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STUDY OF THE REACTION OF POLYSORBATE-20 WITHHETEROPOLYACIDS OF THE KEGGIN STRUCTURE BY THE PHOTOMETRIC METHOD

Mironyak M.O.[1], Volnyanska O.V.[1], Manzuk M.V.[1], Labyak O.V.[1], Nikolenko M.V.[1], Kovalenko V.L.[1, 3], and Kotok V.A.[1, 2, 3]
[1]Department of Analytical Chemistry and Chemical Technology of Food Additives and Cosmetics, Ukrainian State University of Chemical Technology, Gagarin Ave, Dnipro, Ukraine
[2]Department of Processes, Apparatus and General Chemical Technology, Ukrainian State University of Chemical Technology, Gagarin Ave, Dnipro, Ukraine
[3]Competence Center "Ecological Technologies and Systems", Vyatka State University, Moskovskaya St., Kirov, Russian Federation
E-Mail: valeriy_e-ch@ukr.net

ABSTRACT

In this work, the effect of acidity of the working solution on the properties of polyoxyethylene monosorbitan laurate was investigated by a spectroscopic method. Since the substance under study does not absorb light waves in the visible region of the spectrum, the study was conducted in the ultraviolet region. The effect of solution pH on the reaction of the interaction between polysorbate-20 and barium salt to form a cationic particle of polysorbate-barium was also studied by spectrophotometric method. The possibility of reaction between the obtained cationic particle of polysorbate-barium and the anions of 12-molybdophosphate and 12-tungstenphosphate heteropoly acids was investigated and the nature of the bond in the obtained compounds was determined. The composition of the complexes and the ratio of the components were determined by the saturation method at a wavelength of 265 nm. The results of these studies can be used in the development of a new method for the determination of polysorbate-20 in industrial products ionometric method using potentiometric sensors reversible to polysorbate-20.

Keywords: 12-molybdophosphate heteropolyacid, 12-tungstenphosphate heteropolyacid, polyoxyethylene sorbitans, polysorbate, polyoxyethylene monosorbitan laurate, spectrophotometry, surfactants, tween.

INTRODUCTION

Polysorbate-20 (polyoxyethylene monosorbitan laurate), an ester of sorbitan and lauric acid, is a non-ionic surfactant.

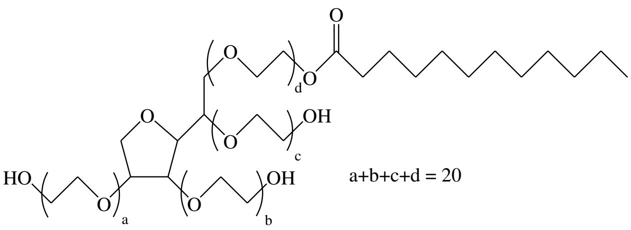

Figure-1. Polysorbate 20 structural formula.

Polysorbates ("tweens")are widely used in industry and medicine as antistatic agents, defoamers, emulsifiers and solubilizers, fiber softeners, dispersing agent and substance that contributes to the dissolution of both water-soluble in the fat phase and waxes in the pharmaceuticals, and fat-soluble in the aqueous phase, in animal feed and soil treatment. [1-6].

In the food and cosmetics industries, polyoxyethylene is used to create fine dispersions of essential oils and fat-soluble flavors in aqueous "pseudo-solutions", in foaming compositions, as emulsifiers in the production of ice cream, confectionery, margarines, canned foods. [7-9]. In acidic products, these compounds play the role of foaming agents and foam stabilizers, in fats antifoaming agents.

The identification of polysorbates in industrial products is carried out by IR spectroscopy [10]. High-performance liquid chromatography is used to determine the quantitative content of oxyethylated sorbitans [11-12].

The results of previous studies show the high efficiency of ion-selective electrodes using heterogeneous acids of the Keggin structure in the quantitative determination of the content of various organic compounds [13-19]. For the correct selection of the counterion of the electrode-active substance of the electrode membrane and to determine the optimal conditions for obtaining the ionic associate, a spectrophotometric study of the reactions of the interaction of the selected object with heteropoly acids is necessary depending on the pH of the solution and the type of heteropolyacid. Also spectrophotometric method allows determining the type of bond and the ratio of the reacting components in the resulting compound [20].

MATERIALS AND DEVICES

Spectrophotometric studies carried out with the spectrophotometer SF-46 (UV- spectra).

The following reagentsare used in the work:

- 12-molybdophosphate acid, $H_3PMo_{12}O_{40}x26H_2O$ (analytically pure);
- 12-tungsten phosphate acid, $H_3PW_{12}O_{40}x31H_2O$ (analytically pure);
- polysorbate-20,$C_{58}H_{114}O_{26}$ (analytically pure);

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- sodium hydroxide (analytically pure);
- chloride acid (conc.) (analytically pure);
- barium nitrate (analytically pure).

EXPERIMENTAL PART

To determine the possibility of obtaining the ionic associate of the determined organic cation with the heteropolyanion, it is necessary to study the nature of the interaction and determine the optimal reaction conditions. Ethoxylated sorbitans (including polysorbate-20) are non-ionic surfactants and, when dissolved in water, do not form positively charged ions. Therefore, to obtain associates with 12-molybdophosphate (MPhA) and 12-tungstenphosphate (TPhA) heteropolyacids, a cationic complex of polysorbate-20 with barium ions was previously obtained.

To select the optimal reaction conditions using a spectrophotometric method, we studied the effect of solution acidity on the properties of polysorbate-20. The ionic associates of the investigated substances with heteropolyacids of the Keggin structure cannot be obtained in highly alkaline solutions since the heteropolyacids are destroyed. The spectral characteristics of the polysorbate-20 solutions were recorded with a solution's own acidity (pH = 6) and a change in pH to an acidic area (pH = 4) and an alkaline (pH = 8) area. Absorption spectra were recorded in the range of 200–350 nm in quartz cuvettes with a layer thickness of 1 cm. A distilled water was used as a solvent and reference solution in all analyzes (Figure-2).

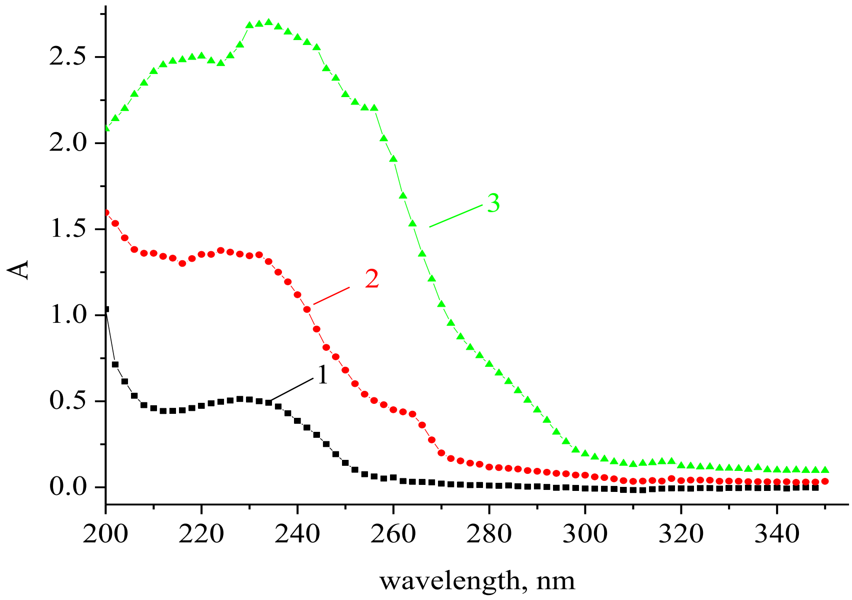

Figure-2. UV absorption spectrum of PS-20 at pH = 6 (1), pH = 4 (2) and pH = 8 (3).

The obtained UV absorption spectra of polyoxyethylene sorbitan monolaurate aqueous solutions, regardless of solution acidity, show the absorption maxima of average intensity at a wavelength of 220 nm ($n \rightarrow \pi^*$ transition characteristic of esters) and a shoulder at 260 nm (Table-1).

Table-1. The spectral characteristics of polysorbate-20 depending on pH.

pH of the solution	wavelength, nm	$E_{exp.}$, l·mol^{-1}·cm^{-1}
4	225	270
	260 (shoulder)	90
6	228	102
	260 (shoulder)	11
8	220 (shoulder)	500
	235	540
	260 (shoulder)	380

The spectral characteristics of polysorbate-20 with barium ions with its own acidity and change of

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acidity into acid and alkaline areas were recorded in order to study the effect of acidity on the reaction of the interaction of polysorbate-20 molecules with barium ions (Figure-3).

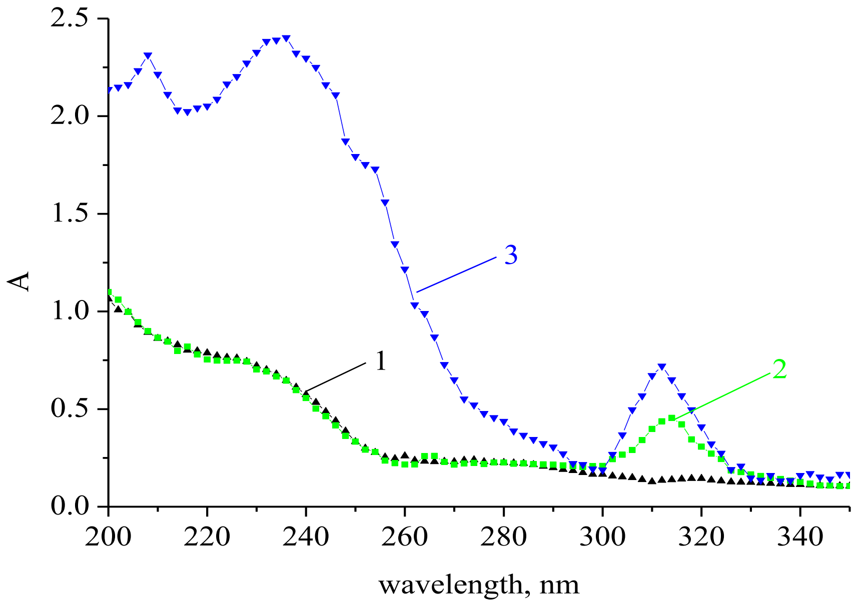

Figure-3. UV absorption spectrum of the cationic PS-Ba^{2+} complex at pH = 4 (1), pH = 6 (2) and pH = 8 (3).

Table-2 shows the spectral characteristics of the cationic complex of polysorbate-20 with barium ions, depending on the acidity of the studied solution.

Table-2. Spectral characteristics of the cationic complex PS-Ba^{2+} depending on pH.

pH of the solution	wavelength, nm	$E_{exp.}$, $l\cdot mol^{-1}\cdot cm^{-1}$
4	222 (shoulder)	1550
	260	520
	320 (shoulder)	290
6	222 (shoulder)	1490
	265	518
	314	910
8	208	4620
	236	4800
	260 (shoulder)	2430
	315	1200

The absorption bands at 220 and 265 nm are preserved in the spectral characteristics with the addition of barium ions to polysorbate-20 (Table-2). This fact indicates the chromophore system of the polysorbate molecules remains unchanged and the absorption significantly increases. An additional absorption band appears at 315 nm which is remained in the alkaline area and almost disappears when the solution is acidified to pH = 4 during the interaction reaction of polysorbate with barium ions with its own acidity.

The spectral characteristics of the complexes of ionic associates (IA) of the PS-Ba^{2+} cationic particle with MPhA and TPhA in the UV area of the spectrum were recorded from pH in order to study the effect of solution acidity on the reaction of the interaction of the cationic PS-Ba^{2+} complex with ions of the 12-molybdophosphate and 12-tungstenphosphate heteropolyacids and to determine the optimal reaction conditions.

After the measurements, it was found that the optimum acidity value of the test solution for the formation of the PS-Ba^{2+}-MPhA associates is 4 and 8 pH units (Figures4,5), because interaction with the cationic particle PS-Ba^{2+} with 12-molybdophosphate heteropolyanion does not occur at the polysorbate-20 solution's own acidity (pH = 6).

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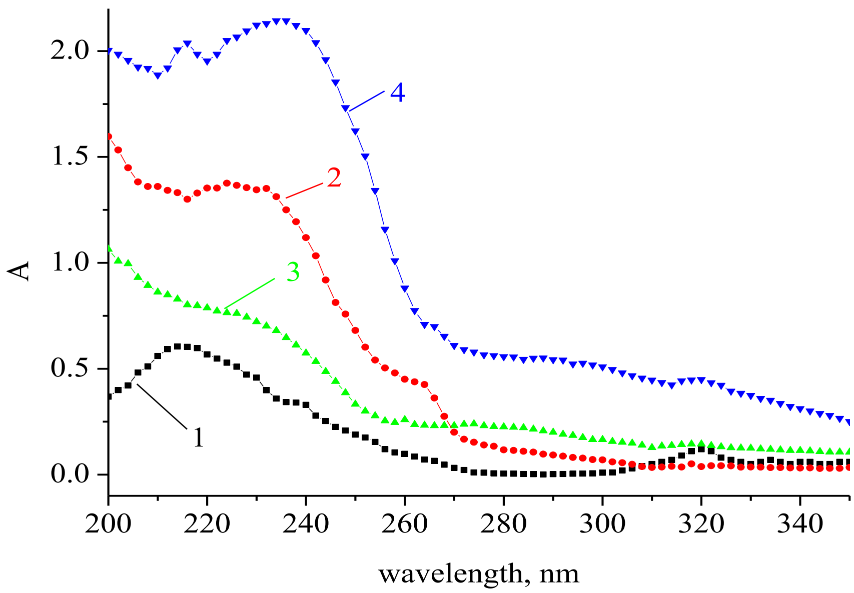

Figure-4. Spectral characteristics of the investigated solutions at pH = 4:1 - MPhA; 2 - cationic complex PS-Ba^{2+}; 3 - PS-20; 4 - associate PS-Ba^{2+} - MPhA.

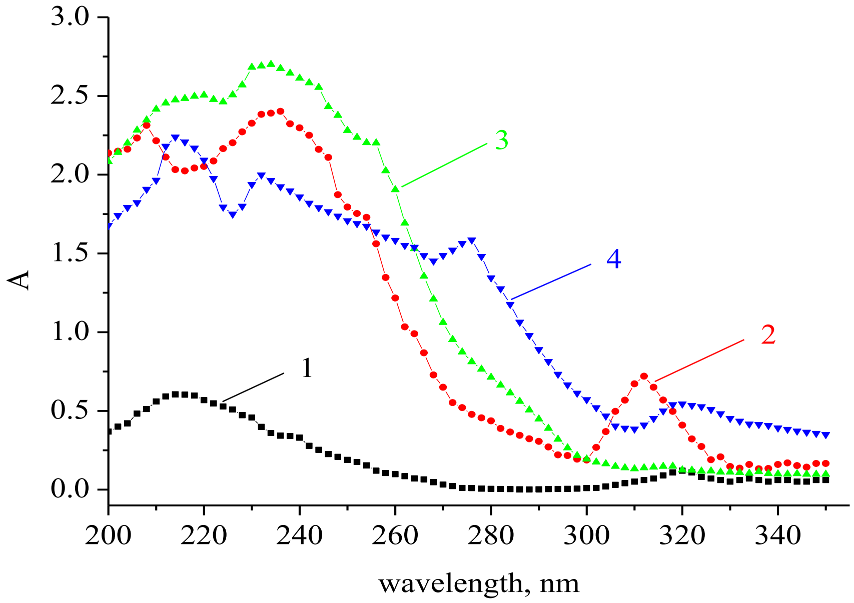

Figure-5. Spectral characteristics of the investigated solutions at pH = 8: 1 - MPhA; 2 - cationic complex PS-Ba^{2+}; 3 - PS-20; 4 - associate PS-Ba^{2+} - MPhA.

The absorption spectrum of the 12-molybdophosphate heteropolyacid has a characteristic intense absorption band at 207 - 220 nm, which corresponds to electron transfer from the orbitals localized on Oxygen atoms to the metal atom of the final bonds O = Me. There are also two bands of medium (260 - 280 nm) and weak (320 - 330 nm) intensities, which correspond to charge transfer along O - Me - O bridge bonds

Similar results were obtained when studying the effect of pH on the reaction of the interaction of a cationic particle PS-$Ba^{2+}$with a heteropolyanion of 12-tungsten phosphate acid. (Figures 6,7).

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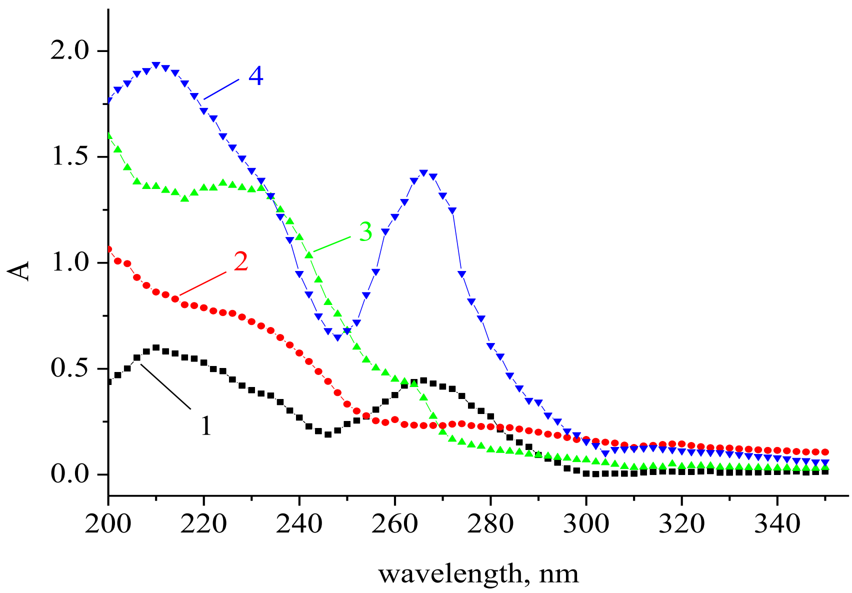

Figure-6. Spectral characteristics of the investigated solutions at pH = 4:1 - TPhA; 2 - cationic complex PS-Ba^{2+}; 3 - PS-20; 4 - associate PS-Ba^{2+} - TPhA.

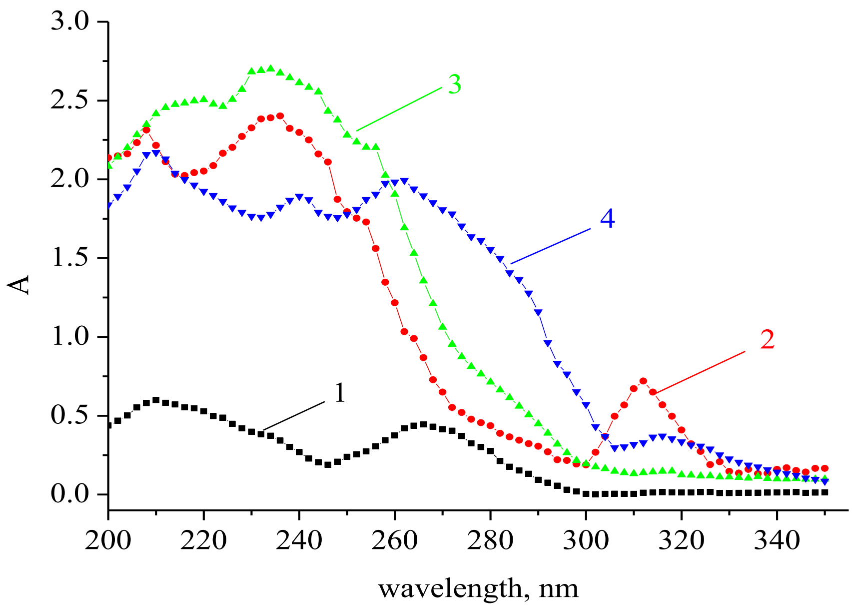

Figure-7. Spectral characteristics of the investigated solutions at pH = 8:1 - TPhA; 2 - cationic complex PS-Ba^{2+}; 3 - PS-20; 4 - associate PS-Ba^{2+}-TPhA

The polysorbate-20 is characterized by low-intensity absorption bands which increase with the formation of the cationic complex of polysorbate with barium ions in the 200-350 nm area as shown by the obtained experimental data (Table-3). The obtained ionic associates with MPhA leads to a significant increase in the UV absorption area, especially in the acidic region. This result can be used to develop of the spectrophotometric methods for the determination of polysorbate-20 in the form of a complex with 12-molybdophosphate heteropolyacid in the future.

The obtained UV spectra of aqueous solutions of associates PS-Ba^{2+}-MPhAand PS-Ba^{2+}-TPhA contain absorption bands characteristic of both polysorbates, its

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cationic complex with barium ions, and of heteropolyacids. Therefore the chromophore system doesn't change during the reaction which with the observed deviation from the additivity law indicates about associative nature of interaction.

Table-3 shows the obtained experimental data of the absorption spectra of polysorbate-20, its cationic complex with barium ions, 12-molybdophosphate and 12-tungstenphosphateheteropolyacids (MPhA and TPhA) and the resulting ionic associates.

Table-3. Spectral characteristics of the studied substances depending on pH.

pH	Substance	wavelength, nm	$E_{exp.}$, $l \cdot mol^{-1} \cdot cm^{-1}$
-	$H_3PMo_{12}O_{40}$	215	60000
		235	34000
		320	12000
-	$H_3PW_{12}O_{40}$	210	58000
		265	43000
4	PS	225	270
		260 (shoulder)	90
	$PS-Ba^{2+}$	222 (shoulder)	1550
		260	520
		320 (shoulder)	290
	$PS-Ba^{2+}$-MPhA	215	40760
		235	42860
		265	14180
		320	8980
	$PS-Ba^{2+}$-TPhA	210	38750
		265	28560
		315	2570
8	PS	220 (shoulder)	500
		235	540
		260 (shoulder)	380
	$PS-Ba^{2+}$	208	4620
		236	4800
		260 (shoulder)	2430
		315	1200
	$PS-Ba^{2+}$-MPhA	215	44780
		232	39980
		275	31720
		315	10880
	$PS-Ba^{2+}$-TPhA	210	43400
		240	37850
		262	39850
		317	7420

A spectrophotometric method was used to study the composition of the associate formed by the interaction of the 12-molybdophosphate heteropolyacid with the cationic $PS-Ba^{2+}$ particle, as well as to establish the ratio of the reacting components.The molar ratio method was used to determine the composition of the complex and the ratio of reacting components in the reaction.To determine the possible composition of the resulting associate, a

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solution of the cationic particle of PS-Ba^{2+} was saturated with a solution of heteropolyacid.

A polysorbate-20 solution with 2.5 ml at $5.0\cdot10^{-4}$ mol/l concentration, 2.5 ml of a barium nitrate solution with a concentration of $1.0\cdot10^{-3}$ mol/l were added in 8 volumetric flasks with a capacity of 25.0 ml. After that an aqueous solution of the 12-molybdophosphate heteropolyacid (respectively 1.0; 2.0; 3.0; 4.0; 5.0; 6.0; 7.0; 8.0 ml) with a concentration of $1.0\cdot10^{-4}$ mol/l was added into flasks and make up to the mark with distilled water. The measurements of the absorption of the obtained solutions at λ = 265 nm were carried out. According to the results, a saturation curve was built (Figure-8) and the ratio of the reacting components was determined.

The ratio of the reacting components in the interaction reaction of the cationic complex PS-$Ba^{2+}$with the heteropolyanion MPhA is 3:2, respectively, an ionic associate of the composition $(PS\text{-}Ba^{2+})_3(PMo_{12}O_{40})_2$ is formed. It was concluded based on the obtained experimental data. These results confirm the previously proposed theoretical assumptions.

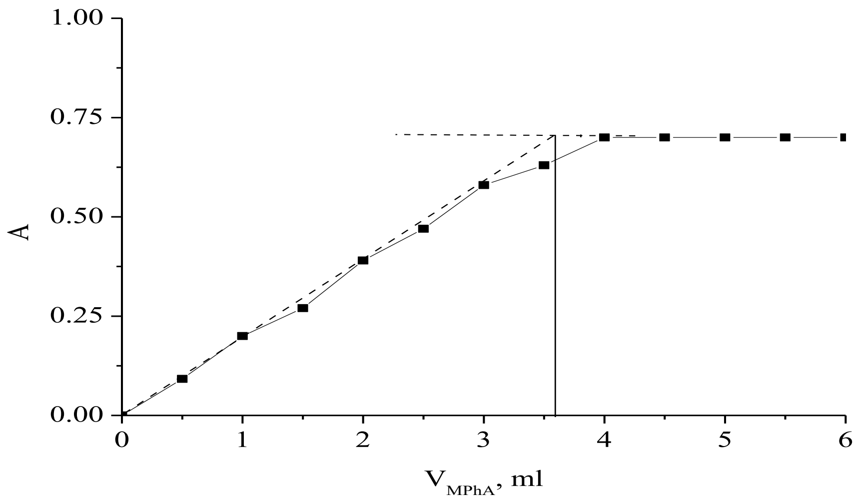

Figure-8. Saturation curve of the cationic complex PS-$Ba^{2+}$with MphA.

It is similarly determined that the ratio of the reacting components in the interaction of the cationic complex of PS-Ba^{2+} with 12-tungstenphosphate heteropolyacid is 3: 2, that is, the ionic associate of the composition $(PS\text{-}Ba^{2+})_3(PW_{12}O_{40})_2$ is formed.

4. CONCLUSIONS

a) The effect of solution acidity on the properties of polyoxyethylene monosorbitan laurate was investigated by UV spectroscopy.

b) The reaction of the interaction of polysorbate-20 with barium ions and the properties of the obtained cationic particle as a function of pH were investigated.

c) The reactions of the interaction of the obtained cationic particle with the anions of heteropoly acids of the Keggin structure were investigated by the spectroscopic method. The associative nature of the interaction of the reacting compounds was confirmed.

d) The composition of the obtained associates formed by the interaction of the cationic particle of polysorbate-barium with the anions of 12-molybdophosphate and 12-tungstenphosphate heteropolyacids was investigated by the method of molar relations. It is established that the ratio of the reacting components in the reaction is 3:2, that is, ionic associates of the composition $(PS\text{-}Ba^{2+})_3(PMo_{12}O_{40})_2$ and $(PS\text{-}Ba^{2+})_3(PW_{12}O_{40})_2$ are formed.

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