

SORPTION ISOTHERMS OF IONS, MOLECULES AND COLLOIDS ON POLYETHYLENE*

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The paper describes adsorption of ions Ba^{2+} , molecules $\text{Hg}(\text{OH})_2$ and colloids of $\text{Fe}(\text{OH})_3$ and HgS on polyethylene in relation to concentration of the adsorbate (10^{-8} to 10^{-3}M), pH , composition and age of the solution. Desorption of molecular $\text{Hg}(\text{OH})_2$ from polyethylene has also been studied. Analysis of the sorption isotherms revealed that the concentration dependence of the sorption of ions and colloids fits the Langmuir equation, whereas the sorption of molecules can be described by the Freundlich sorption isotherm. An exception is the sorption of mercuric sulphide *in statu nascendi*, which obeyed the Sips isotherm. Conclusions are drawn on the adsorption capacity of polyethylene for the given substances and some findings on the character of the sorption linkages are reported.

The objective of this work was to get more knowledge on the regularities of adsorption of traces of elements from aqueous solutions onto polyethylene by studying the adsorption and desorption in relation to concentration of a trace substance. For this study we chose substances whose states in aqueous solutions are sufficiently known and which can represent various forms of the existence of traces in a solution. As a representative of trace cations we selected barium, which forms colloids in aqueous solutions to a negligible extent only¹. The sorption of molecules was studied on divalent mercury, which in neutral and basic solutions occurs mainly in the form² of $\text{Hg}(\text{OH})_2$. To study the sorption of colloids we employed solutions of trace iron, present almost exclusively in the form of colloidal ferric hydroxide^{3,4}, and sulphide solutions of mercury, containing colloidal mercuric sulphide⁵.

The literature gives few data on the concentration dependence of sorption of traces on organic hydrophobic polymers. Belloni⁶ found that the adsorption of promethium onto polyvinyl chloride from 0.01M-HNO_3 can be expressed by the Langmuir sorption isotherm. According to Starik and coworkers⁷ the sorption of zirconium on teflon obeys the Freundlich isotherm. Some authors only state that the absolute value of adsorption increases with increasing concentration of the trace substance⁸. The concentration dependence of sorption is usually complex if the state of the trace element varies with its concentration in the solution. In such cases the sorption isotherm shows

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irregularities; the sorption may, *e.g.*, exhibit a peak⁸, or its relative value increases with the increasing concentration^{3,9}.

EXPERIMENTAL

All solutions were prepared from three times distilled water and A. G. chemicals. Their pH values were adjusted with aqueous sodium hydroxide and hydrochloric acid (Ba, Fe) or nitric acid (Hg). The indicators were radionuclides ¹³³Ba, ⁵⁹Fe and ²⁰³Hg (ref. 1-3). Prior to use the active preparations were suitably diluted with hydrochloric or nitric acid and a standard solution of an inactive isotope of the same element. The solutions for studying adsorption were brought to the desired pH always from the acid side. The stock solution of a labelled trace element was added as the last one. A freshly prepared solution was either employed immediately for an experiment or was left standing in a stoppered bottle for 7 to 14 days. All solutions were prepared and kept in a dust-proof box. The vessels and pipettes had been carefully washed with a hot mixture of concentrated HCl and HNO₃ (1 : 1).

The adsorption was studied on the inner surface of closed polyethylene 30-ml bottles (manufactured by Plastimat, Liberec); the inner surface including the closure was $74 \pm 1 \text{ cm}^2$. Since it had been ascertained that treatment of the polyethylene surface with acids or hydroxides had no significant effects on the adsorption the bottles were washed before experiments in water only. Bottles charged with 10 ml of an adsorbate solution were agitated 15 h on a shaker at 22-25°C. Simultaneously with pipetting the adsorbate solution we always prepared a standard whose activity equalled that of the pipetted solution before the adsorption. When the adsorption ended 5 ml was withdrawn for activity measurement and the rest was used to measure pH. The adsorption was calculated from the activity difference before and after the experiment. If the adsorption is below 10% this method of evaluation is charged with a great error. For this reason the adsorption was determined directly in such cases. The solution was drained out and the radionuclide was desorbed quantitatively with an acid (checked by measuring the activity of the bottle). The activities of the desorption solution and the standard were compared. For other details see^{1,3,5}. The measurement and evaluation of the desorption of mercury is described elsewhere⁵. The activities were measured with a scintillation counter SC-4 (U.S.S.R.) and a well-type crystal of NaJ(Tl). Samples in 5-ml glass ampoules were inserted into the well in the crystal. To prevent adsorption of the radionuclide on the wall of the ampoule, 0.5 ml of 6M-HCl had been pipetted into each ampoule. pH of the solutions was measured with a glass electrode G 202 C and a pH-meter PHM 52 (Radiometer, Copenhagen).

RESULTS

The data given in the present paper are averages of three or more measurements (as many as 15). At low concentrations of barium (10^{-7} to $5 \cdot 10^{-6} \text{ M}$, Fig. 1) the adsorbed quantity of barium (a) was a linear function of its equilibrium concentration in the solution (C), the slope of the line being 1. With increasing concentration the surface got progressively saturated. A constant, final amount of Ba (a_{max}) adsorbed from solutions where the molarity of barium exceeded 10^{-5} M . A similar graph was obtained in evaluating the sorption of colloidal ferric hydroxide. At a starting concentration of Fe $> 10^{-4} \text{ M}$ the precipitate of the hydroxide was clearly seen in the solution. The adsorption of colloids on polyethylene was considerably higher than

the adsorption of ions. In either case the shape of the concentration dependence fits the Langmuir sorption isotherm ($a = a_{\max} kC/(1 + kC)$). The maximum levels of sorption (a_{\max} , corresponding to the adsorption capacity of polyethylene) were calculated from the slopes of the lines obtained by plotting C/a against C ($C/a = a_{\max}^{-1} C + k^{-1} a_{\max}^{-1}$), the adsorption coefficients (k) were obtained from the ordinates delineated by intersections of the y-axis with the lines. These constants were also calculated directly from the curves in Fig. 1 (Table I). The calculations do not take into

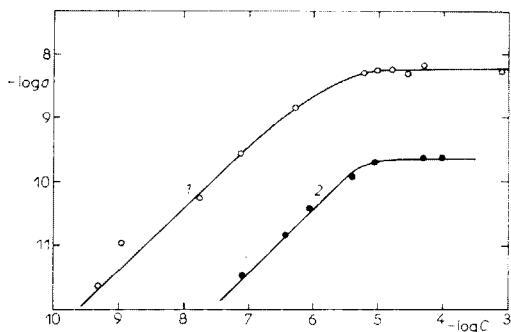


FIG. 1

Isotherms of Sorption on Polyethylene at 22–25°C (a in M/cm^2 , C in M/l)

1 Adsorption of colloidal $Fe(OH)_3$ from 0.0001M-NaCl of pH 7; 2 adsorption of Ba^{2+} from 0.0001M-NaCl of pH 8.

TABLE I

Characteristics of the Adsorption Isotherms

Adsorbate	a_{\max} , M/cm^2	$k \cdot 10^{-5}$, l/M	n^a	Note Fig./Curve
Ba^{2+}	$2.35 \cdot 10^{-10}$	1.60	1.0	b
	$2.44 \cdot 10^{-10}$	1.54	1.0	1/2
$Fe(OH)_3$	$6.53 \cdot 10^{-9}$	7.66	1.0	b
	$5.92 \cdot 10^{-9}$	8.45	1.0	1/1
HgS	$2.8 \cdot 10^{-8}$	—	0.75	2/1
	$1.2 \cdot 10^{-8}$	1.97	1.0	2/2
$Hg(OH)_2$	$>10^{-9}$	—	0.47	2/5
	$>10^{-9}$	—	0.61	2/3
	$>10^{-9}$	—	0.72	2/4

^a The slope of the linear part of the isotherm in logarithmic coordinates. ^b Determined from the graphical plot of the function $C/a = a_{\max}^{-1} \cdot C + k^{-1} \cdot a_{\max}^{-1}$.

account the unevenness of the surface, so that the actual surface was greater than the considered (geometrical) one. For this reason the actual values of a_{\max} were lower.

The adsorption of mercuric sulphide from fresh solutions of Hg concentrations below 10^{-5}M increased linearly in logarithmic coordinates (Fig. 2) with increasing concentration of Hg; the slope of the line is <1 (Table I). With solutions 14 days old the adsorption was somewhat smaller and its concentration dependence fitted the Langmuir sorption isotherm (Fig. 2, Table I).

The concentration dependence of the sorption of $\text{Hg}(\text{OH})_2$ on polyethylene was studied in relation to pH, composition and age of the solution (Fig. 2). The measured values of adsorption fitted lines of slopes <1 and depended on pH of the solution and concentration of sodium nitrate. The age of the solution had little effect on the adsorption. At mercury concentration above $5 \cdot 10^{-4}\text{M}$ the solutions turned turbid by the formation of the colloidal hydroxide, so that the adsorption could no longer be studied.

FIG. 2

Isotherms of Sorptions of Mercury on Polyethylene at $22\text{--}25^\circ\text{C}$ (a in M/cm^2 , C in M/l)

1 Fresh $0.01\text{M}-(\text{NH}_4)_2\text{S}$, pH 4; 2 14 days old $0.01\text{M}-(\text{NH}_4)_2\text{S}$, pH 4; 3 fresh (\ominus) and 7 days old (\oplus) $1\text{M}-\text{NaNO}_3$, pH 7.8; 4 fresh $0.0001\text{M}-\text{NaNO}_3$, pH 7.8; 5 fresh solution 0.0001M in NaNO_3 and 0.01M in NaOH , pH 12.

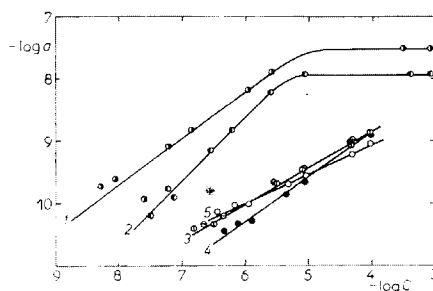


TABLE II

Desorption of Molecules $\text{Hg}(\text{OH})_2$ (in % after 15 h) by $1\text{M}-\text{HNO}_3$ Following Adsorption from Solutions Differing in Composition, Age and pH

Original conc. of $\text{Hg}(\text{OH})_2$ in ads. sol., M	Adsorption pH		Adsorption solution of pH 7.8 containing $1\text{M}-\text{NaNO}_3$	
	7.8	12.0	fresh	7 days old
$5 \cdot 10^{-7}$	—	—	33.8	15.9
$8 \cdot 10^{-7}$	21.9	11.6	39.3	39.9
$1 \cdot 10^{-6}$	26.4	11.7	—	—
$5 \cdot 10^{-6}$	62.4	23.8	59.3	65.5
$1 \cdot 10^{-5}$	55.7	27.0	53.7	71.9
$5 \cdot 10^{-5}$	63.4	31.9	41.7	67.7
$1 \cdot 10^{-4}$	74.2	55.8	60.1	59.5

In addition to studying the concentration dependence of the sorption of molecular $\text{Hg}(\text{OH})_2$ we investigated their desorption effected by the addition of 1M- HNO_3 . Despite the considerable spread of the results (Table II) the desorption seemed to increase with the increasing concentration of mercuric hydroxide in the adsorption solutions (and, consequently, even on the surface), especially in the region of the original concentrations $5 \cdot 10^{-7}$ to $5 \cdot 10^{-6}$ M. This fact corroborates the earlier finding⁵. pH, composition and age of a solution do not have a clear-cut effect on this increase.

DISCUSSION

Comparison of the adsorptions of the individual substances reveals the order $\text{Ba}^{2+} < < \text{Hg}(\text{OH})_2 < \text{Fe}(\text{OH})_3 < \text{HgS}$. This order roughly agrees with the decrease in solubility, and probably even hydrophility, of these substances. It also accords with the general view that a more hydrophobic substance has a greater tendency to deposition on the surface of a hydrophobic solid phase. The tendency to adsorption is evidently different in the early stage of formation of the solid adsorbate (colloid). This might account for the difference in adsorption of mercuric sulphide from fresh and old solutions. The mechanism of deposition of colloids *in statu nascendi* is probably different from that of colloids already formed. This can be deduced from the difference of slopes of the linear increase in adsorption plotted in logarithmic coordinates. The sorption of HgS from old solutions obeyed the Langmuir equation, whereas the concentration dependence of sorption from fresh solutions fitted the Freundlich or, better still, the Sips¹⁰ isotherm. It cannot be ruled out that in the latter case the process involved is aggregation of molecules on the active sites of the surface; such a process would be similar to a molecular sorption. This interpretation is supported by the fact that in logarithmic coordinates the slope of the increase was < 1 , as in the sorption of molecular $\text{Hg}(\text{OH})_2$.

To ascertain the actual cause of this fact would be rather a problem since not even the mechanism of sorption of molecules has yet been satisfactorily elucidated. The low slope of the increase can in principle have one or two reasons: the molecules of the adsorbate on the surface affect one another and/or the sorption sites of polyethylene for molecules are not energetically homogeneous. The first possibility seems less probable, if merely for the fact that the increase in sorption with concentration had a constant slope from even very low concentrations of the adsorbate, at which stage the occupation of the surface was negligible. The other interpretation is also supported by the observation that the facility of desorption of molecular $\text{Hg}(\text{OH})_2$ was enhanced by the increasing occupation of the surface, which is a typical indicator of energetic heterogeneity of the sorption bonds¹¹. Consequently, the sorption sites of polyethylene for molecules can be supposed to be energetically heterogeneous. The determined adsorption isotherm would accord with an exponential distribution of energy of the sorption sites¹².

The concentration dependences of sorption of barium ions and colloidal ferric hydroxide, possibly even of HgS, fit the Langmuir sorption isotherm. Hence it can be inferred that the sorption sites are energetically homogeneous in these cases and that the particles do not affect one another. If only the geometrical surface of polyethylene is considered and the diameter of a hydrated barium ion is set equal to 0.82 nm (ref.¹³) it can be calculated that at the maximum adsorption the occupation of the surface attains nine-tenths of a monoatomic layer of barium ions. Since this is a considerably high extent of surface covering and no aberrations from the Langmuir sorption isotherm (indicative of mutual repellency of the adsorbed ions) were observed it can be assumed that the actual surface of polyethylene substantially exceeds the geometrical one. A similar conclusion was reported by Belloni for poly(vinyl chloride)⁶. However, the degree of occupation of the surface by Pm^{3+} ions calculated by this author was about 2 orders of magnitude lower than that calculated by ourselves. Belloni's results may be charged with an error as they are calculated from the crystallographic radius of the Pm^{3+} ion and it is unlikely that the ions adsorbed in the outer part of the double layer¹ should be fully dehydrated. A similar calculation for colloidal ferric hydroxide and mercuric sulphide colloids can hardly be carried out, since the size of particles of the adsorbate is not known and can moreover vary with concentration of the sorbate. Nevertheless it seems that in the case of colloids the surface does not get fully saturated; if this were so the adsorption capacity of polyethylene would be higher.

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