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ISOPOLYMOLYBDATE- AND ISOPOLYVANADATE ANIONS IN AQUEOUS DIMETHYLFORMAMIDE MEDIUM AND IN SALTS

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According to the data of pH-potentiometric titration, the complexation processes in Na2MoO4 –HCl –NaCl –C3H7ON –H2O and Na3VO4 –HCl –NaCl –C3H7ON (10-40 vol.%) –H2O (Cv = 0.01 - 0.1 mol/L; µ = 0.5 mol/L) and the concentration formation constants of isopolymolybdate- and isopolyvanadate-anions were calculated according to the CLINP 2.1 program; the diagrams of isopolyanion distribution are plotted as a function of acidity and concentration, and schemes for their transformation in aqueous dimethylformamide medium are proposed. The pH (acidity) zones of the dominance of isopolymolybdates and isopolyvanadates are established as a function of the concentration of MoO42 , and VO43– ions; the C3H7ON and H2O ratios in the systems. According to the results of mathematical modeling in aqueous media at a concentration of molybdenum C£0,05 M in the acidity range Z = 0,5-2,5 the tetraiones of the two compositions Mo4O132- and Mo4O144- dominate in the solution, and the protonated hexamolybdates HMo6O215- and H2Mo6O214- are in minor amounts. In the dimethylformamide medium the effect of increasing the concentration of organic solvent on the composition and distribution of isopolymolybdate-anions is shown, namely: protonated hepta- and octa-ions are formed in dilute solutions, unlike aqueous systems, and octa- and tetramolybdate-anions dominate in decimolar solutions with negligible the content of the other ions Mo2O72-, Mo6O216-, Mo4O144-, HMo7O245-.

To confirm the stabilizing effect of dimethylformamide (DMF) on the formation of tetra-, hexa- and octa-molybdate-anions, the synthesis of salts with tetraethylammonium cation in decimolar systems and 25% DMF content was carried out. The composition of crystalline products was determined by chemical, X-ray phase analysis and IR spectroscopy and showed that in the acidity range Z = 1,14 –1,80 white crystals of octamolybdate [N(C2H5)4]4Mo8O26·nC3H7ON·mH2O precipitate after the separation of white crystals of tetramolybdate [N(C2H5)4]2Mo4O13·nC3H7ON·mH2O at Z = 1.50 and yellow hexamolybdate crystals [N(C2H5)4]2Mo6O19·nC3H7ON·mH2O at Z = 1.80. Salts with hexa-, tetra- and octamolybdate anion, which do not precipitate from water solutions, were obtained from the medium with DMF by precipitation with a cation of the inorganic nature –barium.

In the system with vanadium in the aqueous organic medium, as well as in the aqueous medium, it was possible to detect the existence of three-(V3O93-) and tetrametavanadates (HV4O123-) in a narrow range of concentrations (0,01-0,1 mol/L). The decavanadate anion V10O286- is fixed at Z = 2,50, which is marked by an inflection point on the potentiometric titration curve. There are no tetravanadates of composition V4O124- and V4O136-. In the decimolar solution of sodium orthovanadate such polyoxoanions dominate: V4O124-, HV4O135- and V10O286- with an insignificant amount of protonated decavanadate H3V10O283- and V3O93- . With an increase in the DMF concentration of up to 25% by volume, the formation of the un-protonated form of decavanadate anion is stabilized in the system, with the formation of aprotic three- and tetravanadates in larger amounts at Z> 2,5. Crystals of composition: [N(C4H9)4]5V3O10·4H2O·C3H7ON, [N(C4H9)4]4V4O12·4H2O·2C3H7ON, [N(C4H9)4]6V10O28·4H2O·4C3H7ON; In4(V4O12)3·7H2O·3C3H7ON; In2V10O28·5H2O·5C3H7ON were obtained.

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