STRUCTURE OF VANADIUM PHOSPHATE ANION IN SOLUTIONS FROM $^{17}$O, $^{51}$V AND $^{31}$P NMR DATA

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$^{17}$O, $^{51}$V and $^{31}$P NMR studies indicate that the anion structure of sodium vanadophosphate in an aqueous solution is close to that in crystals of the (CN$_3$H$_6$)$_6$HPV$_{14}$O$_{42}$7H$_2$O salt.

Методом ЯМР $^{17}$O, $^{51}$V, $^{31}$P показано, что структура аниона в водном растворе ванадофосфата натрия близка к структуре аниона в кристаллах соли (CN$_3$H$_6$)$_6$HPV$_{14}$O$_{42}$7H$_2$O.

Mixed P-Mo-V heteropolyacids (HPA) H$_{3+x}$PV$_x$Mo$_{12-x}$O$_{40}$ with a high content of vanadium (x $\geq$ 4) are the components of homogeneous catalysts for partial oxidation /1/ and according to Ref. /2/, Mo and V form a continuous set of anions with x = 0–12. The HPA anion has the Keggin structure at x = 0–3 (4 triplets of M$_3$O$_{13}$ octahedra around a PO$_4$ tetrahedron (Fig. 1)) /3–4/. Substitution of Mo$^{6+}$ by V$^{5+}$ increases the anion charge, hence the Keggin structure in high-vanadium HPA can be preserved only via anion protonation. The anion H$_8$PV$_{12}$O$_{40}$$^{7-}$ is assumed /5/ to contain eight non-salt-forming protons. According to Ref. /6/, the composition of the sodium salt anion is PV$_{12}$O$_{36}$$^{-}$, whereas in Na and K salts /7/ the compositions are PV$_{12}$O$_{36}$$^{-}$ and PV$_{14}$O$_{42}$$^{5-}$, respectively. In salts and solutions of vanadium phosphates according to Ref. /8/ the ratio P:V = 1:13 and 1:14. It is seen that the determination of the P:V ratio at a high content of vanadium in the HPA anion is not reliable on the basis of chemical analysis and to determine the total HPA composition, it is necessary to apply physical methods. The $^{51}$V and $^{17}$O NMR spectra of solutions of high-vanadium HPA and PV$_{12}$ /4, 9/ exhibit deviations in their anion structure from the Keggin model, but it appeared impossible to elucidate it. Structural studies of the mixed high-vanadium HPA and sodium vanadophosphate have not been carried out. A recent X-ray study of guanidine vanadophosphate /10/ has shown that its composition corresponds to the formula (CN$_3$H$_6$)$_6$HPV$_{14}$O$_{42}$7H$_2$O and the anion
structure is as in Fig. 1. NMR spectra confirm the existence of a similar structure in aqueous solution of sodium vanadophosphate as well.

To record NMR spectra, the solutions were prepared with a HPA concentration of 0.1-0.2 mol/l from crystals of sodium salts prepared by known methods /6, 7/ (according to the analysis, P:V = 1:13.4). The PMR spectrum at 80 K exhibits a narrow (< 3 G) line which is typical for the OH-groups and a broad line from the strongly bound molecules of water with the intensity ratio of about 1:10 /5/. NMR spectra of the solutions were recorded on a Bruker SXP-4-100 spectrometer at frequencies of 12.21, 36.44 and 23.66 MHz for $^{17}$O, $^{31}$P and $^{51}$V, respectively.

The $^{51}$V NMR spectrum of solutions consists of two lines (Fig. 2) upfield from VOCl$_3$ with chemical shifts (CS) of -529 and 590 ppm and an intensity ratio of about 1:5. The $^{31}$P NMR spectrum consists of a very narrow single line coinciding with H$_3$PO$_4$. It indicates that only one anion with a PO$_4$ tetrahedron inside the polyanion sphere is observed. The absence of the lines associated with the known isopolycompounds in the $^{51}$V and $^{17}$O spectra indicates that the same heteropolycomplex is observed at all nuclei.

A great difference in the CS of the $^{51}$V NMR lines (60 ppm) cannot be attributed to the protonation of a part of anions (as is shown according to the $^{51}$V NMR spectra of V$_{10}$O$_{28}$ /11, 12/), but indicates the structural nonequivalence of V atoms. The $^{51}$V NMR spectrum agrees well with the structure of the anion PV$_{14}$O$_{42}$ in the guanidinium salt /10/, which represents the Keggin anion PV$_{12}$O$_{40}$ with the ad-

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**Fig. 1. Structure of vanadophosphate anion**