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SORPTION PROPERTIES OF MATERIALS BASED ON POLYVINYLPIRROLIDONE COPOLYMERS

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Abstract. Sorption properties of polyvinylpyrrolidone copolymers regarding to different acid-base indicators, as well as heparin and iodine have been investigated. The amount of sorption active centers of synthesized copolymers depends upon synthesis conditions, namely upon temperature and initiator amount, and is determined by the nature of sorbates and copolymers functional groups.

Keywords: copolymers, polyvinylpyrrolidone, sorption, indicators, polystyrene, polymethylmethacrylate.

1. Introduction

The problems of polyvinylpyrrolidone (PVP) copolymers synthesis and usage are very important. These copolymers are widely used in pharmacy, medicine, food industry, that is connected, in its turn, with the whole complex of valuable specific properties peculiar to the mentioned copolymers: high biocompatibility with living cells, selective sorption ability, non-toxicity, thromboresistance, high adhesive properties and coloration ability [1-3].

Sorption properties of PVP copolymers containing polystyrene (PS) or polymethylmethacrylate (PMMA) have not been investigated yet [2]. It should be noted that PVP copolymers are widely used as films: various membranes, insulation bands, film sorbents, etc [3]. Mechanical properties are of relevant aspects, as sorption characteristics. Latex properties depending upon synthesis conditions determine the sorption properties of film materials on their basis.

The aim of the present work was to determine the sorption ability of PVP copolymers, nature and amount of active sorption centers depending upon synthesis conditions and nature of sorbates.

2. Experimental

Among all methods allowing to estimate the sorption ability of solids relative to low-molecular substances the method based on acid-base titration is the most widely used. This method allows to determine the value of sorption ability as well as the effective sorption centers and functional groups participating in the sorption process.

Table 1

Functional groups of indicators and their characteristics

Indicator	pK_a	Functional groups				
Brilliant green (BG)	+1.3	HSO_4^-	$\text{>N}^+=$		>N	
Methyl-orange (MO)	+3.45	$-\text{SO}_3^-$	>N=N		>N	
Methyl-red (MR)	+5.0	>N	>N=N		>C=O	>C=O^-
Bromothymol blue (BB)	+7.3	>C=O	$-\text{OH}$		$-\text{Br}$	
Methylene blue (MB)	+9.7	>N	>N=	>S	=N^+	Cl^-

PVP copolymers were synthesized at 343 K *via* emulsion polymerization of methylmethacrylate and styrene in the presence of PVP and water-soluble radical initiators. To establish the amount of active sorption centers of PVP copolymers, a series of indicators was selected depending on nature of functional groups and pK_a value. Indicators used for the experiments, their functional groups and main characteristics are listed in Table 1.

PVP sorption ability relative to the indicators was determined by photocolorimetry [4]. The indicator concentration in water-alcohol mixture was $(2-6) \cdot 10^{-4}$ M and the film mass was 3–6 mg. Measurements for every indicator were carried out at definite wave length for 70–150 min.

3. Results and Discussion

Kinetic curves of PMMA-gr-PVP and PS-gr-PVP copolymers sorption ability are represented in Fig. 1 using values of active centers amount (q) in copolymers relative to different indicators.

One can see from Fig. 1 that the amount of active sorption centers depends upon the indicator nature. For both copolymers the highest activity is shown using methyl-red and brilliant green indicators and the lowest one – using methyl-orange. On the basis of the mentioned above we may state that sorption ability of investigated copolymers has specific selective character and is determined most of all by the presence of pyrrolidone cycles in copolymers, namely carbamate groups.

In order to establish the effect of pK_a on the amount of active sorption centers as well as to compare copolymers sorption ability we determined the boundary amount of sorption active centers (q_{max}) and sorption value (A). The obtained results are shown in Figs. 2 and 3.

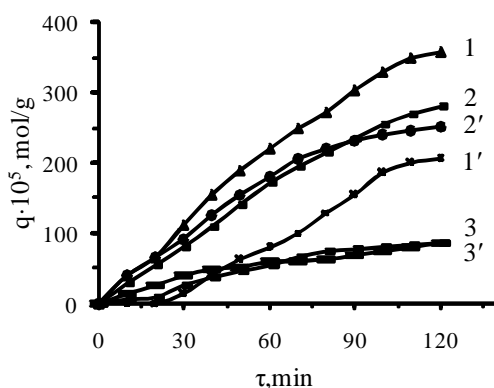


Fig. 1. Kinetic dependencies of active centers amount (q) in copolymers relative to different indicators: BG (1, 1'); MR (2, 2'); MO (3, 3'). PMMA-gr-PVP (1, 2, 3) and PS-gr-PVP (1', 2', 3)

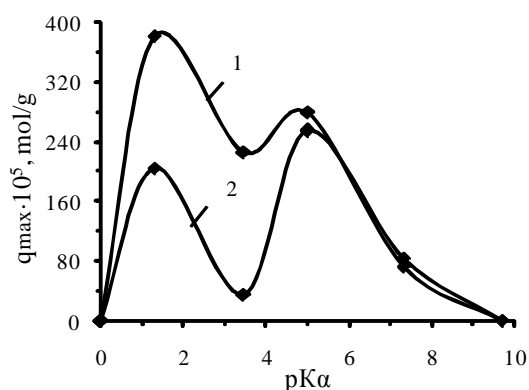


Fig. 2. Dependence of sorption centers amount upon indicators pK_a : PMMA-gr-PVP (1) and PS-gr-PVP (2)

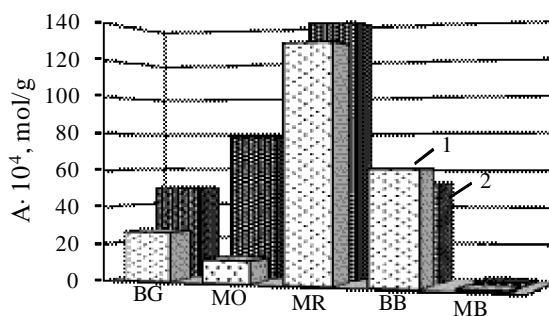


Fig. 3. The effect of indicators nature upon copolymer sorption: PMMA-gr-PVP (1) and PS-gr-PVP (2)

It is obvious that within the range of pK_a from 0 to 5 the amount of sorption active centers is greater for PS-gr-PVP copolymer than that for PMMA-gr-PVP and it is practically the same within the range of 5–10. The essential difference between sorption abilities may be explained by peculiarities of film forming from the latex. It is known [5, 6] that during film formation capillary forces are formed between latex particles which directly contact with each other and consequently get sluggish. These forces compress and deform the particles; they also reduce the porosity of film upper layer. Besides capillary forces, the forces caused by intermolecular interactions, interfacial and surface tensions affect film formation from PMMA-gr-PVP-latex. Intermolecular interactions occur, first of all, as a result of possible interactions due to the PVP carbamate groups and PMMA carboxyl groups able to interact with sorbates and fix them over the film surface. Both phenomena decrease the sorption ability of PMMA-gr-PVP films compared with PVP-polystyrene (PVP-PS) ones.

From the results analysis presented in Fig. 2 the extremal character of the dependence between the amount of active sorption centers and pK_a is evident. It is typical

for both PVP-PS and PVP-PMMA copolymers.

It is necessary to pay attention to those functional groups which are capable to participate in the sorption process and obviously will affect the process on the part of copolymers, as well as of indicators. We can see from Table 1 that several indicators have the same groups (BG and MB— =N^+ and —N ; MR and MO— —N and —N=N). At the same time all indicators have different amount of benzene rings in their structures. However, as it was mentioned above, all investigated indicators have essential difference in sorption ability on PVP copolymers.

It is known [6] that in neutral and alkali media pyrrolidone links of PVP may be in two different forms and the ratio between these forms in macromolecule is influenced by a series of factors: structural and conformational changes in macromolecules, the presence of additional ingredients in the aqueous solution, temperature, difference between values of hydrate shells around pyrrolidone cycles. Apparently the introduction of indicators into the aqueous solution also affects the mentioned ratio, hence the change of sorption characteristics. It should be noted also that in the acid medium PVP hydrolyzes to the poly-N-vinyl- γ -aminobutyric acid.

Thus, investigated PVP copolymers due to the presence of PVP links in their structure may have different functional groups and the indicator nature will affect the ratio between them.

Taking into consideration all mentioned above we examine the extremal dependence between the amount of active sorption centers and pK_a of the indicator (Fig. 2). Brilliant green has the first maximum. Such enhanced activity of the indicator, which has the same functional

groups —N and =N^+ as the indicator with the least activity (MB) may be explained by two reasons. The first one is the possibility of pyrrolidone cycles hydrolysis in the presence of BG which gives the acid reaction. At

the same time —C=O group of poly-N-vinyl- γ -aminobutyric acid is capable to interact with BG, even *via* ionic mechanism. There is no hydrolysis in the presence of MB which has an alkali reaction. The second reason is the presence of anions in the indicator solutions: HSO_4^- in BG and Cl^- in MB. They may block copolymer functional groups in different ways.

The essential difference between sorption ability of methyl-orange and methyl-red may be explained by greater sorption susceptibility on PVP copolymers of group

compared with SO_3^- group of MO.

Thus, the obtained results open up the possibilities of directional purposeful selection of substances during sorption on PVP copolymers. At the same time the addition of water-soluble polymers to latexes at film-formation stage essentially change the film structure, especially its porosity, resulting in the change of sorption and penetrating abilities.

So we investigated sorption abilities of synthesized copolymers by adding PVP (further called “free” PVP) at the film-formation stage. Another reason was the fact that PVP improves mechanical properties (films made of synthesized copolymers have insufficient mechanical strength). The obtained results are shown in Fig. 4.

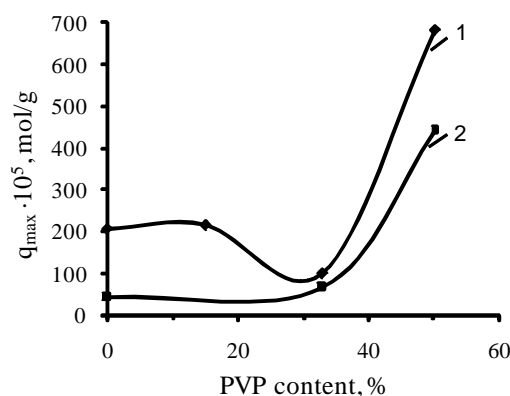


Fig. 4. The effect of “free” PVP on the amount of PMMA-gr-PVP sorption centers. Indicators: BZ (1) and MO (2)

The addition of PVP to the composition leads to the essential change of sorption ability at some concentrations. In our opinion the reason is the change of pores amount in the films, since “free” PVP may be partially washed out during films preparation; and the change of sorption centers activity as the result of their blocking by PVP carbamate groups.

It should be noted that conditions of copolymers synthesis also affect their sorption ability. Table 2 presents the sorption curves of films based on PS-gr-PVP copolymers synthesized at different temperatures and different amounts of initiator (potassium persulphate).

Table 2
Effect of polymerization temperature and initiator concentration on PS-gr-PVP sorption ability

$C_{in.}, \%$	$T_{pol.}, K$	$q_{max} \cdot 10^5, \text{mol/g}$
0.5	333	225
0.8	333	284
1.4	333	360
1.4	323	400

The increase of polymerization temperature decreases the copolymer sorption ability. The reason is the smaller amount of PVP free fragments in the synthesized copolymer at higher temperatures and greater sizes of latex particles. The results from Table 2 show that the increase of initiator concentration also increases copolymer sorption ability. The reasons are the same as mentioned above.

The next step of our experiments was to investigate sorption characteristics of PMMA-gr-PVP and PS-gr-PVP grafted copolymers obtained under heterophase conditions relative to biologically active compounds (heparin and iodine).

To saturate films based on the mentioned copolymers by heparin they were previously washed by the physiological solution (9.0 g of NaCl for 1 l of water), sustained for 24 h in glycerin in a buffer solution (1M of glycine solution in 1 l of water containing 5.8 g of NaCl, pH = 2.7) and placed in the glycine buffer solution containing $25 \cdot 10^4$ of heparin units for 1 l.

The amount of heparin adsorbed by the film is estimated by its decrease in the buffer solution. The amount of washed out heparin is determined after samples stay in the physiological solution for 24 h. The obtained results are represented in Table 3.

Table 3

Heparin and iodine sorption by synthesized copolymers

Copolymer	S_{heparin} , unit/m ²	$S_{\text{iodine}} \cdot 10^2$, mol/g
PMMA-gr-PVP	31250	31,8
PS-gr-PVP	301000	35,7

Investigated PVP copolymers have high sorption ability relative to heparin. At the same time heparin sorbed by films is stable for the physiological solution action for a long time (24 h). Films from PS-gr-PVP copolymer have the greater amount of active sorption centers relative to heparin compared with those from PMMA-gr-PVP. The explanation is the presence of $-\text{O}-\text{SO}_3^-$, $-\text{OH}$, $-\text{C} \begin{array}{l} \text{=O} \\ \text{O} \end{array}$.

>NSO_3^- functional groups in heparin. These groups may be sorbed by investigated copolymers (Table 1). Due to the less mobility of heparin macromolecules caused by their greater sizes (compared with low-molecular compounds) the formation of more stable intermolecular interactions of ion origin is more probable. The $-\text{O}-\text{SO}_3^-$, $-\text{OH}$, groups of heparin and the group of PVP most probably participate in the intermolecular interactions. The presence of group is explained [1] by partial hydrolysis of pyrrolidone cycle in the acid medium.

The experimental results confirm the possibility of the mentioned copolymers use for the production of articles contacting with blood. They will have high thromboresistance and stable in time properties.

At the same time the sorption ability of antiseptics and medical insulation films relative to medical products, especially to iodine is of great interest. Therefore, we investigated the sorption ability of synthesized copolymers relative to the mentioned antiseptic.

It is known [8] that PVP with iodine may form a stable complex where iodine loses its toxicity and ability to burn living tissue but preserves its high antibacterial activity.

The experimental results are represented in Table 3. Both copolymers have sufficiently high sorption properties relative to iodine and they may be controlled by synthesis conditions, including polymerization temperature, changing the structure of synthesized copolymers (graft degree) or sizes of latex particles.

4. Conclusions

Thus, investigations concerning sorption ability of PVP copolymers show that the amount of active sorption centers depends upon synthesis conditions, namely temperature and initiator concentration, and is determined by the nature of functional groups of sorbates and copolymer. It has been established that sorption ability of PS-GR- PVP copolymers is greater than that of PMMA-gr-PVP. It means that they are more effective during their use as sorption materials for antiseptics, medical insulation films and antibody markers.

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СОРБЦІЙНІ ВЛАСТИВОСТІ МАТЕРІАЛІВ НА ОСНОВІ КОПОЛІМЕРІВ ПОЛІВІНІЛПІРОЛІДОНУ

Анотація. Досліджено сорбційну здатність кополімерів полівінілпіролідону відносно різноманітних кислотно-основних індикаторів, а також гепарину та йоду. Встановлено, що кількість активних центрів сорбції синтезованих кополімерів залежить від умов синтезу, а саме температури процесу та кількості ініціатора, і визначається природою функціональних груп сорбованих речовин та кополімеру.

Ключові слова: кополімери, полівінілпіролідон, сорбція, індикатори, полістирол, поліметилметакрилат.