# Investigations on Polymolybdates of Rare Earths. Electrometric Studies on the Compositions of Samarium Polymolybdate

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A survey of the literature reveals that the composition of samarium molybdate, which may be of great significance in the geochemistry of both elements, has not been studied so far by electrometric techniques. The only available reference is that of Cleve,[1] who has thrown some light on the composition of samarium molybdate by adopting analytical means. His results, however, could not be confirmed later. The present investigation has, therefore, been initiated with a view to study the reaction equilibria between $Sm(NO_3)_3$ and various molybdate polyanions by means of amperometic and conductometric titrations. The results have also been substantiated by gravimetric analysis of the compounds formed. These interesting results are a continuation of our similar type of studies.[2,3]

### Appratus and Procedure

Anal. R. (B. D. H.) reagents sodium molybdate $Na_2MoO_4$, lithium chloride LiCl, samarium nitrate $Sm(NO_3)_3$ (Atomic Energy Establishment, Trombay) and gelatine were used. A manual polarograph with a spot galvanometer was used for polarographic and amperometric work. A dropping mercury electrode with the characteristics $m^{2/3}t^{1/6}=4.58\ mg^{2/3}\ sec^{-1/2}$, where $m$ is the weight of mercury in a closed circuit= 7.166 mg/sec, and $t$ is the drop time of the capillary at $-1.0$ V (*vs.* SCE)=3.50 sec, in $Na_2MoO_4$ solution, was used in conjunction with SCE and the proportionality of $i_d$ with respect to concentration was observed. Conductance was measured with the help of a Tesla conductivity bridge, and the procedure adopted was the same as described earlier.[4] Amperometric titrations were carried out between $Sm(NO_3)_3$ and various alkali di, para, tri and meta molybdates at an applied potential of $-1.7$ V (*vs.* SCE) in the presence of 0.1 M LiCl as supporting electrolyte, and 0.005% gelatine as maxima supressor. The end points were located graphically with plots of diffusion current values and conductance drawn as a function of milliliters of titrant added.

### Discussion

The addition of acid to alkalimolybdate causes the formation of various polyanions with regard to the changes occurring in $H^+$ ion concentration. It was considered of importance to ascertain electrometrically whether similar samarium salts can be obtained as a result of reaction between samarium nitrate and various alkali molybdates solutions.

**Normal Molybdate Titration.** Using different concentrations of $Sm(NO_3)_3$ and $Na_2MoO_4$, a series of amperometric titrations were carried out and the well defined breaks in curves (a) and (b) (Fig. 1) at the end points suggested the formation and precipitation of normal samarium molybdate $Sm_2O_3\cdot 3MoO_3$ at a pH range of 5.5—6.0 where the atomic ratio of Sm : Mo is 2 : 3. The reaction proceeds as follows:

$$2Sm(NO_3)_3 + 3Na_2O\cdot MoO_3 \rightarrow Sm_2O_3\cdot 3MoO_3 + 6NaNO_3.$$

Conductometric titration using similar solutions substantiated the formation of the above compound.

**Para-Molybdate Titrations.** The solution of sodium para-molybdate was prepared by adding 1.14 mol of HCl per mole of normal molybdate ($Na_2MoO_4$) at 100°C, and its reaction with $Sm(NO_3)_3$ was studied amperometrically and conductometrically. The well defined breaks obtained in the titration curves (Fig. 2) reveal the formation and precipitation of smarium para-molybdate with the molecular composition $Sm_2O_3\cdot 7MoO_3$ in the pH range 3.5—4.5. The formation can be described as follows:

$$7\ Na_2O\cdot MoO_3 + 8\ HCl \rightarrow 3\ (Na_2O\cdot 2.33\ MoO_3) + 8\ NaCl + 4\ H_2O$$

$$2\ Sm(NO_3)_3 + 3\ (Na_2O\cdot 2.33\ MoO_3) \rightarrow Sm_2O_3\cdot 7\ MoO_3 + 6\ NaNO_3.$$

Similar titrations were also performed with a view to study the reaction between $Sm^{3+}$ and tri and meta alkali molybdates but they could not throw any light on the formation of tri and meta molybdates of samarium. The compositions of the compounds formed were also checked by analyzing the precipitate obtained at the end point gravimetrically, whose results were found to confirm those obtained by electrometric techniques.

$\Delta H$ for the formation of normal and paramolybdates of samrium has also been determined

1) A. Cleve, Oefners, *Akad. Forth*, **58**, 573 (1902).
2) C. M. Gupta, This Bulletin, **38**, 1401 (1965).
3) C. M. Gupta, *ibid.*, **39**, 837 (1966).
4) C. M. Gupta and R. S. Saxena, *J. Inorg. Nucl. Chem.*, **14**, 297 (1960).

TABLE 1. SUMMARY OF THE RESULTS OF AMPEROMETRIC AND CONDUCTOMETRIC TITRATIONS

| Concentrations | | Equivalence points | | |
|---|---|---|---|---|
| $Sm(NO_3)_3$ | $Na_2MoO_4$ | Calcd, m*l* | Obsd, m*l* | |
| Amperometric titrations | | | | |
| Normal molybdate | | Direct titration | | |
| M/40 | M/200 | 2.66 | 2.80 | Fig. 1 (a) |
| M/400 | M/1200 | 4.44 | 4.55 | |
| | | (Reverse titration) | | |
| M/200 | M/20 | 3.00 | 3.00 | Fig. 1 (b) |
| M/800 | M/100 | 3.75 | 3.70 | |
| Para molybdate | | $Na_2O \cdot 2.33\ MoO_3$ | | |
| M/10 | M/46.6 | 2.88 | 2.65 | Fig. 2 (a) |
| M/20 | M/116.5 | 2.28 | 2.20 | Fig. 2 (b) |
| M/40 | M/163.1 | 3.28 | 3.20 | |
| Conductometric titrations | | | | |
| Normal molybdate | | | | |
| M/200 | M/800 | 3.75 | 3.65 | |
| M/40 | M/400 | 1.33 | 1.30 | |
| M/160 | M/400 | 5.33 | 5.25 | |
| Para molybdate | | | | |
| M/160 | M/699 | 3.05 | 3.00 | |
| M/400 | M/1175 | 4.54 | 4.50 | |
| M/400 | M/2330 | 2.30 | 2.20 | |

TABLE 2. COMPOSITION OF THE PRECIPITATES ANALYSED

| Amount of Sm present, g | Amount of Mo present, g | Ratio Sm : Mo | Corresponding compound suggested |
|---|---|---|---|
| 0.0380 | 0.058 | 2 : 3.05 | $Sm_2O_3 \cdot 3\ MoO_3$ |
| 0.0380 | 0.0585 | 2 : 3.07 | |
| 0.0480 | 0.1690 | 2 : 7.04 | $Sm_2O_3 \cdot 7\ MoO_3$ |
| 0.0480 | 1.1685 | 2 : 7.03 | |

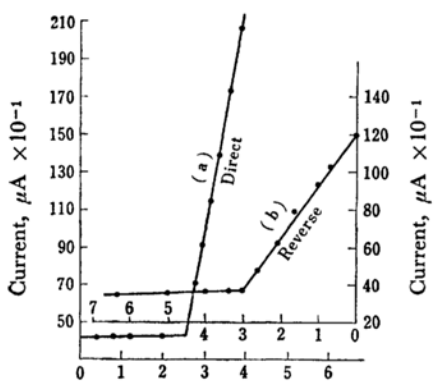


Fig. 1

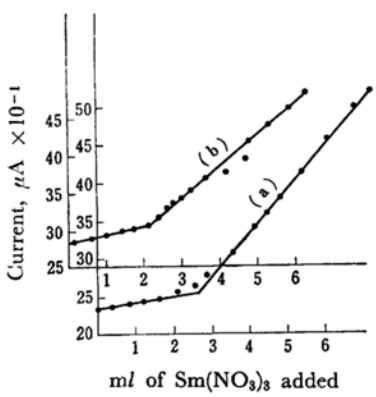


Fig. 2

by the procedure as mentioned by Findlay.[5]

$\Delta H$ for normal compound = −188.8 cal/g mol

$\Delta H$ for para-compound = −183.0 cal/g mol

The present investigation thus confirms the formation and precipitation of normal and para-molybdate of samarium with the molar compositions $Sm_2O_3 \cdot 3MoO_3$ and $Sm_2O_3 \cdot 7MoO_3$ at pH ranges of 5.5—6.0 and 3.5—4.5, respectively, and the heat of formation of the compounds are found to be −188.8 cal/g mol and −183.0 cal/g mol, respectively.

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5) "Practical Physical Chemistry" by A. Findlay, pp. 188—190.