Studies in Rare Metal Tungstates—Amperometric Titrations of Lanthanum(III) with Alkali Tungstate

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In view of the interesting results reported in the amperometric studies of certain isopoly acid salts,[1] it was considered of interest to study the similar rare isopoly tungstate. As no amperometric study on the composition of lanthanum tungstate, appears to have been carried out so far, the present investigation was initiated. Amperometric titrations have been performed between $La(NO_3)_3$ and Na_2WO_4 with a view of studying the possibility of developing the reaction as an analytical method for the determination of lanthanum at a definite pH value. Amperometric methods of analysis possess attributes which extend their value far beyond the direct determination of chemical elements.

AnalR (BDH) reagents sodium tungstate and lanthanum nitrate were used; their solutions were prepared in conductivity water. Lanthanum was estimated as an oxalate[2] by potentiometry, while the tungsten in Na_2WO_4 was determined as its oxinate.[3] A manual polarograph, with a scalamp galvanometer as a current recorder, was used for amperometric titrations. A capillary ($m=2.416$ mg./sec., $t=3.58$ sec. and $m^{2/3}t^{1/6}=2.226\ \mathrm{mg}^{2/3}\,\mathrm{sec}^{-1/2}$) was used in conjunction with a saturated calomel electrode connected to the cell by a low-resistance salt bridge. A series of polarograms of solutions containing lanthanum nitrate in the presence of 0.1 M potassium chloride and 0.01% gelatin were drawn, and the almost limiting current plateau potential was determined to be −1.5 V. (vs. SCE). This potential was applied to the electrodes of the cell throughout the investigations. All the amperometric titrations were carried out in the absence of a supporting electrolyte and in the presence of of 0.01% gelatin. Twenty millilitres of the titre solution was placed in the cell each time, and the cell solution was deaerated by bubbling in hydrogen. The observed current was corrected for the dilution effect, and the end-points were located graphically. The addition of alcohol has often been recommended in these titations, especially because of its favourable influence on the solubility of the precipitate. Therefore, investigations have also been undertaken in this direction. In 50% ethanol, the equivalence point was found to have been much improved.

The precipitation of $La_2O_3\cdot 3WO_3$ is quantitative over the pH range from 5 to 6.5; the results are accurate within an error range of 1% at 10^{-3} M concentrations of the reactants studied. The only product formed at this pH is the normal tungstate of lanthanum, probably due to the fact that normal WO_4^{2-} is predominant over the other species. The present method has limitations, although it is rapid, simple and accurate for the determination of small amounts of La^{3+}. Anions like molybdate, chromate, and vanadate, and such cations as cerium, thorium and silver interfere and hence must remain absent. The work at different pH values did not give satisfactory results.

The above results have been substantiated by pH titrations between alkali tungstate and lanthanum nitrate using glass electrode, both by direct and reverse methods. The electrometric curves reveal a sharp maxima in dpH/dV at the stoichiometric end point corresponding to the formation of normal tungstate. The sharp inflexion in the curve when Na_2WO_4 is added to lanthanum nitrate in the presence of 40% ethanol suggests the possibility of using methyl red for the visual detection of the end point in the 5.0—6.8 pH range.

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