RADIOCHEMICAL STUDY OF THE SORPTION OF TRACE ELEMENTS. X.*

ADSORPTION OF PHOSPHATE ANIONS ON GLASS AND POLYETHYLENE

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The paper describes a study of the adsorption and desorption of trace phosphorus, labelled with ^{32}P, in aqueous solutions on glass and polyethylene. The adsorption has been found to exhibit one or two peaks in the pH range 2 to 9·5, to increase with the age of the solution and to depend on the way of the preparation of the solution and on the concentration of an indifferent electrolyte. Its kinetics changed with the age of the solution. The adsorption on polyethylene was greater than on glass, but in either case its relative degree steeply dropped with the increasing concentration of phosphorus. The most probable mechanism of the sorption on both glass and polyethylene seems to be the physical adsorption of pseudocolloids formed by adsorption of anions $H_2PO_4^-$ (and possibly HPO_4^{2-}) on colloidal impurities in the solution.

The regularities and the mechanism of adsorption of traces of non-metallic elements from aqueous solutions on glass and hydrophobic organic polymers are still rather obscure. Radiochemical studies have revealed that most anions are adsorbed on glass[1-6] and silica[7] to a very little extent. Adsorption on organic plastics has been studied with only a few kinds of anions[6-8]. A significant adsorption on glass and polymers has been found with the phosphate anions only[9-16], but the authors either did not discuss its mechanism or advanced rather contradictious views.

The present paper casts some more light on the regularities and mechanism of the sorption of traces of phosphorus on glass and polyethylene by the description of a systematic study of its dependence on factors characterizing the composition and properties of the solution.

EXPERIMENTAL

Chemicals and methods. All solutions were prepared from three-times distilled water and A.R. chemicals. The ^{32}P preparation used (Na_2HPO_4, carrier-free) was supplied from Zentralinstitut für Kernforschung, Rossendorf ü. Dresden. Unless otherwise stated, the solutions of the preparation were diluted prior to use with 0·001M-HCl. The working solutions were prepared from the stock solutions in such a way that the final solution had the desired composition and the

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required pH was adjusted from the acid side. Unless otherwise specified the stock solutions were mixed only with water and a solution of sodium hydroxide or hydrochloric acid, the final ionic strength being dependent on pH of the solution. The ionic strength was calculated from the concentration of the acid contained in the stock solution of radio-phosphate or from the concentration of sodium chloride formed by neutralization of this acid, from the concentration of the free hydroxide or acid, and from the concentration of ions formed as a result of absorption of aerial gases (*e.g.* HCO_3^-). Using the stock solutions of radio-phosphorus in 0·001M-HCl, the working solutions had the lowest ionic strength (approx. [1 to 3] . 10^{-5}) in the pH range 5 to 9. In certain cases sodium chloride was added to the solutions in such quantities that the ionic strength was constant within some range of pH. Unless non-active phosphorus was added to a solution, the total concentration of phosphorus was given by its contents in the chemicals and the water employed. On the basis of the manufacturers' data on the purity of these chemicals the concentration of phosphorus in the working solutions could be supposed to be (probably much) lower than 5 . 10^{-7}M. These solutions are hereafter referred to as carrier-free. In order to minimize secondary contamination the stock and the working solutions were prepared in a glove box, care being taken that the vessels and pipettes employed were perfectly clean.

The adsorption was studied on the inner surface of sealed, 20-ml glass ampoules (Kavalier, Teplice) or closed 30-ml polyethylene bottles (Plastimat, Liberec). The ampoule glass, Neutral, had a composition 70·2% SiO_2, 7·5% Al_2O_3, 1·8% CaO, 7% B_2O_3, 3% BaO, 9·5% Na_2O, 1% K_2O. The ampoules, sealed in manufacture, were subjected to no treatment before the experiment. Since it had been ascertained that the leaching of polyethylene with hydrochloric acid or sodium hydroxide had no significant effect on the adsorption of phosphorus, the polyethylene bottles were just rinsed out with water before use.

The working solutions were prepared either direct in the adsorption vessels (10 ml) or (greater volumes 100—250 ml) in glass bottles. In the latter case the solution was employed for an experiment immediately after its pH had been measured, or was left standing for 7 days. In an experiment 10 ml of a solution were agitated in the chosen adsorption vessel for 16 h at 25°C. A sample (5 ml) was then withdrawn for the measurement of radioactivity and the remaining solution was employed to measure the value of pH. The empty vessels after finishing the adsorption experiments were used to study the desorption. First they were briefly rinsed out with water, then filled with 10 ml of the desorption solution and agitated again for 16 h. The degree of adsorption was evaluated from the radioactivity difference of the solution before and after the adsorption, the desorption was calculated from the activity of the desorption solution[17]. The radioactivity of a sample was measured with a jacket counter VA-Z-430 (Vakutronik, Dresden, Germany). To minimize the adsorption of phosphorus on the tube, 1M-HNO_3 was added to the measured samples in such a quantity that the final volume of the solution to be measured was 10 ml. The pH values were determined with an apparatus PHM-52 and a glass electrode G 202 C (Radiometer, Copenhagen, Denmark).

RESULTS

The reported data are averages of three or more (as many as 28) experiments. In some typical cases the spread of the results is illustrated by the average error of the arithmetic mean.

Figs 1 and 2 show the adsorption of the carrier-free phosphorus on glass and polyethylene in relation to pH, age and the way of preparation of the solution. As is seen, the adsorption from fresh solutions, prepared from the stock solution of radiophosphorus in 0·001M-HCl, was lower in the pH range 3 to 9 than that from solutions 7 days old, the age of the solution also affecting the dependence of the adsorption on pH. The adsorption from fresh solutions of pH 2 to 9 was considerably dependent on the concentration of hydrochloric acid in the stock solution of radiophosphorus used in the preparation of the working solutions. In solutions of pH > 9 this dependence was not demonstrated, since the differences in sorption above pH 9, apparent from Figs 1 and 2, can be ascribed to the difference in the experimental procedure. For the values represented by curves *3* were obtained with an adsorption solution prepared direct in the adsorption vessel. In its preparation the pH of the finally added solution of radiophosphorus changed already in contact with the adsorbent, so that phosphorus may have been adsorbed to a greater extent than would correspond to the equilibrium pH of the given solution.

The data on the kinetics of the adsorption of phosphorus are plotted in Fig. 3. It shows that with both glass and polyethylene the process was slow in the case of fresh solutions of pH 5 to 6, the adsorption equilibrium being not attained even after 28 hours. The adsorption from older solutions was considerably faster, at least in the beginning. From Fig. 3 it can further be seen that the adsorption of phosphorus on polyethylene at any point of the studied time interval was higher than on glass, in agreement with Figs 1 and 2 (the geometrical area of polyethylene was only 12% greater than that of glass).

The effect of concentration of an indifferent electrolyte on the adsorption is shown in Figs 4 and 5. With glass this effect is not too marked, taking into account the con-

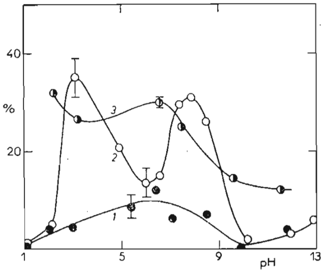

Fig. 1

Adsorption of the Carrier-Free Phosphorus on Glass in Relation to pH and Age (t) of the Solution and Concentration of HCl in the Stock Solution of Radiophosphorus

1 $t = 1-2$ h, 10^{-3}M-HCl; *2* $t = 7$ days, 10^{-3}M-HCl; *3* $t = 0$, 10^{-4}M-HCl.

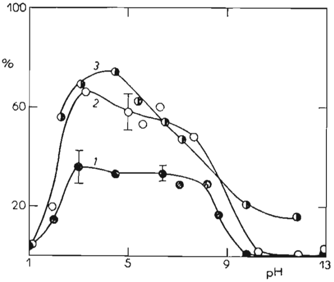

Fig. 2

Adsorption of the Carrier-Free Phosphorus on Polyethylene in Relation to pH and Age (t) of the Solution and Concentration of HCl in the Stock Solutions of Radiophosphorus

1 $t = 1-2$ h, 10^{-3}M-HCl, *2* $t = 7$ days, 10^{-3}M-HCl; *3* $t = 0$, 10^{-4}M-HCl.

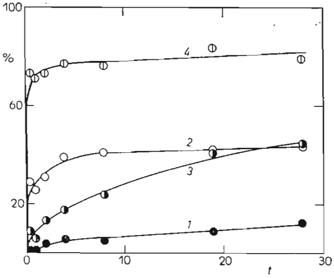

FIG. 3

The Kinetics of Adsorption of the Carrier-Free Phosphorus on Glass and Polyethylene from Fresh and 7 Days Old Solutions of pH 5—6 (t in h)

1 Glass, fresh solution; *2* glass, old solution; *3* polyethylene, fresh solution; *4* polyethylene, old solution.

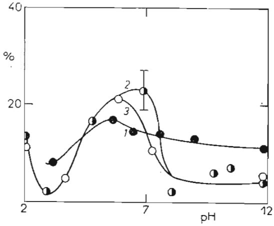

FIG. 4

Adsorption of the Carrier-Free Phosphorus on Glass in Relation to pH and Ionic Strength (I) of the Solution

I: *1* 0·001 (except for pH 11·8), *2* 0·01, *3* 0·1. Fresh solutions, stock solution of radiophosphorus in 0·01M-HCl.

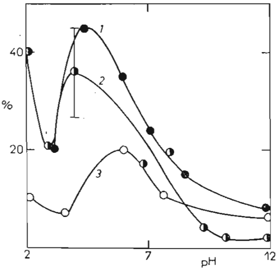

FIG. 5

Adsorption of the Carrier-Free Phosphorus on Polyethylene in Relation to pH and Ionic Strength (I) of the Solution

I: *1* 0·001 (except for pH 11·8), *2* 0·01, *3* 0·1. Fresh solutions, stock solution of radiophosphorus in 0·01M-HCl.

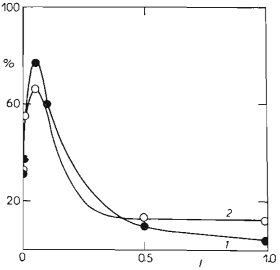

FIG. 6

Adsorption of the Carrier-Free Phosphorus on Glass and Polyethylene from 7 Days Old Solutions of pH 5—6 in Relation to Ionic Strength of the Solution (I)

1 Glass, *2* polyethylene.

siderable spread of data and the low degree of adsorption. In the case of polyethylene, however, the adsorption of phosphorus was suppressed by sodium chloride at concentrations exceeding 0·01M. Comparison of the results in Figs 1, 2, 4 and 5 reveals that the concentration of the acid in the stock solution of radiophosphorus affected not only the degree of adsorption, but even its dependence on pH. The dependence on pH was not appreciably influenced by the indifferent electrolyte.

As in studying the dependence of adsorption on pH it is not possible to maintain a very low ionic strength constant in a sufficiently wide range of pH, the effect of the indifferent electrolyte was investigated on solutions of ionic strengths 0·001 and higher. Figs 4 and 5 do not indicate that in any of the studied regions of pH the adsorption exhibits a peak with the increasing concentration of the electrolyte, in contrast to the observation by Herczyńska[13]. Since this author observed a marked peak on the curve relating the degree of adsorption to the ionic strength at pH 5, the effect of the electrolyte at pH 5 to 6 has been studied under conditions somewhat different from those corresponding to Figs 4 and 5 (with the stock solution of radiophosphorus in 0·001M-HCl). The degree of adsorption as a function of concentration of NaCl did exhibit a peak, but its position and shape differed from one experiment to another. Typical curves are shown in Fig. 6.

The results expressing the degree of adsorption in relation to the concentration of phosphorus are plotted in Fig. 7 for two pH values of the solution. As the lowest concentration of phosphorus was not known, its value is indicated as carrier-free (c.f.) in the graph. Fig. 7 shows that the relative degree of the adsorption steeply decreased with the increasing concentration of phosphorus and was very low even at 10^{-6}M-P. In view of the serious errors in determining such low values of adsorption by the method employed it would have been of little avail to study this concentration dependence in more detail or to plot the data in coordinates suitable for determining

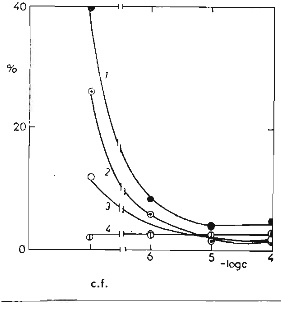

FIG. 7

Adsorption of Phosphorus on Glass and Polyethylene from Fresh Solutions in Relation to the Initial Concentration of Phosphorus in the Solution (*c*)

1 Polyethylene, pH 3; *2* polyethylene, pH 5–6; *3* glass, pH 5–6; *4* glass, pH 3.

the type of the adsorption isotherm. To obtain some idea on the firmness of the linkage of phosphorus to glass and polyethylene the desorption was studied in relation to composition of the desorbing solution and to pH of the solution from which the adsorption had occurred. The results are compiled in Table I. It shows that the values of desorption were rather low with either adsorbent. Desorption of phosphorus with 1M-HCl was more efficient than with water, and desorption from polyethylene was greater than from glass with either desorbing solution. The latter finding agrees with the results published by Hensley[9] and by Baier and Hausmann[12], who reported that the desorption of trace phosphorus from glass was incomplete or slow. On the other hand, Murphy and Riley[16] reported an easy desorption of phosphates from polyethylene, on which phosphorus had been adsorbed from sea water.

DISCUSSION

An interpretation of the adsorption of pentavalent phosphorus from a solution must proceed from its state in the solution. Sedimentation analysis, dialysis and electrophoresis[18] have shown that the carrier-free phosphorus in a 7 days old solution of pH 2·6 to 8·8 is present mainly in the form of pseudocolloidal particles (the real colloids are not formed to a significant extent). They are negatively charged or neutral and are formed by adsorption of anions $H_2PO_4^-$ (and possibly HPO_4^{2-}) on colloidal impurities in the solution. These pseudocolloids are also present in fresh solutions, but their relative content is lower than in the older ones. In addition to the colloids, the solutions contain molecules and the dissociated forms of phosphoric acid. In accordance with these facts the sorption of trace phosphorus can be interpreted as sorption of its pseudocolloidal particles and anions. The adsorption of pseu-

TABLE I

Desorption of the Carrier-Free Radiophosphorus (%) from Glass and Polyethylene in Relation to Composition of the Desorbing Solution, and to pH of the Solution[a] in the Preceding Adsorption

pH	1M-HCl	H_2O	pH	1M-HCl	H_2O
	glass			polyethylene	
3·1	28·0	—	3·0	64·6	—
5·6	27·0	10·1	5·1	58·3	27·8
7·3	27·0	—	6·1	54·0	—
8·0	—	19·6	7·8	47·6	

[a] 7 days old solution of variable ionic strength.

docolloids probably proceeds by a physical mechanism (adhesion), the adsorption of anions by a physical or a chemical mechanism. An electrostatic adsorption of pseudocolloids or ion exchange of phosphate anions in the outer part of the electric double layer can hardly be considered possible in this case, because both glass and polyethylene are negatively charged in the region of a significant adsorption of phosphorus[19,20]. Arguments for the propounded mechanism of the sorption and the conclusions on the proportion of the colloidal and the ionic sorptions are given in next paragraphs, where the individual factors affecting the sorption are discussed.

The very low adsorption of phosphorus in the pH range 1 to 1·5 can be accounted for by the observation that in this range virtually no pseudocolloidal forms of phosphorus are formed[18]. The undissociated phosphoric acid, as its predominant form in this pH region, is evidently little adsorbed on glass and polyethylene. The increase in adsorption starting beyond pH 1·5 may be due to the increasing dissociation of phosphoric acid to the ions $H_2PO_4^-$, or to the greater content of pseudocolloids in the solution[18]. Similarly, the decrease in adsorption beginning at pH values higher than 7 to 8 may be due either to the reduced content of pseudocolloids, demonstrated by centrifugation[18], or to the dissociation $H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$. For it can be expected that a bivalent anion will adsorb less readily on a negatively charged surface[21]. The dependence of sorption on pH between pH 3 and 7, which exhibits a minimum in some cases, is difficult to interpret since the effects of structure and composition of the colloidal particles on their sorption have not been studied yet. Moreover, we do not know the nature of the particles from which the pseudocolloids of phosphorus are formed, and it is possible that their nature varies with pH.

The lower adsorption of phosphorus on glass than on polyethylene is understandable if we consider the electrostatic repulsive forces between the negatively charged forms of phosphorus and the negatively charged surface of the adsorbent. For it is known that the negative charge of glass is higher than that of polyethylene. Thus the zeta potential of glass Jena or Pyrex in the pH range 3 to 12 in the absence of higher concentrations of salt varied[19] between -70 and -185 mV, whereas the zeta potential of polyethylene under similar conditions did not exceed[20] -55 mV. Polyethylene is also known to adsorb even negatively charged colloids to a considerable extent[22].

The adsorption of phosphorus on glass and polyethylene from the old solutions was greater than from the fresh ones in that region of pH where the existence of the pseudocolloids of phosphorus had been demonstrated. Since the content of pseudocolloids increases with the age of the solution, this fact strongly supports the idea of the sorption of pseudocolloids and suggests that phosphate anions are not appreciably adsorbed. For the same reason the assumption of the adsorption of pseudocolloids is substantiated by the determined time dependence of the adsorption. For in the old solutions phosphorus is present in the more adsorbable form, *i.e.* as a pseudocolloid, at the very start of an experiment, and its adsorption is consequently faster than from the fresh solutions, where the pseudocolloids are formed only. Another argument in favour of the adsorption of pseudocolloids is the effect of composition of the stock solution of radiophosphorus on sorption. At pH 2 the content of the pseudocolloids represents a negligible portion of the radiophosphorus, whereas in solutions of pH 4 (*i.e.* radiophosphorus in 10^{-4} M-HCl) the radiophosphorus can be assumed to exist predominantly in the form of pseudocolloids. Consequently, if phosphorus is adsorbed in the form of pseudocolloids, the adsorption will be greater in a fresh solution prepared from radiophosphorus in 10^{-4}M-HCl than in a fresh solution prepared from the stock solution of higher acidity (curves *3* in Figs 1 and 2 with curves *1* in Figs 4 and 5). If these working solutions are left standing prior to adsorption the differences in their relative contents of pseudocolloids tend to disappear, so that the extent of adsorption may not be significantly different. This is a possible explanation of the good agreement of curves *2* and *3* in Fig. 2.

The peaks of the curve relating the extent of adsorption to the concentration of sodium chloride, as an indifferent electrolyte, can be interpreted as follows. With an increase in the concentration of the electrolyte the zeta potential decreases on both the surface of glass[19] and on the surface of polyethylene[20]. This decrease suppresses the repulsive forces between the adsorbent and the adsorbate, both bearing a negative charge, and the adsorption can increase. With further raising the ionic strength of the solution the formation of the pseudocolloids is restricted, as has been proved by the effect of 1M-NaCl on the centrifugation and dialysis of phosphorus[18]. This seems to be the cause of the following decrease in adsorption. The effect of ionic strength on the adsorption from the fresh and from the old solutions is not the same (Figs 4–6). It also changes with pH of the stock solution of radiophosphorus. These variations are probably associated with the different properties of pseudocolloids formed under different conditions. Since the effect of ionic strength on the properties of pseudocolloids of phosphorus has not been studied in detail, the differences in question cannot be interpreted more precisely.

The probable cause of the rapid decrease in the adsorption of phosphorus with its increasing concentration is the decrease in the content of pseudocolloids in the solution. For it can be assumed that the adsorption capacity of colloidal impurities for anions is very low[18]. The anions $H_2PO_4^-$ in higher concentrations cannot obviously be adsorbed on glass or polyethylene either, since the adsorption capacities of these materials for anions are slight, as was shown *e.g.* by the experiments with trace molybdates[21]. The desorption of trace phosphorus has been studied on relatively a few experiments, so that no conclusions can be drawn from them on the state of phosphorus on the surface of the adsorbent. Nevertheless, glass seems to bind the adsorbed phosphorus more firmly than polyethylene does. The comparatively insensitive dependence of the desorption on pH of the solution from which the preceding adsorption has occurred indicates that in the studied range of pH the mechanism of sorption and the state of phosphorus on the surface of the adsorbent do not vary significantly. This conclusion accords with the above interpretation of the sorption.

The described regularities and the propounded mechanism of the sorption of phosphorus on glass are rather at variance with the results reported by Herczyńska[13,14] and with the author's interpretation of them. Herczyńska's fundamental postulate of the exchange of anions in the outer part of the electric double layer is questionable because above pH 2 the charge of glass is negative[19]. For this reason we cannot accept the interpretation (based on this postulate) of the peak on the curve relating the sorption of phosphorus on glass to the ionic strength of the solution. The other possible mechanism, proposed by Herczyńska, is the exchange of anions for the primarily adsorbed OH^- ions, forming the inner part of the electric double layer. As for this exchange, the maximum adsorption should occur, according to this author, in the neutral region of pH. However, there is no reason for the occurrence of a peak in this region, since the concentration of OH^- ions adsorbed on glass no longer significantly changes. Considerable changes in this concentration can be expected in the isoelectric region of the adsorbent, which in the case of glass is around pH 2.

The regular course of the sorption – pH dependence through two maxima, described by Herczyńska, has not been reproduced either. Two maxima were observed in a few cases, but their positions were different from those reported by Herczyńska. Besides, the positions of these maxima have proved to be affected by the way of preparation of the solution, which fact is not implied in Herczyńska's interpretation. In this connexion it should be pointed out that the technique Herczyńska employed[23] did not guarantee a constant composition of the solution and a constant pH in the course of an experiment, since the very small volume of the solution (1 drop) was in contact with the atmosphere and with the relatively large surface of the adsorbent. The author did not measure the pH values after adsorption. This may have distorted the results, especially in experiments with solutions of low ionic strengths and pH 4 to 10. Neither has the author considered the possible changes of state of the trace phosphorus in the solutions and does not mention the preparation and age of the solutions, although these factors, as shown in the present paper, are important.

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