

INVESTIGATION OF SOIL-SOLUTION SYSTEMS ON THE CAPTURE OF RADIOIODINE IN RELATION TO pH*

J. BENEŠ

*Laboratory of Radiological Dosimetry,
Czechoslovak Academy of Sciences, 180 86 Prague 8*

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The paper describes pH changes of solutions brought into contact with soils and the effect of pH on the capture of microconcentrations of iodide in solution (followed with the aid of ^{131}I) by soils. Except for strongly acid media the sorption of iodide was inversely proportional to pH of the solution. Factors affecting the sorption, *viz.* time of the soil-solution contact, concentration of an indifferent electrolyte and the pre-conditioning of the soil, have also been studied. The reduced sorption of iodide from strongly acid solutions is explained and possible mechanisms of the processes are discussed.

There is still some controversy in views on the behaviour of iodine in soils. It is well known that iodine is readily taken in by plants¹, but there are different views as to the capacity of soils to keep it. Some authors² assert that the sorption of iodine by soil is negligible, so that the iodine can be easily eluted. This elution allows the use of some iodine isotopes as tracers in the terrain³. However, Bondarenko and Globus⁴, experimenting with soils, observed losses as high as 50% of ^{131}I from the tracer added. They ascribed these losses to oxidation processes leading to liberation of elementary iodine and its escape by sublimation. Other authors reported evident sorption of radioiodine on soils^{5,6} or on some of their constituents^{7,8}. Of the chemical forms of iodine the most important one in soils is iodide. In measuring the sorption of iodide in relation to the contents of different soil constituents the degree of the sorption proved dependent on pH of the soil⁸.

This paper deals with the behaviour of trace concentrations of iodide in the system soil-solution in relation to concentration of hydrogen ions, covering the whole range of pH.

EXPERIMENTAL

All the chemicals were of A.G. purity and the solutions were prepared using redistilled water. The stock solutions were analysed by the usual methods. Solutions of $\text{K } ^{131}\text{I}$ were obtained by dissolution of carrier-free, commercial (Soviet), fresh preparations, stated to contain specific activities of $1,9$ to $4,4 \cdot 10^8 \text{ s}^{-1} \cdot \text{ml}^{-1}$, 97 to 98% of $\text{K } ^{131}\text{I}$, 1% of the daughter $^{131\text{m}}\text{Xe}$ and less than 0.01% of the other radioisotope admixtures. The contents of SO_4^{2-} and Te were less than

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0.1 mg/ml and 0.01 mg/ml, respectively, and pH was within a range of 7.0 to 8.5. The stability of the iodide form was checked by thin-layer chromatography on plates coated with the Silpearl sorbent, wide-porous silica gel, prepared according to Pitra, and starch as binder (Silufol, Kavalier, ČSSR); the eluant was a system methanol-ammonium hydroxide-acetic acid-water. Prior to experiments the solutions of ^{131}I were tested for the presence of IO_3^- and IO_4^- ; only those solutions which proved free of these ions were employed. The total content of iodide in the starting preparation of ^{131}I was not determined; for in our experience⁹ the sorption of iodide on a soil is not significant unless the analytical concentration of iodide in the solution is greater than 10^{-7}M . Considering the data¹⁰ on the concentration of I^- ions in carrier-free solutions of $\text{K } ^{131}\text{I}$ the analytical concentrations of I^- in the diluted solutions were safely below the critical level. In order to compensate for the possible differences between the individual commercial preparations the solutions of ^{131}I were diluted with a 10^{-9}M solution of KI.

Five fundamental types of Czechoslovak agricultural soil were selected for the study: chernozem, brown soil, brown acid soil, podzolic soil and the illimerized soil. The spots where samples were taken, fundamental characteristics of the soils, their ion-exchange capacities and contents of the ions that could be exchanged were described earlier¹¹. The samples of the soils were allowed to dry in the air, sieved (mesh 2 mm), then dried in a thin layer at 105°C for 60 h in an air-flushed thermostat. The standard chosen for potentiometric titrations was the mineral montmorillonite, *i.e.* Italian bentonite Valdol C 13 (its theoretical composition is 66.7% SiO_2 , 28.3% Al_2O_3 and 5% H_2O , the general formula being $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20} \cdot n\text{H}_2\text{O}$). The total sorption capacity was experimentally determined as 157.74 mval/100 g and the specific surface as $73.7 \pm 1.2 \text{ m}^2/\text{g}$. The organic substances present in montmorillonite were removed by gentle washing of the mineral in a 1% solution of hydrogen peroxide for a week. The samples of the soils and montmorillonite were in their natural ionic forms.

pH of the solutions was measured with a compensation apparatus PHM 4 (Radiometer, Copenhagen, Denmark) employing a glass electrode G 200 B and a saturated calomel electrode K 100 (Radiometer, Copenhagen). The distribution of the radioiodine between a soil and a solution was determined radiometrically. The radioactivities of the dry residues of the aqueous phase (containing Na_2SO_3 as admixture) were measured with GM tubes with terminal windows. The soil samples were measured with a crystal of NaI (TI). Suspensions of the soils and montmorillonite in water were titrated with 0.1M-HCl; the volume of a titrated suspension was 200 ml, so that the volume changes due to the titrations could be neglected. The acid was added at a precisely adjusted rate while the reaction mixture was vigorously stirred with an electromagnetic stirrer. The temperature was kept at $22 \pm 0.5^\circ\text{C}$ and the pH values were measured 5 min after every addition of the acid. The sorption properties of the soils were assessed from the distribution of the radioiodine between the solid and the liquid phases. The ratio of the liquid phase volume to the mass of a soil was invariably 10 ml/g. The systems soil-solution were agitated in closed glass cells on a shaker. The phases were separated by centrifugation. As in most cases the experimental conditions did not allow equilibrium distribution of ^{131}I to establish between the two phases the measured data were not used to calculate the distribution coefficients K_d ; the results are expressed in terms of the relative sorption of $y = ([A]_{\text{tot}} - [A])/[A]_{\text{tot}}$, where $[A]$ designates the concentration of iodine in the solution after the sorption and $[A]_{\text{tot}}$ its total concentration in the system (soil + solution). The values of A were calculated from radioactivity measurements. The symbol Δt denotes the time of contact of the soil with the solution.

RESULTS AND DISCUSSION

The sorption of radioiodine was conducted in media where the desired pH values were adjusted by additions of hydrochloric acid or aqueous potassium hydroxide of known

molarities. Comparison of pH values of the starting solutions (pH_{init}) with those after the sorption (pH_{fin}) shows that the soils affected the hydrogen ion concentrations substantially; both concentration and the time of the soil-solution contact were significant factors. Fig. 1 gives the pH changes ($\Delta\text{pH} = \text{pH}_{\text{fin}} - \text{pH}_{\text{init}}$) in relation to the time a system was agitated. As can be seen pH changes were observed in acid, neutral and alkaline media. If an acid or neutral solution was treated with a soil a rapid increase in pH occurred. With alkaline solutions a decrease in pH was observed. This can be accounted for by the tendency of a soil to bring a solution to the pH corresponding to its ion-exchange function. This tendency is so strong as to affect even pH of weak buffers¹². A sample of soil heated 5 h to 800°C produced no measurable shift of pH (Fig. 1, curve 2). The heat released the chemically bound water and the organic substances decomposed. This suggests that it is mainly the organic component that is responsible for the buffering capacity of soils. Since sorption of iodine by soils was optimum in media of $\text{pH} < 7$ we concentrated our attention on this region.

The curve relating ΔpH to time of the soil-water contact (Fig. 1, curve 4) takes an interesting course. After an initial steep increase pH exhibited an interim decrease.

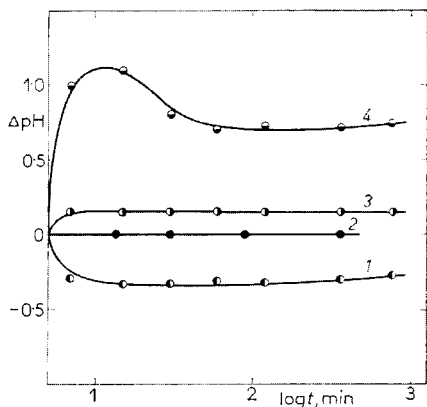


FIG. 1

pH Change of the Starting Solution in the Course of its Shaking with Brown Soil, $\Delta\text{pH} = \text{pH}_{\text{fin}} - \text{pH}_{\text{init}}$

1 Starting solution 0.05M-KOH; 2 annealed soil, starting solution 0.05M-HCl; 3 starting solution 0.05M-HCl; 4 starting solution H_2O .

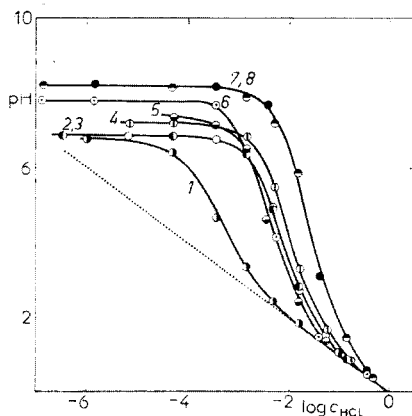


FIG. 2

Relation of Proton Concentrations in the Final (pH) and the Starting ($\log c_{\text{HCl}}$) Solutions for Different Soils

1 Brown soil annealed to 800°C, $\Delta t = 90$ min; 2 acid brown soil, $\Delta t = 90$ min; 3 podzolic soil, $\Delta t = 90$ min; 4 illimarized soil, $\Delta t = 90$ min; 5 brown soil, $\Delta t = 90$ min; 6 brown soil, $\Delta t = 24$ h; 7 chernozem, $\Delta t = 90$ min; 8 chernozem, $\Delta t = 24$ h.

With brown soil it occurred in the period 15 min to 6 h. Later on pH increased again. The curves for soils in hydrochloric acid of very low acidity ($4.5 < \text{pH} < 7$) were qualitatively the same. In experiments in which periods of 7 hours' agitation were followed by 17 h of rest pH of the solution after 3 days' contact with the soil attained the original peak. The time course of pH changes is given by the ion exchange of hydrogen for the alkalis in the mineral particles of the soil, which gradually slows down. The ion exchange is the faster the more acid the solution. The interim decrease of pH in the neutral or mildly acid region may partly be due to neutralization of the alkalis by the absorbed aerial carbon dioxide and possibly even by organic acids extracted from the solid phase, the kinetics of these processes controlling the length of the decreased pH period. Similarly to experiments with the soils, a pH increase with time had been observed¹³ with very dilute solutions of the mineral albite if the starting pH was 4.2 to 5. Since in this case the organic component can be disregarded and since the experimental conditions made it improbable for the pH changes to be due exclusively to aerial carbon dioxide a clear-cut interpretation of the phenomenon in question would require further study. As to the pH decrease in the alkaline region it is possible to ascribe it to adsorption of hydroxyl ions on the mineral surface of the soil particles. A strong adsorption of these ions on clay minerals suspended in alkaline media has been demonstrated.

The relations between the hydrogen ion concentrations in the starting and the final solutions for the given ratio of 10 ml/g and the soils studied are shown in Fig. 2. Experiments with some of these soils were allowed to proceed for different times of the soil-solution contact, so that even the time factor can be evaluated. If no soil-solution interaction had occurred the dependence would be linear, as is shown by the dashed line. A linear character of the dependence was observed in strongly acid media only. The least deviations from the theoretical course appeared with samples which were dehydrated and freed from the organic substances by annealing. In either case, however, the structural lattices of various compounded minerals got upset. Chernozem, shown by grain-size analysis to be the richest in the finest clay fraction, deviated most from the linear course, the deviations being observed even in strongly acid solutions. With increasing pH of the starting solution the curves tend to limit values equalling pH's of aqueous solutions of the soils alone.

If a soil in its natural ionic form gets into contact with ions of hydrochloric acid cations are washed off from the mineral surface, or from the interlayer space of the mineral lattice, and progressively replaced by H^+ ions from the solution. The potentiometric curves of dilute aqueous soil suspensions well reflect this replacing process, by which the minerals are brought into their stable H^+ forms. Fig. 3 shows the titration curves of differently concentrated soil suspensions and of a suspension of montmorillonite. The latter exhibits two inflexion points, characterizing two stages of the cation exchange. The first inflexion point corresponds to exchange of low-bonding-energy cations (here probably Na^+ and K^+); these cations are sorbed mainly

on the surface and edges of the mineral to balance the electrical charge produced by surface deformations of the lattice. The second inflexion point corresponds to elution of cations with a higher bonding energy (probably the cations from the interlayer space of the mineral, mainly Ca^{2+} and Mg^{2+}). The plateau on curve 3 between the two inflexion points can be ascribed to the preceding occupation of the free mineral surface by protons, and the gradual decrease in pH, converging to a limit toward the end of the titration curve, may be due to the formation of a stable H^+ form of montmorillonite, after all the exchangeable cations had passed into the solution. Marshall¹⁴ views the titration of clay in the H^+ -form with an aqueous alkali hydroxide as a process of neutralization. Montmorillonite can then be regarded as a salt of a dibasic acid. The potentiometric titration curves of soil suspensions are similar, but the inflexion points are much less marked; this is probably due to slower establishment of equilibrium in the exchange of cations for protons from the solution. The titration curves of some of the soils exhibit even more inflexion points, so that their suspensions behave as salts of multibasic acids. There is an obvious relation between the course of a potentiometric curve and concentration of the suspension, which is the more marked the easier the release of sorbed cations from the solid phase. Curve 1 in Fig. 3 resembles the titration curve of kaolinite¹⁵, which behaves like a salt of a weak

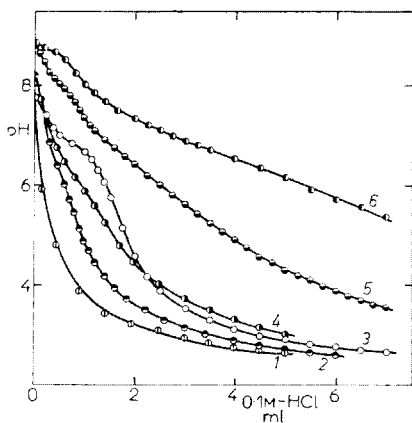


FIG. 3

Potentiometric Titrations of Aqueous Suspensions (in %) of Soils and Montmorillonite

1 Brown soil, 0.5%; 2 chernozem, 0.25%; 3 montmorillonite, 0.06%; 4 brown soil, 2%; 5 chernozem, 1%; 6 chernozem, 2%.

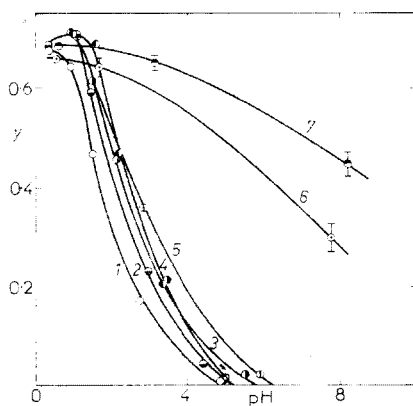


FIG. 4

Sorption of I^- Ions on Soils in Relation to pH

1 Podzolic soil, $\Delta t = 90$ min; 2 acid brown soil, $\Delta t = 90$ min; 3 illimerized soil, $\Delta t = 90$ min; 4 brown soil, $\Delta t = 90$ min; 5 chernozem, $\Delta t = 90$ min; 6 brown soil, $\Delta t = 25$ h; 7 chernozem, $\Delta t = 25$ h.

monobasic acid. From the consumption of acid up to the last inflexion point it is possible to calculate the total exchange capacity of the mineral constituent; the value for montmorillonite is given above and that for kaolinite was determined¹⁵ as 9.86 mval/100 g. As can be deduced from Figs 1, 2 and 3 sorption of a radionuclide on soils is given by pH_{fin} , not by pH_{init} of the solutions.

Sorptions of iodide traces in relation to the final pH values are plotted in Fig. 4 ($\text{pH} = \text{pH}_{\text{fin}}$). The experimental points (marked as circles) represent the mean values from three measurements, the mean-square errors are given if more than eight simultaneous experiments were carried out. In view of the established elution of cations from soils by hydrochloric acid the experiments expressed by Fig. 4 do not refer to a constant ionic strength. All curves demonstrate that pH of a system has a strong effect on sorption of radioiodide by soils. The course (shape) of a curve is influenced chiefly by the time of the soil-solution contact, the kind of soil is a less important factor. For the sorption-pH dependence of iodide traces it invariably applies that the sorption efficiency of a soil increases with concentration of H^+ ions in the solution, *i.e.* $y = f(1/\text{pH})$. Such a course of the curves suggests a positive charge on the soil particles, increasing with decreasing pH. However, mineral particles in soils are normally supposed to have a negative charge, as a result of either isomorphous substitution of ions in the lattice or dissociation of functional groups on the particle surface. The assumption of a negative charge makes it possible to explain the high sorption capacities of soils for cations. According to the present-day views¹⁶ the capture of radioactive isotopes on water-suspended clay particles is controlled by several mechanisms; a possible role of complexing and humine substances is considered, but sorption and heterogeneous exchange are supposed to be the main factors.

In the soil-anion interactions two phenomena should be considered as the most important ones: 1) repellency between anions and the negative charges on the surface of soil particles, and 2) linkage of anions to binding sites, located probably on the edges of the particles. The ion capture may be enhanced both by electrostatic attraction between anions and positively charged sites and by covalent linkages. The first phenomenon is almost ever-present and is nonspecific, whereas the other depends on the properties of the anions. The positive charge on edges of mineral particles in acid media is a result of bond rupture. With clay minerals this rupture is most facile where Si^{4+} is substituted for Al^{3+} . A decrease in pH of the surrounding medium increases the positive charge. The positive charge on the surface of the particles may also account for the observation that in a certain range of the acid region the sorption of cations by soils takes a steep drop, which phenomenon is usually attributed to a competition effect of H^+ ions¹⁷.

The sorption of anions on soils is also interpreted by other mechanisms, but none can fit all experimental facts. For example, there is a view that at $\text{pH} < 7$ electrolytic dissociation of inorganic macromolecules occurs, with the liberation of OH^- ions

and their replacement by anions of the salts present in the solution¹⁶; this view fails to account for the usual drop of pH following addition of a salt, when a strong increase of pH should be expected. The effect of pH on the extent of sorption is quite disregarded by the molecular mechanism of the anion adsorption¹⁸.

Fig. 5 shows the influence of an indifferent electrolyte and ionic strength on the sorption of iodide traces by the brown soil. A constant ionic strength of the solution ($I = 0.6$) was secured for curve 3; in the other cases ionic strength increased with decreasing pH. With curve 4 the value of I went from 0.005 to 0.5, with curve 2 it was constantly higher by 0.3 than the values corresponding to curve 4. In addition to potassium chloride, potassium nitrate was also employed to change the ionic strength of the solution in the sorption experiments. The curves retained their character, they were just shifted in the direction of the axis of ordinates. The decrease in the sorption of iodide on an addition of potassium chloride or nitrate indicates that trace concentrations of iodide occur in the ionic form, so that the capture of radioiodide by soil is a process of ion sorption (a several days' soil-solution contact is not considered here). This is in agreement with the report of Schweitzer and Jackson¹⁹, who, employing the methods of filtration, centrifugation and adsorption, detected no formation of radiocolloids in solutions of I^- . Furnica²⁰ believes that 15 to 25% of the ^{131}I entrapped by natural suspensions in surface reservoirs may be due to colloidal adsorption. The difference in sorption properties of a soil sorbent before and after the heating, by which the organic component is burned out, cannot be ascribed to the non-ionic processes of I^- sorption only; it must be borne in mind that the temperature of 800°C upsets the structure of mineral particles, with the result of changed sorption properties. The sorption of traces of iodide on an annealed soil in relation to pH is described by curve 1 in Fig. 5.

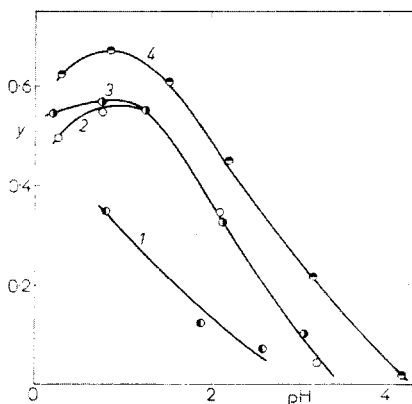


FIG. 5

Effects of an indifferent Electrolyte (Cl^-) and of Degradation of the organic Constituent in Brown Soil on the Sorption of I^- ions

$\Delta t = 90$ min, pH adjusted with hydrochloric acid; 1 annealed soil, HCl, variable I ; 2 HCl, variable I (0.05 to 0.5); 3 HCl-KCl, constant $I = 0.6$; 4 HCl-KCl, variable I (0.3 to 0.8).

The functional dependence of iodide sorption on proton concentration, $y = f(1/\text{pH})$, is not valid at $\text{pH} < 1$. In this region the sorption of iodide ions decreases with pH . According to our findings two factors are responsible for that. In the first place it is the effect of an indifferent electrolyte, in our case high concentrations of Cl^- ions (Fig. 4). The differences in ionic strength, *i.e.* the differences between the analytical concentrations of Cl^- ions referring to the first and the second sets of experimental points of curves 2 and 4 in Fig. 5, are considerable. With curve 2 it is a two-fold value and with curve 4 more than a three-fold one. Naturally the sorption of I^- ions is reduced. However, experiments carried out at a constant ionic strength (Fig. 5, curve 3) reveal another factor, *viz.* a change in quality of the sorbent; the excess of hydrochloric acid attacks and dissolves the structural lattice of mineral components of the soil. As would be expected, this factor depended on the time of the soil-solution contact, which is seen from the curves for different Δt values in Fig. 4. The upsetting and dissolution of the mineral lattice in strongly acid media can also be inferred from the titration curves.

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