

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

ADSORPTION OF BARIUM ON GLASS AND POLYETHYLENE AND ITS STATE IN AQUEOUS SOLUTIONS

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Adsorption and desorption have been studied of traces of barium ($4 \cdot 10^{-8}$ to $2 \cdot 10^{-7}$ M and 10^{-5} M), labelled with ^{133}Ba , on glass and polyethylene in relation to pH, age and composition of the solution, and time. It has been found that adsorption from aqueous solutions begins to increase at pH 4, goes through a maximum and decreases in the alkaline region. The shape of the adsorption curve and the degree of adsorption were considerably dependent on the ionic strength of the solution and on the nature of the adsorbent. Age of the solution has not proved appreciably important. The sorption seems to proceed by ion exchange of Ba^{2+} in the outer part of the electric double layer on the surface of the adsorbent. The decrease of sorption with increasing pH is attributed to a competition effect of the cations of the hydroxide employed for the adjustment of pH. The state of the traces of barium in the solutions was studied by sedimentation analysis, dialysis and electrophoresis. It has been found that in the pH range 3 to 10 the solution contains predominantly the ions Ba^{2+} . At pH > 10 in solutions not protected from aerial carbon dioxide carbonate complexes of baryum are probably formed. The colloidal forms of barium are present in a negligible concentration; these arise by sorption of barium on colloidal impurities in the solution.

The preceding papers of this series dealt with the adsorption of traces of elements that get hydrolyzed in the solutions. To supplement our previous findings on the adsorption behaviour of traces of elements it has been necessary to study the adsorption, under the same conditions, of some trace element whose tendency to hydrolysis and to the formation of true colloids is very weak. We have selected barium whose adsorption on glass and plastics has little been studied yet. Authors dealing with this subject just stated a decrease in the content of barium in very dilute solutions as a result of its adsorption on the wall of the vessel¹ or investigated the possible ways of separating barium from other trace elements^{2,3}. The mechanism of the sorption has been investigated only by Otani and coworkers⁴, who assume an ion exchange of barium on glass.

This paper deals with the adsorption of barium on glass and polyethylene in relation to pH, composition and age of the solution, concentration of barium and time. To facilitate interpretation of the results we have also studied, by the methods of dialysis, centrifugation and electrophoresis the state of barium in the solutions⁵.

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EXPERIMENTAL

Chemicals. The stock solutions were prepared from three times distilled water and A.R. chemicals; they were stored in closed polyethylene or polystyrene bottles. Solutions of sodium hydroxide (1M and 0.01M) were obtained by dilution of a 50% solution of NaOH. The preparation of ^{133}Ba (specific activity 1.5 mCi/mg, in 0.01M-HCl) was purchased from the Radiochemical Centre Amersham. Prior to use it was diluted with 0.01M-HCl or water.

The concentrations of barium in water and the chemicals employed were determined spectrally. From the results and from the known analytical concentration of barium in the preparation of ^{133}Ba it was calculated that in the solutions of $\text{pH} < 11$, without the addition of an isotopic carrier, the total concentration of Ba was constant and within the range $4 \cdot 10^{-8}$ to $2 \cdot 10^{-7}\text{M}$. These solutions are hereafter called carrier-free. In view of the unsafe determination of the barium concentration in the sodium hydroxide employed ($< 10^{-5}\text{M}$ -Ba in 1M-NaOH) it cannot be ruled out that the investigated solutions of $\text{pH} > 12$ had an appreciably greater content of barium. In experiments with a 10^{-5}M solution of Ba the stock solution of radiobarium was mixed with a standard solution of 0.01M-BaCl₂, prepared by dissolving a weighed quantity of the A.R. salt.

The experimental solutions were prepared in two ways: *A.* The stock solution of radiobarium in $\sim 10^{-4}\text{M}$ -HCl was mixed with ten volumes of hydrochloric acid or sodium hydroxide solutions having proper concentrations. *B.* To a greater amount (100–300 ml) of a solution obtained by mixing 0.01M-HCl with 1M-NaOH was added the stock solution of radiobarium in 0.01M-HCl in a ratio of 1 ml per 300 ml of the solution. In some experiments an indifferent electrolyte (2M-NaCl) was added to the solution before the addition of radiobarium. The solution was stirred and after measurement of pH it was employed either immediately or after 7 days' storage in a closed polyethylene bottle. The solutions obtained by procedure *A* were $\leq 10^{-5}\text{M}$ in respect to NaCl and their ionic strength (except for the pH range 5 to 8) was strongly pH-dependent. Solutions *B* contained 0.01M (NaCl + HCl) and their ionic strength in the pH region from 2 to 11 was constant ($\pm 10\%$). The concentration of barium in the two series of solutions was approximately the same.

In order to preserve the normal laboratory conditions the stock solutions were not freed from the colloidal impurities. The solutions for the experiments, however, were mixed and kept in a special box to prevent accidental contamination with dust, but they were not protected from the contact with the aerial CO₂.

Apparatus and Procedures

All the vessels of glass and polyethylene and the pipettes were washed in a hot mixture (1 : 1) of hydrochloric and nitric acids, A.R., then rinsed with three times distilled water. The radioactivity of solutions was measured with a Soviet scintillation counter SČ-4 with a well-type crystal of NaI(Tl). The measurement was carried out with 5-ml glass ampoules, inserted into the hole in the crystal. pH of the solutions was measured with a glass electrode connected to a Multoscop pH meter (Laboratorní potřeby, Prague).

The adsorption was studied on the inner surface of sealed, 20-ml glass ampoules (Kavalier, Teplice) or closed 30-ml polyethylene bottles (Plastimat, Liberec). Unless otherwise stated, the glass of the ampoules (Neutral) had the following composition: 70.2% SiO₂, 7.5% Al₂O₃, 1.8% CaO, 7% B₂O₃, 3% BaO, 9.5% Na₂O, 1% K₂O. With the exception of a few experiments the glass ampoules were submitted to no treatment before use, whereas the polyethylene bottles were washed with 1M-HCl and water. The inner surface of the ampoules was $66 \pm 1\text{ cm}^2$, the inner surface of the polyethylene bottles, including the stopper, was about 74 cm^2 (both values were calculated).

In a typical experiment 10 ml of a solution was agitated in an adsorption vessel for 20 h at room temperature. The adsorption was evaluated from the difference in radioactivity before and after the adsorption⁶. After every experiment pH of the solution was measured. The empty polyethylene bottles after the adsorption experiments were employed for the study of desorption. First they were rinsed with a little water, then filled with 10 ml of a desorbing solution and agitated for 20 h. The time between the starts of the adsorption and the desorption was about 24 h (except when the kinetics of the desorption was studied) and the degree of desorption was estimated indirectly by measuring the radioactivity of the desorbing solution⁶. Desorption from glass was determined directly by measuring the radioactivities of the glass ampoules before and after the desorption⁶.

The sedimentation experiments were carried out with a Janetzki centrifuge (Engelsdorf, Leipzig), model T 14 R. Ten ml of a solution in a plexiglass tube was centrifuged at 15 000 r.p.m. (13 600 g) for 30 min. After the centrifugation 5 ml of the supernatant was withdrawn for the radioactivity measurement. Each centrifugation was accompanied by a parallel experiment without centrifugation. The percentage of sedimentation was evaluated from the activity differences between the centrifuged and the reference samples (parallel experiments).

The method of dialysis was described previously⁷. The porosity of the cellophane (Kalle, Wiesbaden-Biebrich) was 2—8 nm. The dialysis was allowed to proceed for 17 h at room temperature. For studying the electromigration of barium the electrophoresis by Hoyer, Mysels and Stigter⁸ was used, which was modified⁹ to be applicable to trace amounts. The determined mobilities (at 25°C) were corrected for the adsorption of barium on the walls of the apparatus and expressed in absolute units. The conductance of the solutions was measured in a cell with an RLC bridge (Tesla, Czechoslovakia).

RESULTS AND DISCUSSION

The majority of the data given in this paper are averages from a number of experiments (3 to 22). To illustrate the spread of data the mean square deviations of the arithmetical averages are given in some cases.

State of Barium in the Solutions

The results of the study are shown in Figs 1 and 2. From Fig. 1 it follows that barium easily passes through the cellophane membrane and does not sediment in a centrifugal field of 13 600 g. Neither dialysis nor centrifugation depends on the age or ionic strength of the solution. These facts preclude the presence of true colloids of barium in the solutions or a greater quantity of its pseudocolloids with a diameter above 20 nm, which in the centrifugal field employed would be fully sedimented. The existence of pseudocolloidal particles of barium smaller than 20 nm cannot be safely ruled out because in the case of reversible adsorption of a trace element on impurities its state in the solution may appear in the dialysis to be ionic¹⁰. Experience suggests, however, that the formation of such pseudocolloids is improbable¹¹.

Further information on the state of barium was obtained by studying its electrophoresis in relation to pH, age and composition of the solution. As can be seen from

Fig. 2, the mobility of the carrier-free barium in an electrostatic field varies little in the pH range from 3 to 10 and the mobility of 10^{-5}M-Ba is constant. Above pH 10, however, the mobility decreases in either case, but does not depend on the age of the solution. These facts can be explained as follows: up to pH c. 10 the solution contains predominantly barium ions; the content of these ions does not vary with pH (at 10^{-5}M-Ba) or age of the solution. The decrease of electrophoretic mobility of barium is evidently due to the formation of its complex molecules or ions with a lower mobility than that of Ba^{2+} . Such particles may be, e.g., BaHCO_3^+ , $\text{Ba}(\text{HCO}_3)_2$ at $\text{pH} > 5.8$, and especially the undissociated BaCO_3 at $\text{pH} > 10.2$. The carbonates may have been brought into the solution from the hydroxide employed for the pH adjustment or may have been formed from the aerial CO_2 . So long as the absorption of carbon dioxide in the solutions was negligible, or at least constant, the total of carbonates was constant ($\pm 10\%$) within the pH range 3 to 11. Changes in mobility of barium with pH would then be due to stepwise dissociation of carbonic acid, which proceeds approximately in the regions of the two mobility decreases of the carrier-free barium. The decrease of electrophoretic migration above pH 12, where the dissociation is complete, can be ascribed to an increase in the total concentration of carbonates coming from the hydroxide and to the hydrolysis of barium ions¹².

Proceeding from these ideas it is possible to explain the difference between the mobilities of the carrier-free barium and 10^{-5}M barium at $\text{pH} > 11$. Since the

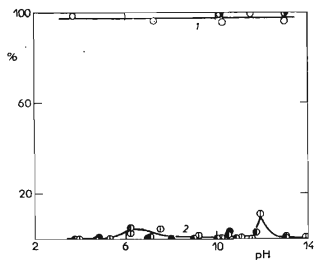


FIG. 1

Dialysis (1) and Centrifugation (2) of Traces of Barium ($4 \cdot 10^{-8}$ to $2 \cdot 10^{-7}\text{M}$) in Relation to pH, Age and Composition of the Solution

○ ○ Fresh solution B, ● ● 7 days' old solution B, ● fresh solution A.

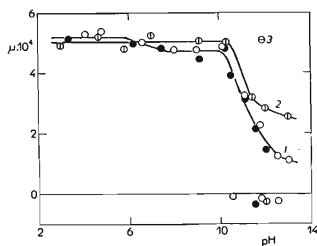


FIG. 2

Mobility of Barium ($\text{cm}^2 \text{s}^{-1} \text{V}^{-1}$) as a Function of pH, Age of the Solution and Concentration of Barium

The solutions were prepared by procedure B. 1 Fresh (○) and 7 days old (●) solutions, $4 \cdot 10^{-8}$ to $2 \cdot 10^{-7}\text{M}$ in Ba; 2 fresh solutions, 10^{-5}M in Ba; 3 fresh and carbonate-free solution, 10^{-5}M in Ba.

concentration of carbonates in the solutions was very probably in the region 10^{-5} to 10^{-4} M, the equilibrium concentration of free CO_3^{2-} ions in the 10^{-5} M solution of Ba decreased, compared to the carrier-free solution of Ba, as a result of the formation of the carbonate complex of barium. Consequently, the portion of the complex forms of barium in its 10^{-5} M solution was lower and the mobility was accordingly higher.

To prove the effect of carbonates on the mobility of barium in the solutions we reduced their concentration to a minimum by adjusting the pH under a nitrogen atmosphere with a 50% solution of NaOH, which is carbonate-free. Fig. 2 shows (point 3) that the mobility of barium in a solution of pH 11.9 prepared in this way was the same as in the solutions of pH 3 to 10. Hence it seems very probable that a decrease in electrophoretic mobility proves the existence of carbonate complexes of barium, not previously mentioned in the literature¹². The exact composition of these complexes cannot be derived from these experiments, but it is probable that they are electro-neutral or bear a low charge. If it is the BaCO_3 complex, the order of magnitude of its dissociation constant should be 10^{-5} .

It is of interest that between pH 10 and 13 barium also migrated to the anode (Fig. 2). This phenomenon proves either the existence of anionic complexes of barium or the formation of its negatively charged pseudocolloids. The latter possibility is supported by the low sedimentation peak of barium at pH c. 12 (Fig. 1), analogous to the peak observed in centrifugation of trace calcium¹³. In view of the low mobility of barium toward the anode the percentual portion of its anionic complexes or pseudocolloids is obviously very small (less than 10%, judging by analogous cases¹⁴ that the minimum mobility of such forms is about $2 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$).

Adsorption of Barium on Glass

The dependence of the adsorption of barium by glass on pH of the solution and on concentration of an indifferent electrolyte (NaCl) is shown in Fig. 3; the region of the increase in adsorption, width of the peak and its height strongly depend on the concentration of the electrolyte. The age of the solution had practically no effect. The observed course of the sorption proves the imperfection of the present knowledge of the sorption of non-hydrolyzed cations on glass^{11,15}, which ignore the decrease of the sorption in alkaline solutions.

The state of barium in the solutions and the sorption properties of glass^{11,15} suggest that the traces of barium are sorbed by an ion exchange for the counter ions in the outer part of the electric double layer. This double layer on glass is very probably formed by dissociation of the surface $\equiv \text{SiOH}$ groups of glass and its charge increases with pH of the solution¹⁶. At pH < 4 the sorption of barium is very small since hydrogen ions, present in a rather high concentration, compete with the Ba^{2+} ions in the exchange. The increase in adsorption with pH (starting from about pH 4)

is evidently due to the diminishing competition of protons and, probably, even to the increasing charge of the electric double layer. Since all the cations present in the solution can participate in the ion exchange in the outer part of the double layer the adsorption of barium depends even on the concentration of the electrolyte. The resultant course of the sorption is given by the competitive equilibria:



where the subscripts *s* and *l* indicate the surface and the solution, respectively. If the concentration of the indifferent electrolyte in the solution is very low (curve 1, Fig. 3) the adsorption increases to approximately pH 7 while only protons compete with barium. At an ionic strength $I = 0.01$ (curve 2) the adsorption increases to c. pH 5.5. At higher pH values the competition equilibrium is controlled mainly by concentration of the electrolyte and since this concentration is constant the adsorption does not change either. If the concentration of sodium chloride is still higher the increase of adsorption with pH is negligible (curve 3).

In an analogous way it is possible to interpret the decrease of adsorption with increasing pH as due to a competitive effect of the cations of the hydroxide employed for adjusting pH. Since the concentration of cations in solution *A* (curve 1) increases above pH ~ 8 , whereas in solution *B* (curve 2) the ionic strength was constant up to pH 11, the decrease of adsorption in both cases is mutually shifted. The increase in ionic strength is the principal but probably not the only cause of the decrease in adsorption of barium with pH. On the basis of the experiments performed it has

TABLE I

Effect of Composition of the Solution on the Sorption of Barium on Glass
Fresh solutions B^a , $4 \cdot 10^{-8}$ — $2 \cdot 10^{-7}$ M-Ba, results in %.

Hydroxide for pH adjustments	pH of the solution	
	6.8 ± 0.2	10.5 ± 0.3
NaOH	26.6 ± 3.2	22.9 ± 2.2
NH ₄ OH	4.4 ± 1.3	10.0 ± 0.5
LiOH	50.1 ± 1.7	26.9 ± 1.9
Ca(OH) ₂	2.9 ± 1.4	3.6 ± 1.8
Sr(OH) ₂	2.4 ± 0.5	6.4 ± 1.0

^a With the exception of the hydroxide.

not been possible to judge how the formation of the carbonate complexes of barium and its hydrolysis affect the decrease of the adsorption. In the pH range 6 to 11, however the effect of the carbonate complexes on the pH dependence of the adsorption was not apparent. The competition with the cations of the hydroxide employed for pH adjustments was usually not considered and the decrease of adsorption of trace cations with pH was ascribed to other reasons, even though less grounded¹⁷.

Comparison of curves 1 and 2 in Fig. 3 suggests the conclusion that in an ion exchange on glass the competition power of protons considerably outweighs that of sodium ions. It was of interest to ascertain the effect of other cations, especially in relation to their charge and hydration. For this reason we studied the adsorption from solutions whose pH was adjusted with different hydroxides (Table I). It appears that with the increasing hydration of an ion its adsorption competition with barium decreases (in the order $\text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$), but increases with the charge of this ion. These facts accord with the current ideas of the ion-exchange mechanism of sorption. As is seen, the competition depends even on pH of the solution, which influences the charge of the glass. A quantitative description of the above mentioned competition equilibria will evidently be rather complex. This can also be inferred from the observation that the adsorption (in %) decreases approximately with the logarithm of the ionic strength (Fig. 3), although this decrease should be steeper. It is probable that the electrolyte considerably influences also the capacity of the electric double

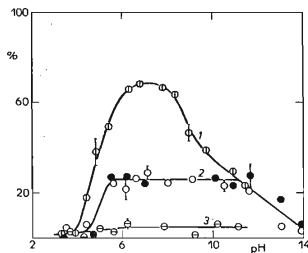


FIG. 3

Adsorption of Traces of Barium ($4 \cdot 10^{-8}$ to $2 \cdot 10^{-7} \text{M}$) on Glass in Relation to pH, Composition of the Solution and Concentration of an Indifferent Electrolyte

1 $\leq 10^{-5} \text{M-NaCl}$, fresh solutions, 2 0.01M-NaCl , fresh (\circ) and 7 days old (\bullet) solutions, 3 1M-NaCl , fresh solutions.

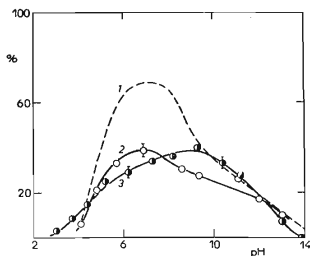


FIG. 4

Adsorption of Barium on Glass in Relation to pH of the Solution, Concentration of Barium and Composition of Glass

The solutions were prepared by procedure A. 1 $4 \cdot 10^{-8}$ to $2 \cdot 10^{-7} \text{M-Ba}$, Neutral glass; 2 10^{-5}M-Ba , Neutral glass; 3 $4 \cdot 10^{-8}$ to $2 \cdot 10^{-7} \text{M-Ba}$, Unihost glass.

layer on the glass surface. The existence of this factor can also be deduced from earlier experiments described by Herczyńska¹⁸.

The increase in adsorption of barium on glass approximately coincides with that of other alkaline earths¹⁹⁻²¹, but it occurs at a lower pH than the increase in adsorption of bivalent cations of some elements of other groups²²⁻²⁴. This phenomenon is an exception from the rule¹⁵ that elements which are more liable to hydrolysis start to be sorbed at lower pH values. It is probably due to a smaller hydration of the ions of alkaline earths, which accounts for their greater activity in the ion exchange.

In order to prove that the sorption of radiobarium is not only its isotopic exchange for the non-active barium contained in the glass Neutral we have also studied the sorption of barium on the glass Unihost, whose content of barium is much smaller. (The approximate composition of the Unihost glass is 68.5% SiO₂, 18.3% Na₂O (K₂O), 6% CaO, 4.1% MgO, 2.8% Al₂O₃). The results (Fig. 4) cannot be explained by the absence of barium in the Unihost glass. The adsorption on this glass at pH > 9.5 is the same as on the glass Neutral and at pH < 4 it is even higher. A possible cause of the lower sorption of barium in the pH range 5-9 is the easier leaching of the Unihost glass. As a result of dissolution of alkalis from the glass the ionic strength of the solution increases and the adsorption of barium ions decreases. This interpretation is supported by the circumstance that in the given region of pH the ionic strength of the solution was the lowest, so that its change could be highest. The decrease in adsorption of caesium on a soda-lime glass with time has been interpreted analogously²⁵. Another interpretation, which seems to be the only possible one accounting for the different adsorption at pH < 4, is based on the difference between the two sorts of glass in the properties of the electric double layer. The observed difference in sorption is at variance with the data reported by Otani and coworkers, who found a greater sorption of barium from neutral solutions on an alkaline glass than on a boron-silicate glass⁴. It must be borne in mind, however, that these authors studied the adsorption on a specially prepared glass and employed a different method.

Curve 2 in Fig. 4 illustrates the dependence of the adsorption of barium on pH of the solution, which was 10⁻⁵M in respect to Ba. Its course agrees with curve 1 for the strongly alkaline region. (At lower values of pH the relative sorption of barium from its more concentrated solution is lower.) This agreement proves that the decrease in sorption of barium with pH cannot be caused by a possible increase in the concentration of barium in solutions of pH > 12. For the sorption decreases even in the solution of 10⁻⁵M-Ba, where no essential change in the concentration of barium can occur. The decrease in the relative sorption of barium compared to its carrier-free solution follows from the gradual saturation of the ion exchange capacity of glass. The relatively high degree of adsorption even in more concentrated solutions, suggests that the capacity of glass for the ion exchange of cations is considerable.

The time courses of the adsorption of barium on glass in relation to pH, age and composition of the solution are shown in Fig. 5. The sorption of barium from neutral solutions of a low ionic strength (curve 1) proceeds in two stages. In the first stage the sorption is very rapid (the half-time is a few minutes). In the second stage the adsorption increases very slowly and continues to increase even after 10 h. Such a course of sorption is essentially in agreement with the findings reported earlier⁴. In the other cases the adsorption reached a certain degree in 1–2 hours, which no longer changed even after 20 to 50 h. It is of interest that both the fresh and the old solutions of pH 12 exhibited a peak of the barium sorption in the early stage. To account for this fact it is necessary to assume that the decrease of sorption with time is a consequence of the reaction of barium in the solution with a substance that is leached from the glass. Obviously the product of this reaction is not adsorbed on the glass. A possible explanation is dissolving of the surface layers of the glass by the action of the alkaline solution and the consequential entry of the silicate ions into the solution. This interpretation is supported by the suppression of the peak on the sorption curve and by the increase in adsorption if the glass has been exposed for some time to a solution of pH 12 before the experiment (curve 2). This treatment removed

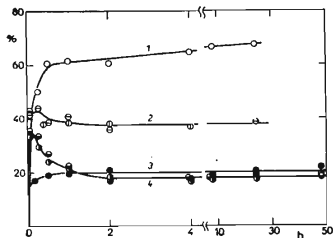


FIG. 5

Time Dependence of the Adsorption of Traces of Barium ($4 \cdot 10^{-8}$ to $2 \cdot 10^{-7}M$) on Glass

1 pH 6.7, fresh solution A; 2 pH 12, fresh (○) and 7 days old (⊖) solution B; before the adsorption the ampoules were exposed to 0.01M-NaOH; 3 pH 6.7, fresh solution B; 4 pH 12, fresh (●) and 7 days old (⊙) solution B.

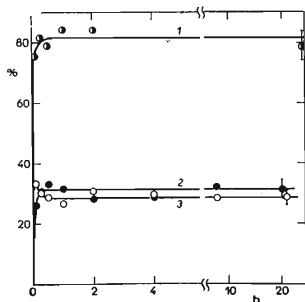


FIG. 6

Time Dependence of the Adsorption of Traces of Barium ($4 \cdot 10^{-8}$ to $2 \cdot 10^{-7}M$) on Polyethylene (2) and Unihost Glass (3) and the Course of Desorption from Polyethylene (1) 1 Desorption with 1M-HCl after adsorption from a fresh solution A, pH 11; 2, 3 adsorption from a fresh solution A, pH 6.7.

from the glass the readily soluble components, so that in the subsequent experiment they did not contaminate the solution to an appreciable extent. With the Unihost glass there appeared a small peak on the time dependence of the sorption even at pH 6-7 (Fig. 6). This observation is in keeping with the lower leach-resistance of this sort of glass and, consequently, greater contamination of the solution.

Desorption (20 h) of barium from glass proceeds as follows:

pH ^a	3.8	5.4	9.8	11.8
Ba, % ^b	94.4	~ 100	~ 100	~ 100
Ba, % ^c	68.1	67.2	56.8	56.6

^a Fresh solution B, $4 \cdot 10^{-8}$ – $2 \cdot 10^{-7}$ in Ba. Desorbing solution, ^b 1M-HCl, ^c H₂O.

A solution of 1M-HCl desorbs barium quantitatively. These facts accord with the data reported by Otani and coworkers⁴ and with the above interpretation of the sorption as an ion exchange, characterized by a high reversibility. According to the current ideas^{11,15} the small dependence of the desorption on pH of the preceding adsorption supports the un- changing character of sorption in the studied range of pH.

Adsorption of Barium on Polyethylene

The dependence of the adsorption of barium on pH, age and ionic strength of the solution is shown in Fig. 7 for two concentrations of barium. The start of this adsorption (curves 1 and 2) coincides with the start of the adsorption on glass, but its increase with pH is more moderate and the decrease appears at higher values of pH. Consequently the maximum adsorption is shifted to a higher pH. Suppression of the adsorption with an indifferent electrolyte proves that even on polyethylene the traces of barium are adsorbed by an ion exchange, probably in the outer part of the electric

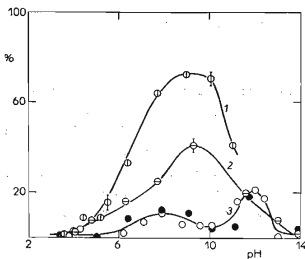


FIG. 7
Adsorption of Barium on Polyethylene in Relation to pH, Age and Composition of the Solutions

$1 \cdot 10^{-8}$ to $2 \cdot 10^{-7}$ M-Ba, fresh solution A; $2 \cdot 10^{-5}$ M-Ba, fresh solution A; $3 \cdot 4 \cdot 10^{-8}$ to $2 \cdot 10^{-7}$ M-Ba, fresh (○) and 7 days old (●) solution B.

double layer. The course of the adsorption with pH can be interpreted like in the case of glass, but there are some differences in adsorption between the two adsorbents. These differences are due mainly to the different chemical compositions of the two adsorbents, with the consequential difference in properties of the electric double layers. This is evidently also the cause of the unequal effect of ionic strength on the adsorption, and of the different course of the adsorption from 0.01M-NaCl (Figs 3 and 7), which in the case of polyethylene exhibited two peaks.

The decrease in the relative degree of adsorption with the increasing concentration of barium can be explained, like with glass, by a partial saturation of the ion-exchange capacity of the electric double layer. However, the adsorption is still considerable, which suggests a rather high capacity of polyethylene for the ion exchange. These observations substantiate the conclusions we have arrived at before²⁶.

The desorption (20 h) of barium from polyethylene is more difficult than from glass:

pH ^a	6.3	9.4	12.3
Ba, % ^b	71.0	80.9	77.7
Ba, % ^c	50.1	73.0	65.6
Ba, % ^d	23.5	47.0	38.7

^a Fresh solution A, $4 \cdot 10^{-8}$ — $2 \cdot 10^{-7}$ in Ba. Desorbing solution; ^b 1M-HCl, ^c 0.01M-NaCl, ^d H₂O.

Even after desorption with 1M-HCl part of the barium remains attached to the surface of polyethylene. There are evidently two modes of the binding of barium, since part of it desorbs readily and fast (Fig. 6, curve 1). The extent of the desorption does not depend on the time interval between the starts of the adsorption and the desorption. Thus desorption after 20 hours' adsorption was the same (within the range of experimental error) as that after 15 minutes' adsorption. (Owing to the rapid course of the adsorption (curve 2, Fig. 6) its extent in the two cases was the same). These facts prove that the incomplete desorption is not caused by diffusion of barium into polyethylene, but that it is probably due to the formation of some firm linkage of barium to the surface of polyethylene. However, the nature of this linkage remains for the present unclear.

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