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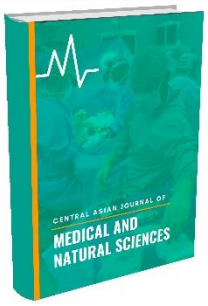

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INVESTIGATION OF THE PROCESS OF INTERACTION OF V(+5)WITH CAPROHYDROXAMIC ACID IN AQUEOUS ALCOHOL SOLUTIONS

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ABSTRACT: The article presents the findings of the study of the interaction of salt V(+5) with caprohydroxamic acid in water-alcohol solutions. The compositions of the resulting complex compounds were determined by the method of A.K.Babko, their instability constants in water and its mixtures with 20; 40; 60; 80 volume percent content of methanol, ethanol and propanol were calculated. It was found that the stability of complex compounds V(+5) increases with an increase in alcohol content in the mixture. The optical density of the solution at λmax = 450 nm is the highest in aqueous propanol solutions. It has been concluded that the data obtained can be used in the development of conditions for the determination of vanadium content by photocolorimetric method.

KEYWORDS: Ammonium vanadate, caprohydroxamic acid (CapHA), optical density, spectrophotometric method, instability constant of complex compounds, dielectric constant of solvents.

INTRODUCTION

Tungsten, molybdenum and vanadium are d-element analogues, which leads to their association in mineral raw materials and soil, biomaterials. Therefore, the analytical determination of one element in the presence of another presents great difficulties.

In this regard, a systematic study of the process of interaction of molybdenum (6+) [1,2], tungsten (6+) [3] with caprohydroxamic acid was carried out, and the data obtained were used to develop a photocolorimetric determination of molybdenum [4].

The remains of some plants and animals contain significant amounts of vanadium ions. Hemovanadin in blood contains up to 15% vanadium. Vanadium ions in body are involved in redox processes, contributes to the respiration process. The addition of small amounts of vanadate salt to the foods of pigs and cattle increases the productivity of animals [5]. In this regard, the determination of vanadium content in biomaterials, in the diet of animals is of particular interest.

Vanadium salts (+5) with benzhydroxamic acid in aqueous solutions, at pH=2 forms a colored complex compound with a maximum optical density in the region of λ_{max} = 450-500 nm, and the data obtained were used to develop a photocolorimetric method for determining vanadium [6].

The absorption spectra of solutions of the reagents and their mixtures were recorded on an EPS-3T instrument from Hitachi. FEK-56M was used to plot optical saturation curves. The values of dielectric constant (E) of water-alcohol mixtures were calculated using the formula given in [7]. The instability constants of complex compounds of vanadium with caprohydroxamic acid in water-alcohol solutions were calculated by the methods of equilibrium shift [8] and R. Foster [9].

RESULTS AND THEIR DISCUSSION

Spectrophotometric investigation of solutions of NH_4VO_3, CapHA and their mixtures in aqueous-methanol, aqueous-ethanol and aqueous-propanol solutions containing 20,40,60,80 volume percent alcohols at pH = 2 showed that the maximum absorption band at λ_{max} = 220 nm is characteristic for CapHA solutions, and the ammonium vanadate solution has an absorption band at λ_{max} = 260 nm. Their mixtures at pH = 2 in aqueous solution have λ_{max} = 465 nm. In water-alcohol solutions, with an increase in the volume percentage of alcohol content, a shift of λ_{max} towards the short-wavelength region of the spectrum (up to 450 nm) is observed, while a noticeable increase in the intensity of the absorption band is observed. In water-propanol solvents, a shift in the absorption band and an increase in its intensity with an increase in the propanol content is observed up to 40 volume % (in water-ethanol up to 60 and water-methanol up to 80 volume % of ethanol, respectively) in water. A further increase in the propanol content does not affect the intensity and the position of λ_{max} = 450 nm of the band maximum. This fact is apparently explained by the interaction of vanadium caprohydroxomate with alcohol molecules in water-alcohol solvents, as a result of which compounds of other compositions can be formed.

*Table 1 shows the data of the dependence of the optical density (OD) of solutions on the concentration of CapHA in water-propanol solutions (the data were obtained in Cv (5+)=1.57*10^{-4} mol/l, PhEC-56m, light filter No. 4, the cuvette thickness =10 mm).*

Table 1

№	CCapHA * 10^{-2}mol/l	Value of the optical density (D) at 20,40,60, and 80 volume percentage of propanol in the systems			
		20	40	60	80
1	0,02	0,035	0,100	0,120	0,160
2	0,04	0,063	0,177	0,228	0,305
3	0,06	0,115	0,260	0,332	0,418
4	0,08	0,144	0,312	0,395	0,469
5	0,12	0,218	0,394	0,455	0,514
6	0,16	0,271	0,438	0,488	0,535
7	0,20	0,317	0,470	0,503	0,547
8	0,30	0,375	0,501	0,528	0,561
9	0,40	0,410	0,518	0,541	0,568
10	0,50	0,430	0,528	0,548	0,569

11	0,60	0,450	0,535	0,553	0,570
12	0,80	0,467	0,545	0,561	0,571
13	1,00	0,476	0,554	0,565	0,570
14	1,20	0,482	0,561	0,568	0,572
15	1,60	0,485	0,568	0,572	0,571

It can be seen from the data in the table that in all studied systems, with an increase in volume % of the propanol content, the concentration of the CapHA, at which the OD of the solution reaches the maximum value, decreases. Apparently, with the decrease in the dielectric constant (DC) of the medium, the equilibrium of the reaction of complex formation shifts towards the complete binding of vanadium (5+) into the complex with CapHA.

Using the data in Table 1, the composition of complex compounds of vanadium (5+) CapHA was determined by the method of A.K.Babko [8]. Based on the obtained results, it is concluded that in water-propanol systems, the process of complex formation occurs stepwise and, depending on the content of C_{CapHA} in the solution, the compounds with molar ratios V(+5) with CapHA 1:1 or 1:2 are respectively formed with small and moderate CapHA contents [Fig. 1].

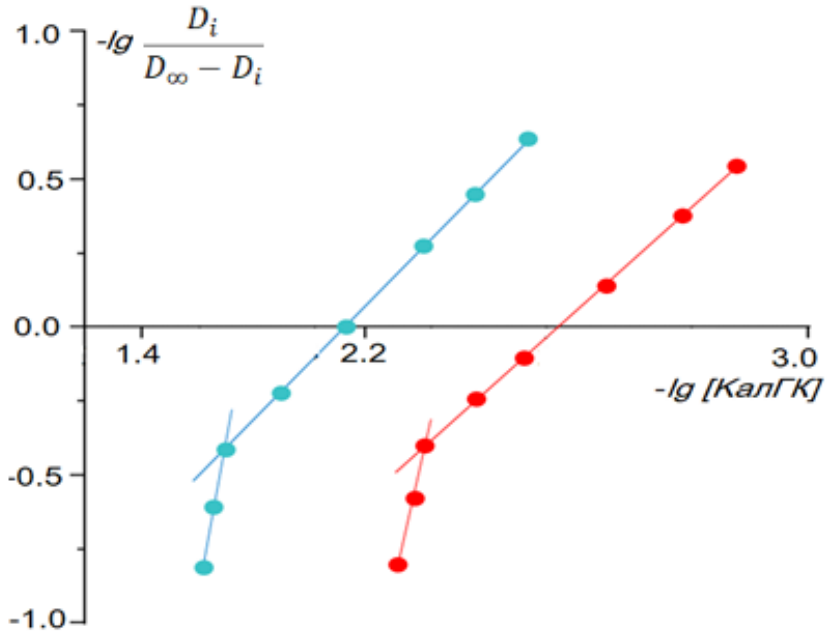

Fig.1. Determination of molar ratios of compounds V(+5) with CapHA in aqueous (1) and 40 vol. % propanol content solutions

Depending on the content of the ligand in the solution, there are compounds of a certain composition, which makes it possible to calculate the values of the instability constants of the complexes V(+5) with CapHA.

The instability constants of the complex compounds were calculated by the method of equilibrium shift [8,9]. The dependence of the pK instability of complexes V(+5) on 100 / DP the values of water-

propanol mixtures have a graphical dependence shown in Fig.2, which is markedly different from the direct character.

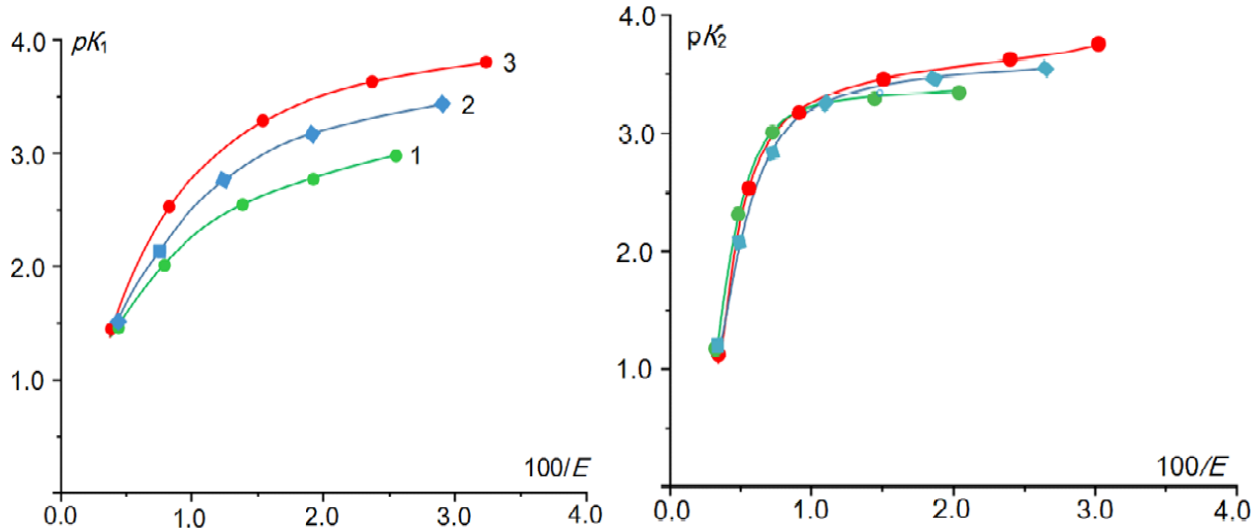

Fig.2. Dependence of concentration of pK_1 and pK_2 instability of complex compounds V(+5) with CapHA on 100/E medium for water-methanol (1), water-ethanol (2) and water-propanol solutions.

This is the result of a significant influence of the chemical and physical nature of the solvent on the stability of [10] complex compounds of vanadium (+5) with CapHA. The DP values for water-alcohol mixtures of the solvents were calculated according to the formula given in [7]

$$E = \frac{V}{100} E_1 + \frac{100-V}{100} E_2$$

where: V and E_1 are the volume percentages and DP of the first liquid, and (100-V) and E_2 are the second.

Determination of the composition of vanadium complexes with CapHA in water-alcohol solvents shows that the shift from λ_{max} = 450 nm is not a consequence of a change in the composition of vanadium complex compound exists in an aqueous solution. Apparently, a sharp shift of λ_{max} = 465 nm to 450 nm at low alcohol contents and an increase in the OD of the solution as the volume content of the non-aqueous solvent increases. This is the result of the formation of solvate complexes of vanadium caprohydroxamate with alcohol molecules.

CONCLUSIONS

Spectrophotometric studies of the process of complex formation of ammonium vanadate and CapHA in water-alcohol systems have shown that the resulting solvate complex is most stable in a mixture of water with 40 or more volume percent propanol content. In this system, the OD of the solution is the highest and stable. These data can be used in the development of a photocolorimetric method for determining the vanadium content in samples.

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