Notes

Prediction of Ksp sequence for some sparingly soluble salts from K_d values of metal ions on some inorganic ion exchangers based on tin and silicon- A new approach

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The distribution coefficients of twelve heavy metal ions such as Cu^{2+}, Mn^{2+}, Pb^{2+}, Hg^{2+} etc. have been determined on various ion exchange adsorbents based on Silicon and Tin. The materials used have been Stannic arsenosilicate, Stannic tungstosilicate, Stannic molybdosilicate, Stannic phosphorsilicate, Stannic selenosilicate and Stannic antimonysilicate. These double salts possess adsorption ion exchange properties and have been found to be selective for one or more metal ions. On the basis of the adsorption behaviour for metal ions, the Ksp sequence of various double salts with heavy metal ions have been predicted. A number of analytically useful separations including Cu^{2+}-Hg^{2+}, Cu^{2+}-Ni^{2+}, Pb^{2+}-Al^{3+}, Zn^{2+}-Mn^{2+}, Pb^{2+}-Zn^{2+}, Cu^{2+}-Zn^{2+}, Cu^{2+}-Al^{3+}, Cu^{2+}-Mn^{2+} etc., have also been achieved on these materials by the column chromatographic method.

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Environmental pollution and its control is of current interest. The contamination of ground water, (a principal source of potable water) is a serious environmental problem. The analysis and removal of heavy metals such as Cu, Mn, Pb, Hg etc. which are the chief pollutants in ground water is, therefore, of much analytical significance.

The ion exchange column chromatography is a simple, versatile and comparatively inexpensive analytical technique, and can be effectively utilized for the solution of metal pollution problems. The inorganic ion exchange adsorbents, by virtue of their high selectivity for metal ions in general, have been proven to be important for such a purpose. The synthesis, characterization and thermal stability of tin and silicon based ion exchange materials have been carried out earlier in our laboratories[1-3].

Apart from metal ion separations, column chromatography can be useful as a means for obtaining physical data such as solubility products (Ksp) using K_d values. Earlier, we have predicted the Ksp of various metal arsenates from R_f values of corresponding metal ions on stannic arsenate papers[4] as well as stannic arsenate[5] and titanium arsenate[6] thin layers. The prediction of Ksp from Ri values have also been reported by performing cation chromatography on Sn (II) hexacyanoferrate (II) papers[7].

As far as we are aware, no effort has been made to predict the Ksp sequence of the metal salts from K_d values. The present study is therefore an attempt to explore such a possibility on various double salts of metal ions studied on the basis of their corresponding distribution coefficients. Some metal ion separations which are important from the pollution control viewpoint have also been achieved on the columns of these materials.

Experimental

Reagents and chemicals

All the reagents and chemicals used in this study were of Analar grade. Stannic chloride penta hydrate (PPH Poland), Sodium selenite, Sodium arsenate heptahydrate (Reidel), Sodium tungstate, Sodium molybdate, Sodium phosphate and Potassium antimonate (BDH) were used. The metal ions used for the distribution studies were used in the form of nitrates dissolved in demineralized water. Uranyl nitrate was used to give UO_2^{2+} ion in the solution. Vanadyl sulphate was dissolved in demineralized water to give VO^{2+} ion.

Preparation of ion exchange materials

The ion-exchange materials viz stannic arsenosilicate, stannic tungstosilicate, stannic molybdosilicate, stannic phosphorsilicate, stannic selenosilicate and stannic antimonysilicate were prepared as described earlier[1-3].

Ion exchange capacity (IEC)

The K^+ ion exchange capacity was determined by taking 1 g of the dry ion exchange material by column experiments (saturation method) as reported earlier[1]. The value for each ion exchange material (meq g^{-1}) is given in parenthesis: Stannic arsenosilicate [SnAsSi-1(1.23), SnAsSi-6 (1.24), SnAsSi-11 (1.60),

SnAsSi-12 (1.38)], Stannic tungstosilicate (0.82), Stannic molybdosilicate (0.30), Stannic phosphorsilicate (1.50), Stannic selenosilicate (0.52) and Stannic antimonysilicate (0.88).

Distribution studies

The distribution coefficients of twelve metal ions were determined on stannic molybdosilicate, stannic selenosilicate and stannic tungstosilicate in demineralized water. The K_d values for the metal ions on stannic arsenosilicate, stannic phosphorsilicate and stannic antimonysilicate were taken as reported earlier[1-3]. The loading[8] of the cation was not more than 3% of the ion exchange capacity of each exchange material. 0.5 g of the sample was shaken for 6 h in 50 mL of the cation solution. The amount of the cation in solution was determined by titration with 0.001 M EDTA and the K_d values (Table 1) were calculated from the usual formula-

$$K_d \text{ (mL/g)} = \frac{I-F}{F} \times \frac{50}{0.5}$$

Where 'I' is the volume of EDTA consumed by the original solution and 'F' is the volume of EDTA consumed after equilibrium.

Separations

Quantitative separations of some metal ions were achieved on different ion exchange materials using the column technique. Two grams of 60-100 mesh sized particles of the ion exchanger (H^+ from) were filled in the column of 0.6 cm bore on a glass wool support. It was washed with demineralized water and the mixture of the cation solution was introduced from the top. The flow-rate was maintained as 0.6 to 0.8 mL/min. The adsorbed cations were then eluted with suitable solvents and the effluent titrated with 0.001 M EDTA solution. Qualitative tests of tin, silicon, arsenic, tungsten, molybdenum, phosphorus, selenium and antimony in the effluent for the respective ion exchange materials were negative. The separations achieved experimentally on each ion exchange material are given in parenthesis: Stannic arsenosilicate [SnAsSi-1(Mg^{2+}- Al^{3+}), SnAsSi-6 (Al^{3+}- Pb^{2+}), SnAsSi-11 (Hg^{2+}- Cu^{2+}), SnAsSi-12 (UO_2^{2+}- VO^{2+})], Stannic tungstosilicate (Ni^{2+}- Cu^{2+}, Ga^{3+}- In^{3+}, Zn^{2+}- Mn^{2+}), Stannic molybdosilicate (Pb^{2+}- Zn^{2+}, Mg^{2+}- Zn^{2+}, Cu^{2+}- Zn^{2+}), Stannic phosphorsilicate (Al^{3+} - Cu^{2+}, UO_2^{2+} - Zn^{2+}, VO^{2+} - UO_2^{2+}, Ni^{2+} - Cu^{2+}), Stannic selenosilicate (Pb^{2+} - UO_2^{2+}, Zn^{2+} - Cu^{2+}, Mn^{2+} - Cu^{2+}) and Stannic antimonysilicate (Mn^{2+} - Zn^{2+}, Cu^{2+} - Zn^{2+}, Ni^{2+} - Zn^{2+}).

Results and discussion

The essential feature of these studies is to determine the selectivities of some heavy metal ions on the silicon based inorganic ion exchangers and to explore the different rates of adsorption in obtaining quantitative separations of these metal ions.

The distribution coefficients of twelve metal ions were determined in demineralized water on different ion exchangers (Table 1). The selectivities of the four samples of stannic arsenosilicate for various metal ions as shown by K_d values were found to be almost the same. They show higher adsorption for Pb^{2+}, VO^{2+} and Cu^{2+} while negligible or no adsorption for UO_2^{2+}, Mg^{2+} and Hg^{2+}, thus facilitating their separations.
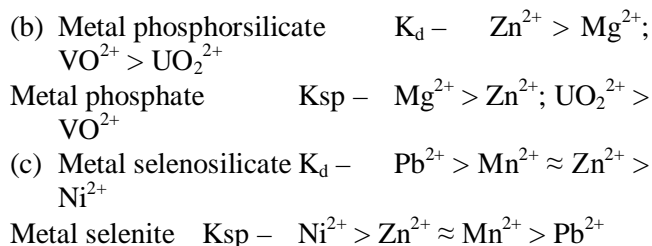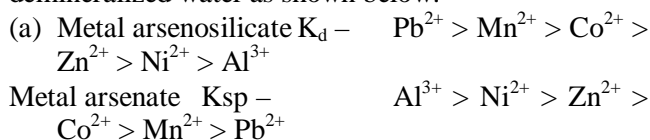
Stannic tungstosilicate shows a higher selectivity for Zn^{2+} as it is completely adsorbed on the exchanger column while the other metal ions are much less adsorbed. Similarly stannic molybdosilicate also exhibits selectivity towards Zn^{2+} though to a much lesser extent. However, for all other metal ions it shows zero adsorption. Zn^{2+} is, therefore, separated from other metal ions by using these materials.

Table 1 — Distribution coefficients of some metal ions on different exchange materials in demineralized water (mL g^{-1})

Metal ion	SnAsSi-1	SnAsSi-6	SnAsSi-11	SnAsSi-12	Stannic tungsto silicate	Stannic molybdo silicate	Stannic phosphor silicate	Stannic seleno silicate	Stannic antimony silicate
Pb^{2+}	2150.0	2230.0	1950.0	2040.0	100.0	0	80.2	75.4	160.2
Ni^{2+}	70.8	88.2	57.5	150.0	0	0	70.6	0	183.0
Co^{2+}	300.0	330.0	400.0	400.0	0	0	100.0	0	150.2
UO_2^{2+}	0	0	0	0	200.0	0	66.5	300.0	200.0
VO^{2+}	12400.0	11800.0	12150.0	12000.0	0	0	66.5	300.0	200.0
Cu^{2+}	16150.0	15100.0	14400.0	16040.0	320.0	0	400.0	300.2	550.0
Zn^{2+}	50.0	133.3	50.0	810.0	11050.0	1500.0	230.0	11.4	14320.0
Mn^{2+}	400.0	300.0	400.0	280.0	0	0	0	0	0
Mg^{2+}	0	0	0	0	48.6	0	30.6	60.2	0
Hg^{2+}	0	0	0	0	0	0	10.6	150.0	0
Ga^{3+}	200.0	50.0	100.0	100.0	0	0	0	0	0
Al^{3+}	220.0	50.0	100.0	100.0	0	0	0	0	0

Among others, stannic phosphorsilicate shows almost no adsorption for Mn^{2+}, Ga^{3+} and Al^{3+} whereas for some other metal ions, the adsorption is significant. Moderate adsorption of UO_2^{2+}, VO_6^{2+}, Cu^{2+} and Hg^{2+} is observed on stannic selenosilicate. The other ions show a negligible or no adsorption. Besides this, stannic antimonysilicate is highly selective for Zn^{2+} whereas Mn^{2+}, Mg^{2+}, Hg^{2+}, Ga^{3+} and Al^{3+} are not adsorbed. The selectivity sequence for some pairs of metal ions on these exchange materials is given in Table 2.

The chromatographic behavior of metal ions on these exchange columns has been found to be interesting. When the K_d is higher, the ion is more strongly held by the ion exchange material and moves less readily. However, the elution sequence of the metal ions also depends on the solubility (Ksp) of the metal salts formed by the interaction of the metal ion loaded and the anion of the exchange material. Though, the Ksp of various metal arsenosilicates, tungstosilicates, molybdosilicates, phosphorsilicates, selenosilicates and antimonysilicates are not known and as such no relationship can be established between the Ksp of these double salts of metal ions with the K_d of the corresponding metal ions on their columns. Interestingly, however, a correlation has been observed between the K_d values of the metal ions on different exchange materials and the known Ksp values of their corresponding arsenates, tungstates, molybdates, phosphates, selenites, and antimonates. It is presumed that the higher is the solubility of the metal salt, lower will be the K_d for that metal ion, which is supported by earlier observation on niobium arsenate ion exchanger[9]. This trend is confirmed by the behavior of some common metal ions. The K_d values for metal ions are given in Table 1. For these metal ions, the sequence of the K_d values is the same as the ones predicted from Ksp values of the corresponding metal salts in demineralized water as shown below.

(a) Metal arsenosilicate K_d – $Pb^{2+} > Mn^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+} > Al^{3+}$

Metal arsenate Ksp – $Al^{3+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+} > Pb^{2+}$

(b) Metal phosphorsilicate K_d – $Zn^{2+} > Mg^{2+}$; $VO^{2+} > UO_2^{2+}$

Metal phosphate Ksp – $Mg^{2+} > Zn^{2+}$; $UO_2^{2+} > VO^{2+}$

(c) Metal selenosilicate K_d – $Pb^{2+} > Mn^{2+} \approx Zn^{2+} > Ni^{2+}$

Metal selenite Ksp – $Ni^{2+} > Zn^{2+} \approx Mn^{2+} > Pb^{2+}$

On stannic molybdosilicate, most of the ions are not adsorbed ($K_d = 0$) (Table 1) whereas the Ksp values of various metal antimonates are not known. As such, these exchange materials have not been included in the above sequence relationship.

However, the above prediction of sequence does not hold good for some ions on stannic tungstosilicate. Thus, if we consider that the eluction sequence can be predicted from Ksp values, it follows that the Ksp values are reliable to a certain degree for such predictions because:

(a) The Ksp values of metal arsenates etc., are taken for the sequence purpose and not that of metal arsenosilicates, on which the K_d values have been determined. The same is true for the other double salts of Sn (IV) used for column chromatography.

(b) Some of the metal ions under study interact in a different manner with the exchange material.

Thus, the K_d values are a rough guide for the prediction of sequence of Ksp values, especially when they differ from one another considerably.

On the basis of distribution coefficients of various metal ions on different exchange materials, some possible column chromatographic separations were tried. The metal ions retained on the column were eluted with HNO_3 solutions (0.01 M HNO_3, 1–3 % of HNO_3) and mixtures of HNO_3 and NH_4NO_3 solutions of different concentrations in the volume ratio (1:1). A number of useful binary separations have been achieved experimentally.

It is evident from the above studies that these materials can be used advantageously for obtaining some difficult metal ion separations. Analysis of alloys and rock samples containing these metals can

Table 2 — Selectivity sequence of some pairs of metal ions for the exchange materials based on Silicon and Tin (IV)

Pair of metal ions	Stannic arsenosilicate	Stannic tungstosilicate	Stannic phosphorsilicate	Stannic selenosilicate	Stannic antimonysilicate
Mg^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}	$Cu^{2+}>Zn^{2+}>Co^{2+}>Mn^{2+}>Ni^{2+}>Mg^{2+}$	$Zn^{2+}>Cu^{2+}>Mg^{2+}>Ni^{2+}$ or Co^{2+} or Mn^{2+}	$Cu^{2+}>Zn^{2+}>Co^{2+}>Ni^{2+}>Mg^{2+}>Mn^{2+}$	$Cu^{2+}>Mg^{2+}>Zn^{2+}>Ni^{2+}$ or Co^{2+} or Mn^{2+}	$Zn^{2+}>Cu^{2+}>Ni^{2+}>Co^{2+}>Mn^{2+}$ or Mg^{2+}
UO_2^{2+}, VO^{2+}	$VO^{2+} > UO_2^{2+}$	$UO_2^{2+} > VO^{2+}$	$VO^{2+} > UO_2^{2+}$	$UO_2^{2+} > VO^{2+}$	$UO_2^{2+} > VO^{2+}$
Pb^{2+}, Hg^{2+}	$Pb^{2+} > Hg^{2+}$	$Pb^{2+} > Hg^{2+}$	$Pb^{2+} > Hg^{2+}$	$Hg^{2+} > Pb^{2+}$	$Pb^{2+} > Hg^{2+}$

be carried out on these exchange materials. These can also be utilized for the removal of toxic metals from industrial wastes.

Acknowledgement

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