CHAPTER VI
AN EFFORT AT THE CORRELATION OF Kd VALUES WITH
BASIC PROPERTIES OF SOME INORGANIC
ION EXCHANGERS

INTRODUCTION

In order to arrive at a useful correlation of the basic properties such as ion exchange capacity, ionic radius, atomic number ionic charge with the Kd values of inorganic ion exchangers an effort has been made to summarise these properties of some inorganic ion exchangers in the form of suitable plots.

Let us consider first the case of metal antimonates as inorganic ion exchangers. The log Kd vs atomic number for ten antimonate ion exchangers are plotted in Figs. 18-27, the average Kd values vs atomic number in Fig. 28 and the average Kd vs atomic number for alkaline earth metal ions in Fig. 29. There are some general characteristics to be noted. Na⁺ has the maximum average log Kd for the antimonate exchangers which is larger than that of any other ion. Thus these exchangers can be used for the separation of Na⁺ from K⁺, Li⁺, Rb⁺ and Cs⁺. This has been done by Abe[1,2]. Similarly these exchangers have high Kd values of Ag⁺, Hg⁺² and Pb⁺². Very low Kd values are reported for Mg⁺². It therefore appears that the Kd values depend upon the interaction of the counter ions with the anion
Fig. 18—A plot of log kd vs Atomic number. Exchanger: Ceric antimonate, Form: H\(^+\) form, Nature: Amorphous, Size: 100–200 mesh, pH: 2–3.
Fig. 19 - A plot of log kd vs Atomic number. Exchanger: Chromium antimonate, Form: H⁺ form, Nature: Amorphous, pH: 3–4.
Fig. 20 – A plot of log kd vs Atomic number. Exchanger: Titanic antimonate, Form: H⁺ form, Nature: Amorphous, Size: 100–200 mesh, pH: 2–3.
Fig. 2.1 – A plot of log $kd$ vs Atomic number. Exchanger: Zirconium antimonate, Form: $H^+$ form, Nature: Amorphous Size: 100-200 mesh, pH: 2-3
Fig. 2.2 – A plot of log k_d vs Atomic number. Exchanger: Iron antimonate, Form: H⁺ form, Nature: Amorphous, Size: 150-250 mesh, pH: 1.
Fig. 2.3 - A plot of log kd vs Atomic number. Exchanger: Stannic antimonate, Form: H+ form, Nature: Amorphous, Size: 50-100 mesh, pH: 2-3
Fig. 24—A plot of $\log k_d$ vs Atomic number. Exchanger: Niobium antimonate, Form: $H^+$ form, Nature: Semi crystalline, pH: 1.
Fig. 25 - A plot of log $k_d$ vs Atomic number. Exchanger: Antimonic acid, Form: $H^+$ form, Nature: Crystalline, Size: 100–200 mesh.
Fig. 26 – A plot of log kd vs Atomic number. Exchanger: Lead antimonate, Form: H⁺ form, Nature: Amorphous, Size: 200 mesh, pH: 2.
Fig. 27 - A plot of log $k_d$ vs Atomic number. Exchanger: Lead antimonate, Form: $H^+$ form, Nature: Crystalline, pH: 2-3.
Fig. 28 – A plot of log ave. kd vs Atomic number for metal ions on various antimonate exchangers.
Fig. 29 - A plot of log kd vs Atomic number for Alkaline earth metal ions.
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Fig. 29—A plot of log $kd$ vs Atomic number for Alkaline earth metal ions.
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Fig. 29 - A plot of log kd vs Atomic number for Alkaline earth metal ions.
Fig. 29 - A plot of log kd vs Atomic number for Alkaline earth metal ions.

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Fig. 29 - A plot of log ave. $k_d$ vs Atomic number for metal ions in a group.
Fig. 29 - A plot of log ave. kd vs Atomic number for metal ions in a group.
matrix. In order to bring about the dependence of Kd values on atomic number, plots have been made for the Kd values of Mg$^{+2}$, Ca$^{+2}$, Sr$^{+2}$ and Ba$^{+2}$ on various antimonates. In most cases Mg$^{+2}$ shows the lowest Kd value where as Ba$^{+2}$ shows the highest. A comparison of the Kd values on the amorphous and crystalline lead antimonates is instructive. While the crystalline material shows a regular trend the amorphous lead antimonate shows an erratic behaviour.

Similar trends are noticed for plots of log Kd vs ionic radii (Figs. 30-41). Thus as the ionic radius increases there is a regular increase in Kd values. This is because the ions are exchanged as hydrated ions and the ions with the lowest ionic radii have the largest hydrated ionic radii. The trend of niobium antimonate, chromium antimonate, titanium antimonate, iron antimonate and lead antimonate are similar. Once again the difference between the crystalline and amorphous lead antimonates is worth noticing.

The plots of ion exchange capacity vs hydrated ionic radii are instructive (Fig. 42). The ion exchange capacity depends upon two factors:

1. Hydrated ionic radii
2. Selectivity

As the hydrated ionic radius increases the ion exchange capacity decreases as the exchange now becomes more difficult. Thus for
Fig. 30 - A plot of log $k_d$ vs Ionic radius. Chromium antimonate.
Fig. 3.1 - A plot of log _kd_ vs Ionic radius. Titanium antimonate.
Fig. 32 - A plot of $\log k_d$ vs ionic radius. Stannic antimonate.
Fig. 33 - A plot of log kd vs Ionic radius. Zirconium antimonate.
Fig. 34 - A plot of log kd vs Ionic radius. Niobium antimonate.
Fig. 35 – A plot of log kd vs ionic radius. Ceric antimonate.
Fig. 36 - A plot of log kd vs ionic radius. Iron antimonate.
Fig. 37 - A plot of log kd vs ionic radius. Lead antimonate(a)
Fig. 38 - A plot of log kd vs Ionic radius. Crystalline antimonic acid.
Fig. 39—A plot of $\log k_d$ vs ionic radius (Å). Crystalline lead antimonate.
Fig. 40 - A plot of log ave. $kd$ vs ionic radius for metal ions on various antimonate exchangers.
Fig. 40 - A plot of log ave. $k_d$ vs. ionic radius ($\text{Å}$) for metal ions in a group.
Fig. 40 - A plot of log ave. kd vs Ionic radius (Å) for Lanthanides and Actinides.
Fig. 41 - A plot of log kd vs ionic radius (Å) for Alkaline earth metal ions.
Fig. 41 - A plot of log k_d vs Ionic radius (Å) for Alkaline earth metal ions.
Fig. 41 – A plot of log kd vs Ionic radius (Å).
Crystalline lead antimonate.

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Fig. 42 - A plot of Hydrated ionic radius (Å) vs Ion exchange capacity (meq/g).
Fig. 42—A plot of Hydrated ionic radius (Å) vs ion exchange capacity (meq/g).
Fig. 42 - A plot of Hydrated ionic radius (Å) vs ion exchange capacity (meq/g).
Fig. 42 - A plot of Hydrated ionic radius (Å) vs Ion exchange capacity (meq/g).

Cont'd. Hydrated ionic radius (Å)
AMORPHOUS LEAD ANTIMONATE (Sb/Pb = 5)

ALKALI METALS

ALKALINE EARTH METALS

CRystalline Lead Antimonate (Sb/Pb = 2.5)

ALKALI METALS

ALKALINE EARTH METALS

Cont'd. Fig. 42. A plot of Hydrated ionic radius (Å) vs Ion exchange capacity (meq/g).
alkali metals the trend is $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ . This trend is noticeable for cerium antimonate, nickel antimonate, niobium antimonate, titanium antimonate and to some extent lead antimonate.

The second factor is the specific selectivity of antimonic acid. Antimonic acid is known to be highly selective for $\text{Na}^+$ ions. This effect is apparent in stannic antimonate, zirconium antimonate and antimonic acid. Let us now discuss each case separately. For titanium antimonate the authors state that "Except for $\text{Li}^+$ and $\text{Ba}^{+2}$ the ion exchange capacity is negligibly affected by the size and charge of the exchanging ion"[3]. This is not true as the plot of ion exchange capacity vs hydrated ionic radii shows (Titanium antimonate in Fig.42). Further the authors state "As the mixing ratio of antimony to titanium increases the exchange capacity also increases. This becomes maximum at antimony to titanium ratio of 4:1". This has not been explained by the authors but is understandable considering that antimonic acid loses its ion exchange capacity for cations on partial replacement by metal ions. This replacement is minimum at the high $\text{Sb/Ti}$ ratio of 4.0. A plot of the ion exchange capacity vs hydrated ionic radii shows that the ion exchange capacity decreases as the hydrated ionic radius is increased. This is the normal sequence.

Zirconium antimonate synthesized by Tandon and Mathew[4] shows a higher exchange capacity for $\text{Na}^+$ ions than for $\text{K}^+$ and
Li$^+$ ions as is the case for antimonic acid. This is probably because Sb/Zr ratio is 1.03. Abe and Ito had remarked that in the zirconium antimonate which they had synthesized normal selectivity was observed for the alkali metals\[5\]. They further showed that if Sb/H ratio is greater than 1, then unreacted antimonic acid is present in the antimonate. This observation is in consonance with the data of Tandon et al. on zirconium antimonate. Further confirmation is obtained from their data on stannic antimonate. Mathew and Tandon synthesized stannic antimonate and determined the ion exchange capacity for Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Rb$^+$, Cs$^+$, Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$ [6]. They remarked "No regular trend is observed in the case of alkali metals, however in the case of alkaline earth metals the exchange capacity increases with increasing the ionic radii". This is not correct. A plot of ion exchange capacity vs hydrated ionic radii (Stannic antimonate in Fig. 42) shows that the ion exchange capacity is maximum for Na$^+$ ions and in fact the order of selectivity is the same as for antimonic acid. This supports the observations of Abe and Ito. The Sb/Sn ratio for stannic antimonate is 5.0 and therefore it contains a large amount of antimonic acid. The exchange of Sn$^{4+}$ with H$^+$ ions of antimonic acid may be represented by the equation

$$2\text{H}_2\text{Sb}_2\text{O}_5(\text{OH})_2 + \text{Sn}^{4+} \rightarrow \text{SnSb}_2\text{O}_5(\text{OH})_2$$ (eq.6)
giving a product of the Sb/Sn ratio of 1. These observations are applicable to cerium antimonate, nickel antimonate and niobium antimonate also. All the three have Sb/M ratio of less than 1 and show the normal order of preference.

This explanation does not apply to amorphous and crystalline lead antimonates. The exchange reaction in this case will be

\[
(H_3O^+)_2\text{Sb}_2\text{O}_6\cdot2\text{H}_2\text{O} + \text{Pb}^{+2} \rightleftharpoons \text{PbSb}_2\text{O}_6\cdot2\text{H}_2\text{O} \quad \text{(eq. 7)}
\]

For complete replacement Sb/Pb ratio should be 2. Thus if Sb/Pb ratio is greater than 2, then some antimonic acid should be left unreacted and the material should show some selectivity for Na\(^+\) ions. However it appears that the crystal structure of lead antimonate is so rigid that after most of the protons have been blocked out by Pb\(^{2+}\) the material no longer shows the selectivity associated with antimonic acid.

A number of interesting features can be seen in the plots of log ave. Kd vs charge on the exchanging ion (Fig. 43). Cr(III)Sb shows the largest Kd values for metal ions of 2, 3 and 4 valencies and Ce(III)Sb shows the minimum. The Kd adsorption curve of the crystalline lead antimonate is almost a mirror image of the curve for amorphous lead antimonate. As a general
Fig. 43—A plot of log ave. kd vs Charge on the ion for various antimonate exchangers.
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Fig. 43 - A plot of log ave. kd vs Charge on the ion for various antimonate exchangers.
rule the Kd values should increase with the charge on the ion. This is shown by Zr(IV)Sb and Ti(IV)Sb. However, in most cases the ave. Kd first decreases and then increases as in the case of Cr(III)Sb, Sn(IV)Sb and Nb(V)Sb. This may be due to two contradictory factors. (1) Increase in charge increases the attraction for the cation for the exchanger. (2) Increase in the hydrated radius decreases the initial attraction of the cations to the ion exchanger.
References

1. Abe, M.

2. Abe, H., Ahmad Chsau, E.A. and Hayashi, K.

3. Gill, J.S. and Tandon, S.N.

4. Mathew, J. and Tandon, S.N.

5. Abe, M. and Ito, M.

6. Mathew, J. and Tandon, S.N.