

STUDIES ON ORGANO-METALLIC INTERACTIONS IN THE MARINE ENVIRONMENT *

Part 2. Interaction of Metallic Ions with Humic Acid from a Marine Sediment

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ABSTRACT

Sorption of radionuclides in sea-water by humic acid prepared from a marine sediment yielded distribution coefficient values (K_d) of the order of 10,000 for Mn, Co, Zn and Y. Solubilization of Ba, Mn, Zn, Co, Fe, Y and Zr-Nb was observed in ammonium humate; Ba was in the form of cationic and/or cationic complexes, whereas Mn, Zn, Co, Fe, Y, Zr-Nb formed significant proportions of 'nonionic' or 'anionic' complexes. These complexes were comparable to EDTA complexes in their behaviour on the ion exchange column. The attainment of equilibrium in the solubilization or complexing process has been observed to be slow, ranging from days to a month.

INTRODUCTION

HUMIC ACID is an ion exchange material, but adsorption or solubilization of metal ions and metal compounds by the acid (or humate) is not necessarily associated with its exchange centres or related to its exchange properties. Pillai *et al.*¹ observed the presence of trace elements even in highly purified humic acids indicating sites within the humic acid for bonding metal ions. Alexandrova² suggested that aluminium and iron are included in the anionic part of the humus compound. Kononova³ indicated the association of trace elements and rare elements with humic substances in the form of chelates. Schnitzer and Skinner⁴ reported that soil organic matter (the NaOH extract, mainly of humic substances) forms stable water-soluble complexes with elements such as Fe^{+++} , Al^{+++} , Ca^{++} , Mg^{++} , Cu^{++} and Ni^{++} . Basu *et al.*,⁵ in their studies with humic acid, found that the ion desorption curves were always lower than the adsorption curves indicating the possible formation of a complex. Zinc was found to be more strongly bound on humic acid than calcium, but less strongly than copper or ferrous iron by Randhawa and Broadbent.⁶ Mortensen⁷ stated that the studies which have suggested that soil organic matter is able to chelate metals have relied on indirect evidence. The present work was conducted, in this context, namely, to study the sorption and solubilization of metal ions present by humic acid extracted from a marine sediment.

EXPERIMENTAL

Preparation of Humic Acid

Humic acid was extracted repeatedly from a marine sediment (collected from near-shore region of Bombay) by a 0.2 N NaOH- Na_2CO_3 solution. Treatment was for 6 hours at 80° C. in air, the insoluble sediment centrifuged out and the humic acid was precipitated by HCl at pH 2. The precipitate was purified by repeated dispersion in alkali, filtration (all filtrations in this preparation and in experiments to follow were also carried out with 0.22 μ Millipore membrane filters), precipitation by acid, dialysis, and prolonged electrodialysis at 200 V. The stock humic acid (pH 3.2 and base exchange capacity of 383 meq./100 gm.) thus prepared was stored in a glass bottle which was rigorously cleaned with aqua regia followed by steam cleaning for 80 hours and repeated washing with DDW.

Sorption of Radionuclides by Humic Acid in Sea-Water

Freshly collected sea-water from Bombay Harbour was allowed to settle for 24 hours and the supernatant water was filtered. The filtered sea-water (pH 7.8) was used for the sorption experiments. Doubly concentrated sea-water (DCSW—pH 8.4) was prepared by evaporating the sea-water to half its original volume under an infrared lamp and then filtering it. (This water was used in the experiments to compensate for the dilution on the addition of a volume of sodium humate to the filtered sea-water.) The sodium humate (pH 7.9) was obtained by dropwise

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addition of caustic soda to humic acid solution. Aqueous solutions of the compounds (see Table I) of the following isotopes, Mn^{54} , Fe^{59} , Co^{60} , Cu^{64} , Zn^{65} , Y^{90} and Cs^{134} were used in the experiments.

To two steam-cleaned 250 ml., wide mouth reagent bottles were respectively added:

Bottle 1—Control: 90 ml. sea-water; 5 ml. DCSW, 5 ml. DDW (pH of mixture 8.0).

Bottle 2—Sample: 90 ml. sea-water and 5 ml. DCSW (pH of mixture 8.0).

A known measured equal volume ($\sim 100 \lambda$) of the isotope solution was added to each of the bottles, shaken well, and left to equilibrate. The total carrier of each element present in the system is given in Table I. There was no

TABLE I

Chemical forms, decay characteristics and carrier contents of the isotopes used in sorption experiments

Isotope	Half-life	Mode of decay	Chemical form	Total carrier ($\mu g/l.$)
Mn^{54}	291 d.	EC, gamma	$MnCl_2$	2
Co^{60}	5.27 y.	Beta, gamma	$CoCl_2$	1.7
Cu^{64}	12.8 h.	Beta, EC, gamma	$CuSO_4$	225
Zn^{65}	245 d.	Beta ⁺ , EC, gamma	$ZnCl_2$	60
Y^{90}	64.2 h.	Beta	YCl_3	756.6
Cs^{134}	2.2 y.	Beta, gamma	$CsCl$	110.5
Fe^{59}	45 d.	Beta, gamma	$FeCl_3$	15.2

added to Bottle 2, shaken well, and set aside for coagulation and settling (~ 4 hours) of humic acid. A very faint straw yellow colour, indicating solubilization of a part of humic acid in the medium was observed in the clear supernatant liquid. The control and sample bottles were shaken, specific volumes were withdrawn and filtered and aliquots (1 ml.) of the filtrate were counted. The difference between the two counting rates multiplied by the total volume of liquid in the sample bottle was calculated to show the extent of sorption of activity by humic acid in sea-water. All counting statistics were below the standard deviation of $\pm 2\%$. Solution of any precipitated activity in Bottle 2 by the humate has not been considered in the discussions to follow. The values of the distribution coefficient,

$$K_d = \frac{\text{Sorption of activity per g. of humic acid}}{\text{Activity per ml. filtrate of the sample}}$$

for a particular radionuclide were determined at different time intervals over prolonged periods. Results are shown in Tables II and III. The activity (625 cpm/ml.) of the filtrate from Fe^{59} -humic acid mixture, during the sorption experiments as above, was about four times higher than that of the filtrate from the control (144 cpm/ml.). This anomalous behaviour of Fe^{59} suggested the possible solubilization of Fe by the dissolved fraction of the humic acid.

TABLE II

Sorption of Mn^{54} , Co^{60} , Zn^{65} , Y^{90} and Cu^{64} by humic acid in sea-water

Mn^{54}		Co^{60}		Zn^{65}		Y^{90}		Cu^{64}	
Time (days)	K_d	Time (days)	K_d	Time (days)	K_d	Time (days)	K_d	Time (hours)	K_d
0.17	1285	0.17	10640	0.17	11140	0.17	12230	17	4625
2	2133	2	11350	3	11150	1	15360	24	5308
6	4059	7	11320	7	13030	2	15385	40	5981
12	5885	14	10970	10	13450	5	15440	48	7034
19	7825	21	12370	18	13080			65	7909
27	10189								
46	11780								
54	11370								
61	11140								
70	11210								

change in pH on addition of the isotope solutions. Definite volumes from Bottle 1 were withdrawn at 24-hour intervals immediately after thorough shaking, and aliquots (1 ml.) were counted before and after filtration. Equilibrium was assumed in both the bottles when the activity in the control filtrate remained unaltered for two successive days. Sodium humate (5 ml., 12.84 mg.) was then

TABLE III

Sorption of Cs^{134} by humic acid in sea-water

Time (days)	Activity in cpm. per ml. filtrate of	
	Control	Sample
6	1541	1533
13	1453	1480
27	1459	1462
35	1419	1411

Solubilization of Elements by Humic Acid

Fe in Sea-Water.— Fe^{59} (100 λ , 107400 cpm.) was added to each of:

5 ml. DDW	.. Control
5 ml. Sodium humate	.. Sample I, and
5 ml. DCSW	.. Sample II,

each contained in 250 ml. bottle, mixed well and kept for 1 hour with intermittent shaking.

To the control bottle was then added 5 ml. DCSW and 90 ml. sea-water, to Sample I bottle was added 5 ml. DCSW and 90 ml. sea-water, and to Sample II bottle was added 90 ml. sea-water and 5 ml. sodium humate.

The pH of the contents in the bottles was found to be 8.1. These were shaken well and kept for 24 hours with intermittent mixing. Aliquots were withdrawn at intervals immediately after thorough mixing, filtered and 1 ml. filtrate counted. Results are shown in Table IV.

TABLE IV

Solubilization of Fe^{59} by humic acid in sea-water

100 λ of Fe^{59} : 107400 cpm (1.8 μg . Fe)

Time (days)	Activity in cpm per ml. filtrate of		
	Control	Sample I	Sample II
1	26	223	35.5
4	20	200	46
9	26	201	59.4
16	23	171	54
39	16.5	113.5	58

Fe Zr-Nb and Ce in water and dilute alkali.—For each isotope, two well-cleaned centrifuge tubes were taken:

Tube 1 .. Control : 5 ml. DDW,
Tube 2 .. Sample : 5 ml. sodium humate (12.84 mg.; pH 7.9).

Each tracer (100 λ) was added to the tubes, pH was adjusted to 7 and the tubes were allowed to stand for 24 hours with intermittent shaking. Well-mixed solutions (2 ml.) were filtered and 1 ml. aliquots of the filtrates counted. The pH of the remaining 3.1 ml. solution in the tubes was raised to 10 with strong caustic soda, allowed to stand for 24 hours, 2 ml. of the well-mixed solutions were again filtered and 1 ml. aliquots counted. The balance of 1.1 ml. remaining in the tubes was diluted with 9.9 ml. of pH 10 water (i.e., dilution by a factor of 10), allowed to stand for 24 hours, filtered, and 1 ml. aliquots were counted. Results are shown in Table V,

TABLE V
Solubilization of Fe^{59} , Zr^{95} and Ce^{144} by humic acid in water and dilute alkali

	Fe^{59}	* $\text{Zr}^{95}\text{-Nb}^{95}$	* Ce^{144}
Added activity (cpm)	1174 (0.07 μg .)	26349	23619
	Activity in cpm per ml. filtrate of		
	Fe^{59}	$\text{Zr}^{95}\text{-Nb}^{95}$	Ce^{144}
Control:			
pH 7 ..	225	4273	12462
pH 10 ..	82	444	4538
pH 10: dilution 10	8	32	449
Sample (humic acid):			
pH 7 ..	1152	25955	23894
pH 10 ..	1161	26510	23829
pH 10: dilution 10	112	2506	2395

* Separated from fission products.

Ba, Fe, Y and Zr-Nb in ammonia water.—Experiments were conducted in 2% ammonia and comparison was made with ammoniacal EDTA. Ba^{133} as BaSO_4 , Fe^{59} and Y^{90} as chlorides and $\text{Zr}^{95}\text{-Nb}^{95}$ as $\text{ZrO}(\text{NO}_3)_2$ were used. To 1 ml. each of ammonium humate and ammoniacal EDTA, both equivalent to 1.7 mg. each, were separately added 1 ml. of 20% ammonia, the respective isotopes and the volumes were made up to 10 ml. They were shaken well, kept for 24 hours with intermittent mixing (10 days for $\text{Zr}^{95}\text{-Nb}^{95}$), filtered and aliquots (5 ml. for Ba, 1 ml. for others) of the filtrates counted. Aliquots (2 ml. for Ba, 1 ml. for others) of each were separately passed through Dowex 50 W- \times 8 (50-100 mesh) cation exchange columns (2 cm. \times 1 cm.) conditioned with 2% ammonia water, columns washed with 2% ammonia; effluent (including interstitial volume) and washings collected, evaporated to the volume necessary for the standard geometry (5 ml. for Ba, 1 ml. for others) and counted. Results are shown in Tables VI and VII.

TABLE VI

Solubilization of Ba^{133} , Fe^{59} , Y^{90} and $\text{Zr}^{95}\text{-Nb}^{95}$ in ammonium humate

	Ba^{133}	Fe^{59}	Y^{90}	* $\text{Zr}^{95}\text{-Nb}^{95}$
Added activity (cpm)	4352 (1217 μg .)	24715 (98 μg .)	284200 (170 μg .)	18854
	Activity in counts per minute in filtrate of			
	Ba^{133}	Fe^{59}	Y^{90}	$\text{Zr}^{95}\text{-Nb}^{95}$
Control ..	Nil	Nil	10444	4468
Ammonium humate	3198	13698	172760	20140

* Separated from fission products.

TABLE VII

Ion exchange behaviour of metal ion complexes with humic acid and EDTA on a Dowex 50 cation column in NH_4^+ form

Sample	Activity in cpm in		% passing through the column
	Influent	Effluent and washings	
Ba ¹³³ -H.A.	.. 639	Nil	..
Ba ¹³³ -EDTA	.. 634	Nil	..
Fe ⁵⁹ -H.A.	.. 1370	1362	100
Fe ⁵⁹ -EDTA	.. 1300	1290	100
Y ⁹⁰ -H.A.	.. 17276	10711	62
Y ⁹⁰ -EDTA	.. 12174	1080	97
Zr ⁹⁵ -Nb ⁹⁵ -H.A.	.. 2014	1917	95.2
Zr ⁹⁵ -Nb ⁹⁵ -EDTA	.. 1440	948	65.8
Mn ⁵⁴ -H.A.	.. 203	197	100
Co ⁶⁰ -H.A.	.. 1944	1774	91.3
Zn ⁶⁵ -H.A.	.. 4623	639	20.3

Mn, Co and Zn.—Humic acid, which sorbed Mn⁵⁴, Co⁶⁰ and Zn⁶⁵ in the earlier experiments in sea-water (see sorption experiments above), was filtered, washed free of sea-water, dissolved in 5 ml. of 2% ammonia and filtered. 1 ml. of these filtrates were directly counted and 1 ml. aliquots of each were passed through Dowex 50 W- \times 8 (50–100 mesh) cation exchange columns in NH_4 form as above; columns washed with 2 ml. of 2% ammonia; effluents (including interstitial volume) and washings were collected, evaporated to 1 ml. and counted. Results are shown in Table VII.

RESULTS

Sorption of Radionuclides by Humic acid in Sea-Water

There was an increase in the sorption of elements by humic acid with time; K_d values became constant after a certain period. For Mn⁵⁴, saturation value was reached after 46 days with the K_d in the range of 11200 to 11800; Co⁶⁰, 4.5 hours and K_d of 11400 to 12400; Zn⁶⁵, a week and K_d of 12300 to 13500; and Y⁹⁰, 2 days and K_d of 15400 (see Table II). Sorption of Cu⁶⁴ increased with time, but the saturation value could not be observed with good counting statistics because of its short half-life. The maximum K_d value obtained in the course of 65 hours was about 8000 (Table II). Cesium was not sorbed by humic acid; this may be attributed to the presence of high concentrations of competing ions (Table III). Szalay and Szilagyi⁸ observed the quantitative release of Cs¹³⁷ from a humic acid column in presence

of 0.1% NaCl. Ganapathy *et al.*⁹ reported a high sorption of Cs¹³⁷ by a marine sediment, however, he did not observe any influence of organic matter in the sorption.

Solubilization of Elements by Humic Acid

Fe in sea-water.—Table IV shows the results obtained on the solubilization of Fe in sea-water in presence of humic acid. The control filtrate shows only 2.5% of the added activity whereas the filtrate from Sample I shows 22.3% of the Fe to be in solution. The ratio of Sample I activity to the control filtrate activity is approximately 7 to 10, whereas the filtrate of Sample II shows about 3.5% in solution on the first day and this progressively increases to about 10 to 11% in the course of 39 days. From the order of addition of the different solutions in the experiment, it is apparent that in Sample I, interaction between iron and sodium humate predominantly takes place in the dissolved phase of the two reactants, and in Sample II, sodium humate interacts with precipitated iron hydroxide. The progressive dissolution of this precipitated iron is quite demonstrative in the results whereas the Sample I results indicate completion of interaction in the very early stages of addition.

Fe, Zr-Nb and Ce in water and dilute alkali.—Solubilization of Fe⁵⁹, Zr⁹⁵-Nb⁹⁵ and Ce¹⁴⁴ by humic acid is well illustrated in Table V. Fe⁵⁹, Zr⁹⁵-Nb⁹⁵ and Ce¹⁴⁴ precipitated in the control tubes to the extent of about 81%, 84% and 47% respectively at pH 7 while at pH 10 precipitation increased to about 93%, 98% and 81% respectively. Further dilution with pH 10 water had no significant effect on their precipitation. At pH 7, Fe⁵⁹, Zr⁹⁵-Nb⁹⁵ and Ce¹⁴⁴ were all retained completely in solution by sodium humate while rise in pH did not effect any precipitation of the elements to any appreciable extent. Further dilution with water at pH 10 by a factor of 10 had no influence on the solubilization of the elements by humic acid.

Ba, Fe, Y and Zr-Nb in ammonia water.—Results are shown in Tables VI and VII. In ammoniacal medium, significantly large quantities of the insoluble barium sulphate, iron, yttrium and zirconium-niobium were solubilized by ammonium humate, the amount of Y⁹⁰ and Zr⁹⁵-Nb⁹⁵ solubilized being respectively 17 and 4–5 times that obtained in the respective controls.

The column studies indicate that the solubilized Ba, being retained completely on the

column, must be present in a cationic complex and/or in exchangeable cationic form. The column behaviour of humic acid complex bears a very close similarity with the column behaviour of BaSO_4 -EDTA complex.

Column studies with Fe indicate 100% escape of Fe^{59} activity through the column, i.e., Fe-humic acid complex is completely 'non-ionic' or 'anionic'. The behaviour is closely similar to the Fe-EDTA complex.

62% of solubilized yttrium passed through the column indicating a 'non-ionic' or 'anionic' complex state of the Y-humic acid compound. This can be compared with 97% of Y-EDTA complex passing through the column.

This column behaviour of trivalent elements-humic acid complex gives support to the observation of Alexandrova² that these are usually present in the anionic part of the humic acid.

It is interesting to compare the 95% of Zr-Nb-humic acid complex with the 66% Zr-Nb-EDTA complex passing through the column. The equivalence and the chemical nature of humic acid complexes not being established, it was not possible to compare, on the basis of results obtained in these experiments, the stability constants in quantitative terms with those of EDTA complexes. In the relative scale, however, one can see that the humic acid complexes of stability equal to, less than and greater than EDTA complexes, are possible.

In separate experiments it was observed that the activities in the dissolved part of Mn^{54} , Co^{60} and Zn^{65} in ammonia are quantitatively retained on the column, but in presence of humic acid, 100% Mn^{54} , 91% Co^{60} and 20% Zn^{65} came down with the effluent.

It is to be noted, in these experiments, that elutions were not carried out with large volumes of the eluant in order to follow the elution characteristics of the constituents retained on the column. Rather, the objectives of the experiments were to obtain the fraction of the solubilized product which passed through the column simultaneously with humic acid.

DISCUSSION

Initial concentrations of the elements at which the sorption experiments were carried

out with humic acid in sea-water were in the range of 10^{-6} M to 10^{-8} M; humic acid concentration was 0.1284 mg./ml. Mn, Co, Zn, Y and Cu were practically completely sorbed. Fe remaining in solution with the dissolved fraction of humic acid in sea-water was observed to be about 3×10^{-8} M. Although the total exchange capacity of added humic acid was far in excess of the equivalents of the trace elements under consideration, the equilibration was observed to be a slow process ranging from days (for Co, Zn, Cu, Y, etc.) to a month (for Mn). The precipitated humic acid when dissolved in ammonia and passed through the cation column in NH_4 form (see Table VII), Mn and Co passed through the column quantitatively and Zn partly, indicating that the elements sorbed by humic acid are not necessarily at the ion exchange sites.

Similar observations apply in respect of the column experiment with humic acid solubilized Fe, Y and Zr-Nb in ammoniacal medium. Of the elements studied, only BaSO_4 , solubilized by humic acid in ammonia medium, is retained on the column quantitatively and it is interesting to note that the equivalents of Ba solubilized by humic acid (383 meq./100 gm. of humic acid) correspond to the ion exchange capacity of the humic acid (383 meq./100 gm. of humic acid) obtained by potentiometric titration. However, these complexes were comparable to EDTA complexes in their, column behaviour.

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