INTERACTION OF YTTRIUM AND LANTHANUM CATIONS WITH ANIONS OF HYPOPHOSPHORIC ACID IN AQUEOUS SOLUTION

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Equilibrium systems $Y(ClO_4)_3$–$Na_4P_2O_6$–H_2O and $La(NO_3)_3$–$Na_4P_2O_6$–H_2O were investigated by means of conductivity and potentiometric measurements. Experimental results were interpreted assuming the formation of normal, $M(III)_4(P_2O_6)_3$, double, $NaMP_2O_6$, and basic, $La_x(OH)_y$. $(P_2O_6)_{(3x-y)/4}$, salts. The existence of normal salts and in the case of yttrium also of the double salt was demonstrated by their isolation from the above-mentioned systems.

Quinty[1] described isolation or normal yttrium hypophosphate, $Y_4(P_2O_6)_3.6\ H_2O$ from the system $Y(NO_3)_3$–$Na_2H_2P_2O_6$–H_2O in the form of poorly soluble, crystalline precipitate. Analogously, the salt of neodymium, $Nd_4(P_2O_6)_3.4\ H_2O$ was prepared in crystalline form and that of thorium, $ThP_2O_6.x\ H_2O$ as amorphous product. Their isolation was preceded by potentiometric and conductometric measurements of the system $M(III)(IV)$–$Na_2H_2P_2O_6$–H_2O (or 30% ethanol). In interpreting the results the author assumes the formation of the above-mentioned normal salts. From the literature data it is evident that the nature of the salts of trivalent elements with anions of multibasic oxoacids of phosphorus (normal, hydrogen, double, complex and basic salts) is predominantly a function of pH of the system under study.

The present paper is therefore devoted to the study of the reaction of yttrium and lanthanum ions with anions $HP_2O_6^{3-}$ and $P_2O_6^{4-}$. According to the distribution diagram of hypophosphoric acid, a $0.01M$ solution of $Na_4P_2O_6$ (pH_{exp} 11·10) contains 9% of $HP_2O_6^{3-}$ and 91% of $P_2O_6^{4-}$ ions[2].
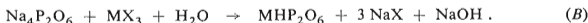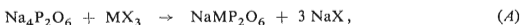
EXPERIMENTAL

Solution of tetrasodium hypophosphate was prepared by neutralization of disodium dihydrogen hypophosphate solution with an equivalent amount of sodium hydroxide. The solution was standardized cerimetrically[3,4]. The solid acid salt, $Na_2H_2P_2O_6.6\ H_2O$, was prepared according to Remy and Falius[5] by oxidation of red phosphorus with sodium chloride solution. The purity of sodium salts was checked by means of one-dimensional paper chromatography[6]. Yttrium perchlorate (in solution) was obtained by dissolving yttrium oxide (Lachema) in 60% perchloric acid and was standardized complexometrically against xylenol orange[7]. Lanthanum nitrate (in solution) was standardized complexometrically against eriochrom black according to Schwarzenbach[8]. Conductivity measurements were carried out on Conductivity meter, type OK-102/1 (Radelkis, Hungary) equipped with commercial conductivity cell with Pt electrodes. The resistance capacity of the cell was not determined since the only task was to obtain the dependence of $1/R$

on n [n = amount of substance (in mol) of hypophosphate per mol of metal, $H_xP_2O_6^{x-4}$: M(II))]. Potentiometric measurements were performed using a laboratory compensation pH-meter (Laboratorní přístroje, Prague) with glass and calomel electrodes. The electrode system was calibrated with a 0·1M borax solution (pH 9·18) and with phosphate buffer Radiometer (pH 6·5). Both conductivity and potentiometric experiments were performed at 25°C ± 0·2°C. Equilibrium systems were prepared by adding 0·1M-Y(ClO₄)₃ or La(NO₃)₃ to 25 ml of 0·01M-Na₄P₂O₆. Total number of the samples prepared from each system was twenty, of which the last one contained 5 ml of the metal salt solution (n = 0·5). The samples were thermostated at 25°C for 200 h. Conductivity and pH were measured directly in the heterogeneous systems in the solutions above the precipitate. Besides, direct conductivity and potentiometric titrations of 0·005M-Y(ClO₄)₃ or La(NO₃)₃ with a 0·05M solution of Na₄P₂O₆ were also carried out. The values of pH and of conductivity were always taken 5 minutes after the last drop of the solution had been added.

RESULTS AND DISCUSSION

System Y(ClO₄)₃–Na₄P₂O₆–H₂O. In the region of $n \geqq 0·5$ a white, gel-like precipitate is formed immediately, which at $n > 1$ changes into the crystalline form. Both the inflex and the break on potentiometric and conductivity curves in the region of $n \geqq 0·95$ (Fig. 1) support the formation of a compound with $n = 1$. Theoretically, the formation of a double or acid salt can be supposed, according to Eqs (A) and (B), respectively.

$$Na_4P_2O_6 + MX_3 \rightarrow NaMP_2O_6 + 3\,NaX, \qquad (A)$$

$$Na_4P_2O_6 + MX_3 + H_2O \rightarrow MHP_2O_6 + 3\,NaX + NaOH. \qquad (B)$$

From Eq. (B) it is evident that the formation of acid salt must necessarily be accompanied by an increase of the pH of the system. However, it was found that with decreasing n the value of pH_{exp} diminishes (Table I). Unlike to Eq. (B), Eq. (A) does not, at the first sight, imply any change of the pH of the system. The formation of double salt, however, must be connected with a pH decrease, owing to depletion of $P_2O_6^{4-}$ ions from the system. Using the function $pH = f(K_3, K_4, K_w, C_p, C_{Na^+}, C_{X^-})^*$ the changes in the pH's of the systems were calculated for the region of $n \geqq 1·04$, assuming the formation of double, acid and normal salts (Table I). Experimentally found changes of pH and electric conductivity in the region of $n > 0·95$ are therefore explained as the result of double salt formation which in the region $0·75 < n < 0·95$, is transformed into normal salt, according to equation

$$3\,NaMP_2O_6 + MX_3 \rightarrow M_4(P_2O_6)_3 + 3\,NaX. \qquad (C)$$
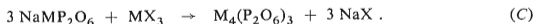
*. K_3, K_4 are the third and fourth dissociation constants of hypophosphoric acid, K_w is the ion product of water, $C_p = \sum_{x=0}^{2} (H_xP_2O_6)$, C_{Na^+} is the equilibrium concentration of Na^+, C_{X^-} is the equilibrium concentration of ClO_4^- or NO_3^-, respectively.

Interpretation of the results of potentiometric and conductivity measurements in the system $Y(ClO_4)_3$–$Na_4P_2O_6$–H_2O was confirmed by the isolation of crystalline double salt as well as of the normal salt in amorphous form.

System $La(NO_3)_3$–$Na_4P_2O_6$–H_2O. In the region of $n \geqq 0.5$ a white, gel-like precipitate is formed immediately. No crystallisation of this product was observed even after 3 months. The dependence of pH on n (Fig. 2) does not prove so decisively (position of inflex in the region of $n \geqq 1$) the formation of double salt, as it is in the case of yttrium. The decrease of pH in the region of $n > 1$ cannot be regarded as a sufficient evidence of the formation of double salt as the only compound formed in the system (Table I). We suppose that in the region of $n > 1$ both double and
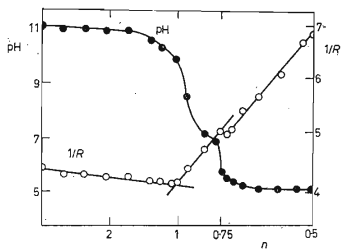

Fig. 1

Conductivity and Potentiometric Measurements in the System $Y(ClO_4)_3$–$Na_4P_2O_6$–H_2O

n Amount of substance (in mol) of hypophosphate per mol of yttrium.
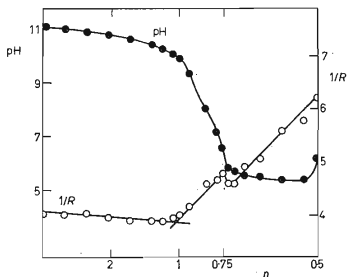

Fig. 2

Conductivity and Potentiometric Measurements in the System $La(NO_3)_3$–$Na_4P_2O_6$–H_2O

n Amount of substance (in mol) of hypophosphate per mol of lanthanum.
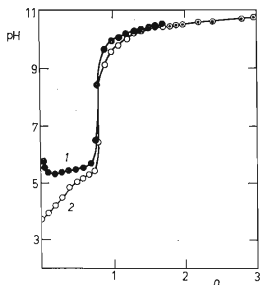

Fig. 3

Potentiometric Titration of 50 ml of 0.005M Solutions of MX_3 with 0.05M Solution of $Na_4P_4O_6$

1 $La(NO_3)_3$, 2 $Y(ClO_4)_3$. n Amount of substance (in mol) of hypophosphate per mol of metal.

TABLE I

Dependence of pH_{exp} and pH_{theor} on n [$n = (H_xP_2O_6^{x-4})$: (MIII)]

n	pH_{exp}^{a}	pH_{exp}^{b}	pH_{theor}^{c}	pH_{theor}^{d}	pH_{theor}^{e}
∞	11·10	11·10	—	—	—
2·50	10·90	10·88	10·87	11·74	10·90
1·25	10·40	10·45	10·59	11·87	10·76
1·042	10·02	10·11	10·16	11·94	10·67

[a]System $Y(ClO_4)_3–Na_4P_2O_6–H_2O$. [b]System $La(NO_3)_3–Na_4P_2O_6–H_2O$. [c]Values calculated according to Eq. (A), [d]according to (B), [e]according to: $4 MX_3 + 3 Na_4P_2O_6 \rightarrow M_4(P_2O_6)_3 + 12 NaX$.

normal salts are formed. With increasing concentration of MX_3 ($n > 0.75$) the double salt is gradually transformed into normal salt according to Eq. (C). Only the roent-genographically amorphous normal salt was successfully prepared from the system. The effect of cation of M(III) on the nature of the salt formed is manifested also in direct potentiometric and conductometric titrations of 0·005M solutions of $Y(ClO_4)_3$ or $La(NO_3)_3$ with 0·05M-$Na_4P_2O_4$ (Fig. 3). In both cases an immediate formation of gel-like precipitates takes place, which do not change during the titration. The course of the potentiometric titration curve in the system $Y(ClO_4)_3–Na_4P_2O_6–H_2O$ supports the formation of normal salt $Y_4(P_2O_6)_3$. In the case of lanthanum first portions of the reagens added cause an apparently contradictory decrease of pH (pH of 0·05M-$Na_4P_2O_6 = 11.65$). We explain this effect by transition of the $[La_x(OH)_y]^{3x-y}$ ions into the precipitate of $La_x(OH)_y(P_2O_6)_{(3x-y)/4}$ which results in the decrease of the pH of the system. With increasing concentration of the titration reagent these basic salts of variable composition are eventually transformed into the normal salt $La_4(P_2O_6)_3$. An analogous phenomenon was also observed in titrations of LaX_3 with solutions of alkali metals di- tri- and tetraphosphates[9].

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