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Selective Adsorption of Dimethylarsinic Acid by Synthetic Inorganic Ion Exchangers[1)]

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Six ion exchangers were studied for selective uptake of dimethylarsinic acid from aqueous media at around neutral pH. Hydrous oxides of multivalent metals showed very high selectivity towards dimethylarsinic acid in 0.01 mol dm^{-3} NaCl.

Many inorganic ion exchangers have been synthesized for their potential use in separation chemistry. Among these, oxides and hydroxides of multivalent metals have received much attention owing to the excellent selectivity, chemical and radiation stabilities.[2,3)] Recently, very high selectivity was found for oxoanions of As^{V}, Sb^{V}, etc. on hydrous titanium dioxide ion exchanger of amorphous type(HTDO) and increased in the order:[4)] Cl^- , Br^- << Mo^{VI} < W^{VI} <As^{V} < P^{V} <Sb^{V}. Also the HTDO showed much higher selectivity for As^{III}.[5)]

Organometallic compounds and oxides of heteroelements, e.g., Hg, As, Sb, Sn, Se, Pb, etc., are beneficially used in high-tech industry, biomedical fields, and agriculture and marine product industries.[6)] Dimethylarsinic acid(DMAA) is increasingly used in the basic microbiology and related fields. It cannot be effectively separated from waste solution containing DMAA by a usual coprecipitation with $Fe(OH)_3$, etc.

The present paper describes selectivity profiles for dimethylarsinic acid along with inorganic As^{III} and As^{V} ions on various ion exchangers (a-f). For the latter two ions, As_2O_3 dissolved in NaCl solution and NaH_2AsO_4 were used. a)Strong-acid type cation exchange resin, Dowex50W-X8 (H^+ form, 100-200 mesh). b)Strong-base type anion exchange resin, Dowex2-X8(Cl^- form, 100-200 mesh). c)Amorphous hydrous titanium dioxide (HTDO), $TiO_2 \cdot 2.3H_2O$[7)]: Liquid $TiCl_4$ (100

cm^3) was prehydrolyzed by adding slowly demineralized water(300 cm^3). The resultant clear solution was hydrolyzed by adding dropwise 2.8 M (1 M=1 mol dm^{-3}) NaOH (1600 cm^3) with stirring vigorously. A precipitate formed was percolated, washed thoroughly with water and air-dried. The semitransparent product was ground and sieved to 100-200 mesh. Incorporated Na^+ in the product was removed as much as possible by the conventional column method using 0.1 M HNO_3, washed with water and air-dried. d)Amorphous hydrous zirconium dioxide (HZDO), $ZrO_2 \cdot 1.76H_2O$: This was synthesized by adding zirconium tetrabutoxide(50 cm^3) to demineralized water(1 dm^3). A precipitate formed was washed thoroughly with water and air-dried. e)Boehmite-type hydrous aluminum oxide (HAO), $Al_2O_3 \cdot 1.2H_2O$[8]: Four M NH_3 aq. solution was added to 10% $AlCl_3$ aqueous solution upto pH 8-10 to form a precipitate. The precipitate was repeatedly washed with NH_3 aq. solution of pH 9 until free from Cl^- , and then aged for 30 d at room temperature in NH_3 aq. solution of pH 9. After washing, it was hydrothermally heated for 5 h at 200 °C, air-dried and sieved to 100-200 mesh. f)Hydrotalcite (KYOWAAD 500, HT), $Mg_6Al_2(OH)_6CO_3 \cdot 4H_2O$.

The ion exchangers, a and b, and hydrotalcite were supplied by Wako Pure Chemical Ind. and by Kyowa Chemical Ind., respectively. All other chemicals were of analytical grade.

The products prepared (c-e) were identified by an X-ray powder diffraction analysis using a JEOL X-ray diffractometer model JDX-7E with Ni-filtered CuKα radiation. Adsorption of arsenic compounds on these ion exchangers was studied as follows. A sample(0.10 g) was immersed in 10 cm^3 of a mixed solution containing As^{III}, As^V or DMAA of various concentrations with the ionic strength adjusted to 0.01 M by NaCl at 30 °C. Arsenic compounds were determined by neutron activation analysis using ^{76}As($T_{1/2}$ 26 h, 556 keV) at the Japan Atomic Energy Research Institute. The uptake in mmol/g was calculated from the difference in the concentration between the sample and the reference. The distribution coefficient (Kd, in cm^3/g) was calculated by the ratio of uptake of ions in mmol/g to concentration of ions in mmol/cm^3

Both organic ion exchangers (a, b) showed a negligible uptake for DMAA at pH > 7 (Fig.1), though a low percentage of arsenic acid was adsorbed at pH>4 on both the cation and anion exchangers. Therefore, these organic ion exchangers will not be effective for selective separation of DMAA in an aqueous environmental and industrial waste solutions containing a large amount of matrix.

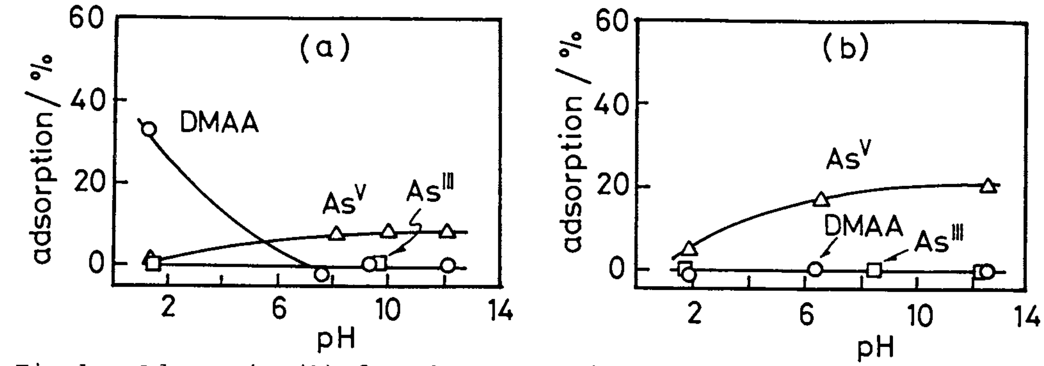

Fig.1. Adsorption(%) for three arsenic compounds. Initial concn.:0.01 M.

An uptake of DMAA was examined for inorganic ion exchangers(Table 1). The adsorption selectivity on these materials increased in the order of HT<HAO<HZDO<HTDO. Hydrotalcite known as an anion exchanger showed a low selectivity for DMAA. HAO and HZDO had a relatively small capacity for DMAA (<0.2 mmol/g). On the contrary, HTDO showed a large capacity of 0.66 mmol/g at pH 6.68. Thus, synthetic inorganic ion exchangers (especially HTDO) were found to be an effective adsorbent for DMAA.

An uptake for As^V ion increased in the order of HAO<HT<HZDO<HTDO (Table 2). Of these materials, HTDO was most selective for As^V ion and showed the uptake of 0.69 mmol/g at pH 6.88. HAO was selective for As^V ion at 10^{-4} M, but the capacity was very small.

Table 1. Adsorption(%) of DMAA on Various Inorganic Ion Exchangers

	Initial concentration and equilibrium pH					
Ion exchangers	1.0×10^{-4}M	pH	1.0×10^{-3}M	pH	1.0×10^{-2}M	pH
c) HTDO	100±1	5.92	100±1	5.75	66±1	6.68
d) HZDO	80±16	6.38	70±3	7.46	16±1	8.30
e) HAO	10±20	6.00	10±5	6.88	3±1	7.60
f) HT	0±20	9.03	10±4	8.97	4±1	8.84

An uptake for As^{III} ion increased in the order of HAO<HT<HZDO<HTDO(Table 3). Quantitative uptake for As^{III} was observed on HZDO and HTDO at the initial concentration of 1.0×10^{-2} M.

The pKa values of these arsenic compounds in 0.1 M KCl are pK 6.2 for DMAA; pK_1 2.22, pK_2 6.98, pK_3 11.50 (25 °C) for $AsO(OH)_3$; and pK 9.06 for $As(OH)_3$ (30 °C).[8] Their predominant species at pH 8-11 are $(CH_3)_2AsOO^-$, $AsO_3(OH)^{2-}$, and $As(OH)_4^-$. The plot of log Kd for these ions vs. log$[OH^-]$ should show the same slope as the

Table 2. Adsorption(%) of As^{V} Ion on Various Inorganic Ion Exchangers

	Initial concentration and equilibrium pH					
Ion exchangers	1.0×10^{-4}M	pH	1.0×10^{-3}M	pH	1.0×10^{-2}M	pH
c) HTDO	100±1	5.99	100±1	6.30	69±1	6.88
d) HZDO	80±11	5.90	94±2	7.68	35±1	8.85
e) HAO	100±11	6.98	25±4	7.43	0±1	8.90
f) HT	100±11	9.04	94±2	9.04	25±1	9.13

Table 3. Adsorption(%) of As^{III} on Various Inorganic Ion Exchangers

	Initial concentration and equilibrium pH					
Ion exchangers	1.0×10^{-4}M	pH	1.0×10^{-3}M	pH	1.0×10^{-2}M	pH
c) HTDO	100±1	6.08	100±1	5.93	97±1	5.08
d) HZDO	100±15	6.23	100±2	7.13	95±1	8.25
e) HAO	30±18	6.29	40±3	8.38	0±1	9.42
f) HT	70±18	9.03	60±3	8.93	15±1	9.28

charge in case of an infinitesimal anion-exchange. The slopes of straight lines obtained at an initial concentration of 10^{-4} M on the HTDO were -0.96 for DMAA at pH>7, -0.85 for As^{V} at pH>7.5 and -0.92 for As^{III} at pH>9.5. Therefore, the ion-exchange process is predominant in the adsorption of DMAA and As^{III}. A relatively high concentration may be responsible for the slope for As^{V}. The uptake of these arsenic compounds on HTDO was reversible and a repeated use may be feasible.

References

1) Synthetic Inorganic Ion-exchange Materials. LV.

2) V. Veselý and V. Pekárek, Talanta, 19, 219 (1972).

3) M. Abe, Bunseki Kagaku, 23, 254, 1561 (1974).

4) M. Tsuji and M. Abe, J. Radioanal. Nucl. Chem., 102, 283 (1986).

5) M. Tsuji and M. Abe, The 48th Symposium of the Japan Society for Analytical Chemistry, Abstr. p.477, June 1987.

6) J. M. Wood, Science, 183, 1049 (1974).

7) M. Abe, M. Tsuji, S. P. Qureshi, and H. Uchikoshi, Chromatographia, 13, 626 (1980).

8) M. Abe and T. Ito, Nippon Kagaku Zasshi, 86, 818, 1259 (1965).

9) C. F. Baes and R. E. Mesmer, "The Hydrolysis of Cations," John Wiley and Sons, New York (1976).

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