SPECIATION AND STABILITY OF POLYOXOMETALATES: NMR INVESTIGATION OF PW_{11} AND PMo_{11} BEHAVIOR IN AQUEOUS SOLUTIONS

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Polyoxometalates (POMs) are inorganic, discrete, nanoscale polyatomic metal-oxo anions, known for their diverse structures and solubility in polar media [1, 2]. Their well-defined molecular architectures, high charge density, redox activity make them particularly valuable for applications in solutions, especially in homogeneous catalysis and as biologically active agents beneficial to human health. Upon dissolution in aqueous media, POM anions can undergo protonation, hydrolysis, and occasionally redox processes, which influence the presence and activity of the species [2]. The aim of this study is to determine the optimal pH for the synthesis of transition-metal substituted Keggin types anions $[X^{3+}(H_2O)P^{V}M_{11}O_{39}]^{4-}$ ($X = Ga^{3+}$, Fe^{3+}, etc., $M = Mo^{VI}$, W^{VI}), which shape and charge are supposed to be crucial in cell membrane penetration with potential applications in medicine [3]. Considering the hydrolysis of X^{3+} transition metals and a pH-dependent transformation of monolacunary $[PW_{11}O_{39}]^{7-}$ (**PW_{11}**) and $[PMo_{11}O_{39}]^{7-}$ (**PMo_{11}**), a systematic study of POM speciation in solution is essential. The behavior of **PW_{11}** and **PMo_{11}** in aqueous solutions (10^{-2} M) at varying pH values was investigated using quantitative nuclear magnetic resonance (^{31}P NMR) spectroscopy, a widely accessible and effective method for studying solution-phase processes [4]. After investigating sodium **PW_{11}** solutions at various pH levels using ^{31}P NMR spectroscopy, it was observed that the **PW_{11}** anion remains its stability between pH 3 and 6. Below pH 3, protonation of **PW_{11}** is initiated, ultimately leading to the formation of $[PW_{12}O_{40}]^{3-}$ at pH 1.5. In turn, **PMo_{11}** is more stable than **PW_{11}** at lower pH values, being the predominant phase from pH 2 to 4. Below pH 1.5, $[PMo_{12}O_{40}]^{3-}$ anion is identified, while at pH above 5, a tri-lacunary anion $[PMo_9O_{31}(OH)_3]^{6-}$ appears. These results are crucial for optimizing synthesis conditions that involve templating metals such as Ga^{3+}, which undergo significant hydrolysis above pH = 2–3. The synthesis using **PW_{11}** as a ligand for Ga^{3+} is feasible at pH 3, whereas the synthesis with its molybdenum analogue, **PMo_{11}**, can be conducted at even lower pH levels, around 2–3, where Ga^{3+} hydrolysis is minimized.

References

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