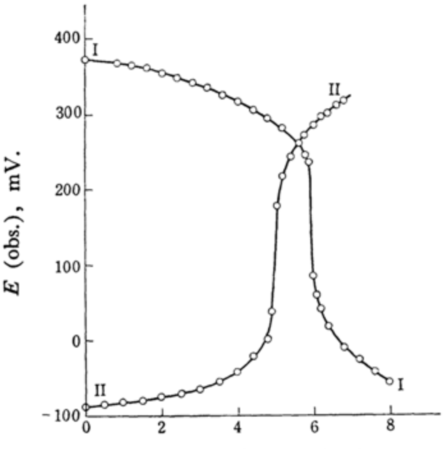

Fig. 1. Direct (curve I, M/9 Na_3AsO_4 vs. M/10 $HgNO_3$) and reverse (curve II, M/15 $HgNO_3$ vs. M/180 Na_3AsO_4) potentiometric titrations between mercury(I) nitrate and sodium arsenate in the absence of ethanol.

Discussion

Figure 1 illustrates the direct and reverse potentiometric titrations between mercury(I) nitrate and Na_3AsO_4. In the case of inverse titrations, when the mercury(I) nitrate solution is added to the Na_3AsO_4 solution, the arsenate ions are removed from the solution by precipitation and the E. M. F. gradually rises up to the addition of about 2.5 mol. of mercury(I) nitrate per mole of Na_3AsO_4, but at the stoichiometric end-point which corresponds to the formation of Hg_3AsO_4 a sharp upward jump in potential is noted, after which the E.M.F. becomes practically constant. In direct titration (curve I), i. e., when Na_3AsO_4 solution was added to the mercury(I) nitrate solution taken into a cell, the E. M. F. of the cell gradually decreases up to the vicinity of the end-point which is indicated by a sharp fall in E. M. F.; after this the E. M. F. assumes a practically constant value. Both the direct and reverse potentiometric titrations yield a sharp inflection at the point where the molecular ratio of mercury(I) and AsO_4^{3-} is 3 : 1, corresponding to the formation of mercurous arsenate, Hg_3AsO_4, in the 8.2—9.4 pH range. The accuracy and reproducibility of these titrations have been found to be excellent, and the precipitation of the compound is almost quantitative.

It has been noted that each titration takes about half an hour for completion, and that a thorough stirring in the vicinity of the end-point has a favourable effect. The presence of ethanol increases the sharpness of the end-point and, consequently, the magnitude of the d*E*/d*V*, as it reduces the solubility of the precipitates formed and decreases the hydrolysis and adsorption of AsO_4^{3-}.

It is apparent from the above study that, when mercury(I) nitrate reacts with Na_3AsO_4, the formation of mercury(I) arsenate, Hg_3AsO_4, takes place in the 8.2—9.4 pH range. As the precipitation of the compound is quantitative, the reaction can be successfully utilised for the determination of Hg_2^{2+} or AsO_4^{3-} ions in solutions at suitable concentrations and pH range.

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