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Studies of Rare Earth Polyphosphate Glasses of Composition $[Na_xM_{(1-x)/2a}Dy_{(1-x)/2a}PO_3]_n$

GITA SETH* and ANJANA AGRAWAL
Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

Fusion technique was used for the preparation of derivatives of composition $[Na_xM_{(1-x)/2a}Dy_{(1-x)/2a}PO_3]_n$ [where M^1 = bivalent metal like Cu(II), Ca(II), Zn(II) and Mg(II) and X = 2/3 and 3/4 and a = valency of metal]. Compositions of these polyphosphate glasses were confirmed by their analysis for metals and phosphorus. The polymeric nature of all polyphosphate glasses was confirmed by determination of number average molecular weight (Mn). The characteristic frequencies in the IR spectra are supportive of the presence of polyphosphate indicative of the polymeric nature of these derivatives.

Key Words: Rare earth polyphosphate, glasses.

INTRODUCTION

Due to numerous applications of polyphosphate glasses in industries as well as in agriculture, it has received considerable attention of many research workers[1,2]. Polyphosphate derivatives of lanthanides have been studied by many workers.[3,4] A persual of literature revealed that complex polyphosphates containing rare earth cations and bivalent metal ions have not been studied in detail. In the present communication we report the studies on polyphosphate of bivalent metal like Cu(II), Ca(II), Zn(II) and Mg(II) with Dy(III) of composition $[Na_xM_{(1-x)/2a}Dy_{(1-x)/2a}PO_3]_n$.

EXPERIMENTAL

Fusion method[5] is being used for the preparation of various complex polyphosphates. Compositions were confirmed by estimation of the bivalent metals, dysprosium and phosphorus, by the method reported in literature.[6] Thin-layer chromatography was done using dioxane as eluent. Molecular weight (number average) was determined by end group titrations[5]. IR spectra were obtained on FTIR spectrophotometer (IR Magna 550, Nicolet) in the region 4000–400 cm^{-1}.

Method of preparation of polyphosphate derivatives

The reaction mixture in required molar ratio (keeping in view that metal-phosphorus ratio is equal to one) was taken in a platinum crucible and mixed well with a stirrer. It was gradually heated first at low temperature and then the crucible was placed in a muffle furnance maintained at 900 ± 10°C (thermostatically controlled) for 2 h. The products were obtained in the form of a transparent melt,

which was immediately chilled between two stainless steel plates. The weight of the products corresponded to those calculated on the basis of the equation used for the reaction.

When x = 2/3:

$$24\,NaH_2PO_4 + 12(NH_4)_2HPO_4 + 3MO + Dy_2O_3 \rightarrow Na_{24}M_3Dy_2(PO_3)_{36}]_n + 24NH_3 + 42H_2O$$

When x = 3/4:

$$36NaH_2PO_4 + 12(NH_4)_2HPO_4 + 3MO + Dy_2O_3 \rightarrow Na_{36}M_3Dy_2(PO_3)_{48}]_n + 12NH_3 + 54H_2O$$

RESULTS AND DISCUSSION

Various polyphosphate derivatives systhesized above were analysed for the constituents, *i.e.*, phosphorus, alkali-bivalent metals and dysprosium. Results are reported in Table-1. In TLC studies R_f values were measured in dioxane-solvent system (30 mL dioxane + 75 mL water + 5 g trichloro-acetic acid and ammonia solution). Dioxane is preferred over other solvent systems due to its miscibility in water, low dielectric constant and moderately low viscosity. In this solvent excellent resolution is obtained in comparatively lesser running time. The R_f and R_g values for various complex polyphosphates are calculated and listed in Table-2. Two spots of very weak intensity along with those of polyphosphates in chromatograms correspond to ortho and trimetaphosphates which can be attributed to initial hydrolysis of polyphosphate chain in aqueous solution, which has been considered to be less than 2–2.5%. This is in agreement with observations reported in literature.[7] The plot of R_g values *vs.* negative log of chain length is straight line which indicates the long chain polymeric character of the polyphosphate glasses. The chain length was calculated by using the simple equation.

$$\text{Chain length } (n_c) = \frac{\text{Number-average molecular weight}}{\text{Weight of single phosphate unit}}$$

End group titration

The number average molecular weights were determined by the end group titration technique[8] with the help of Systronics pH-meter having a glass and a calomel electrode. The aqueous solutions of the complex polyphosphate were prepared by dissolving about 0.1–0.15 g of the sample in 100 mL of double distilled water. The solution thus obtained was then titrated after adujsting the pH 3.0 with 0.01 N HCl, with 0.1 N NaOH solution. The volume of alkali consumed between two inflections in the titration curve around pH 4.5 and 9.0 units was used to calculate the number average molecular weight (M_n) as per formula and reported in Table-3.

$$M_n = \frac{20{,}000 \times \text{weight of polymer sample}}{\text{mL of 0.1 N NaOH used}}$$

TABLE-1
ELEMENTAL ANALYSIS OF COMPLEX POLYPHOSPHATE GLASSES

S.No.	Compounds	% Analysis							
		P		Na		M′		Dy	
		Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
1.	$[NaPO_3]_n$	3.29	3.15	4.43	4.21	–	–	–	–
2.	$[Na_{24}Mg_3Dy_2(PO_3)_{36}]_n$	29.40	29.35	14.55	14.48	3.13	3.22	8.56	8.50
3.	$[Na_{24}Ca_3Dy_2(PO_3)_{36}]_n$	29.04	29.16	14.37	14.46	1.90	1.80	8.46	8.35
4.	$[Na_{24}Ni_3Dy_2(PO_3)_{36}]_n$	28.62	28.55	14.17	14.25	4.51	4.44	8.34	8.27
5.	$[Na_{24}Cu_3Dy_2(PO_3)_{36}]_n$	28.52	28.47	14.11	14.23	4.87	4.74	8.31	8.44
6.	$[Na_{24}Zn_3Dy_2(PO_3)_{36}]_n$	28.48	28.53	14.09	14.17	5.00	5.09	8.30	8.21
7.	$[Na_{36}Ca_3Dy_2(PO_3)_{48}]_n$	29.36	29.47	16.35	16.26	2.37	2.27	6.41	6.35
8.	$[Na_{36}Ni_3Dy_2(PO_3)_{48}]_n$	29.04	29.18	16.17	16.09	3.44	3.55	6.34	6.26
9.	$[Na_{36}Cu_3Dy_2(PO_3)_{48}]_n$	28.95	28.87	16.12	16.25	3.71	3.79	6.33	6.25

TABLE-2
M_n –log n_c (n_c = CHAIN LENGTH) R_f AND R_g VALUES OF VARIOUS COMPLEX POLYPHOSPHATE DERIVATIVES IN DIOXANE SOLVENT

S.No.	Complex poly phosphate	M_n	–log n_c	R_f	R_g
	NaH_2PO_4	–	–	0.92	–
1.	$[NaPO_3]_n$	4725	2.2286	0.039	0.042
2.	$[Na_{24}Mg_3Dy_2(PO_3)_{36}]_n$	3840	2.4382	0.051	0.055
3.	$[Na_{24}Ca_3Dy_2(PO_3)_{36}]_n$	3483	2.4848	0.051	0.055
4.	$[Na_{24}Ni_3Dy_2(PO_3)_{36}]_n$	3042	2.5510	0.053	0.058
5.	$[Na_{24}Cu_3Dy_2(PO_3)_{36}]_n$	3871	2.4480	0.041	0.044
6.	$[Na_{24}Zn_3Dy_2(PO_3)_{36}]_n$	4380	2.3949	0.040	0.043
7.	$[Na_{36}Ca_3Dy_2(PO_3)_{48}]_n$	3080	2.4343	0.049	0.053
8.	$[Na_{36}Ni_3Dy_2(PO_3)_{48}]_n$	3113	2.5347	0.055	0.060
9.	$[Na_{36}Cu_3Dy_2(PO_3)_{48}]_n$	3630	2.4692	0.052	0.056

TABLE-3
NUMBER AVERAGE MOLECULAR WEIGHT (M_n)
DETERMINED BY END GROUP TITRATION

S.No.	Complex poly phosphates	W (g)	V (mL)	M_n
1.	$[NaPO_3]_n$	0.1701	0.72	4725
2.	$[Na_{24}Mg_3Dy_2(PO_3)_{36}]_n$	0.1574	0.82	3840
3.	$[Na_{24}Ca_3Dy_2(PO_3)_{36}]_n$	0.1375	0.79	3483
4.	$[Na_{24}Ni_3Dy_2(PO_3)_{36}]_n$	0.1490	0.98	3042
5.	$[Na_{24}Cu_3Dy_2(PO_3)_{36}]_n$	0.2167	1.12	3871
6.	$[Na_{24}Zn_3Dy_2(PO_3)_{36}]_n$	0.1314	0.60	4380
7.	$[Na_{36}Ca_3Dy_2(PO_3)_{48}]_n$	0.1386	0.90	3080
8.	$[Na_{36}Ni_3Dy_2(PO_3)_{48}]_n$	0.1291	0.83	3113
9.	$[Na_{36}Cu_3Dy_2(PO_3)_{48}]_n$	0.2014	1.11	3630

W = Weight of the polymer sample used in titration.

V = Volume of 0.1 N NaOH consumed between 4.5 to 9.0 pH.

The existence of two inflections in the titration curve is indicative of the presence of strongly and weakly acidic groups in these derivatives. As the nature of the titration curves obtained is similar to that of Graham's salt, it can be concluded that the polyphosphate derivatives consist of the end and middle groups in the chain-like polymeric anion. The M_n values lie in the range of 2000–4000 indicating a chain length (n_c) equal to 20 to 40 units and are in the same range as found in the case of polyphosphates reported in literature.[8]

Infrared spectra

The spectra of these polymeric derivatives show broad bands which may be ascribed to their amorphous polymeric character. The absorption frequencies observed are in close agreement with the values reported for Graham's salt.[9,10] The IR spectra of all long chain polyphosphate derivatives contain a very strong broad band, with absorption maxima at 1270 cm^{-1}, which is ascribed to the P=O stretching vibration. Absence of triplet band at *ca.* 1330 cm^{-1} and sharp band at 770–745 cm^{-1} attributed to trimetaphosphate and cyclic phosphate indicates the absence of trimetaphosphate anion and cyclic phosphate. The absorption bands in the region 1100–1080 cm^{-1} and 1115–1170 cm^{-1} related to PO_2 or P—O^- ionic character attributed to long chain polyphates are observed in these derivatives. A weak broad band, characteristic of amorphous phosphates, is also observed at 1030–990 cm^{-1}. The absorptions at 890–870 and 720 cm^{-1} are ascribed to vibration in the P—O—P chain.[11]

From IR spectral studies and other studies mentioned above it can be suggested that these complexes are long chain polymers containing polyphosphate $(PO_3)_n^{-n}$ chain.

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