CHAPTER VII

Summary and conclusion

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VII.1. Summary

Experimental details with corresponding findings of the present dissertation have been presented in **Chapter II** to **Chapter VI** in an extensive way. Radiochemical separations on newly synthesized exchangers based on tungstate, molybdate and vanadate salts of Aluminium(III) and two other systems containing Cerium(IV)iodotungstate and quinoline phospho molybdate, for obtaining radioactive daughters in no-carrier-added states have been reported. Due to non-availability of wide varieties of genetically related radioisotope pair, we had to depend on few limited number of systems in which a secular equilibrium between parent and daughter exists and at the same time $T_{1/2}$ of daughter is not too high, so that growth of daughter through parent decay over the exchanger bed takes place rapidly.

The strategy of synthesis of the exchangers used here was to adopt the simple and readily reproducible techniques, even for the cost of degree of crystallinity of the solid phase exchanger. Moreover the amorphous or gel varieties of previously reported exchangers are known to function in a very smooth way particularly in column operation. Mixing of requisite chemicals however, needs continuous agitation followed by dilution with water so that precipitation process becomes as homogeneous as possible. Care has to be taken again for washing the unabsorbed acid as foreign ions so that selective ion exchange behavior is reached as far as practicable. Even, the pH of washing liquids was strictly maintained in acidic range, keeping in mind its application to the adsorption of metal ions. Drying temperatures have also shown by previous workers to have an effect on characteristics of ion exchangers and we selected to dry all the exchangers at room temperatures.

Exchangers were characterized by elemental analysis, physical and chemical stabilities including thermal and radiation dose and also through IR-spectroscopy to search for appropriate functional groups. For elemental analysis, conventional analytical techniques were applied after dissolution of exchanger in suitable solvents. Thermal analysis shows the presence of water molecules with the insoluble salt and also the point at which cleavage of solid matrix takes place. Such studies as reported in earlier chapters show that all the exchangers are quite stable toward heat and also toward radiation doses. Where the materials were subjected to high intensity γ-ray (~35-40 kGy) there was no apparent fall in exchange capacities. These indicated that they are sufficiently stable when radioactive isotopes are inserted into the matrix, and as such radiochemical separations could be tried over such materials. I.R spectra show the presence of metal-oxygen (most cases) bond in the insoluble polyoxometallates confirming the composition of exchanger.

The most important step of characterization in respect to the ion exchange behaviors of these solid phase exchangers is the determination of ion exchange capacities, which were later, confirmed by pH metric titration. Exchange capacities are not comparable with those of organic counter parts e.g. sulphonic acid derivative of divenyl benzene-styrene co-polymer. Nevertheless capacities are not too poor for the study of ion exchange properties of alkali and alkaline earth cations.

Results of such determination are not same for all the exchangers. Thus on the aluminium molybdate, the trends for alkali metal cation is $Li^+ < Na^+ > K^+ > Cs^+$ while for alkaline earth metal cation, it decreases with increasing in atomic number with slight fluctuation in Ba(II) mare correlation with hydrated ionic radious of metal ions may not be justified in all cases, however replacement of (H_3O) unit by Na^+ may be preferential in the structure of $Na_2 (H_2O)_4(H_3O)[Al(OH)_6Mo_6O_{18}]$. The fact may be viewed parally with the highest capacity for Mg^{2+}, among alkaline earth metals, an ion similar Na^+ (e/r). In general, alkali cations are more firmly bound than their alkaline earth counter parts. These arguments are, however, not very strong for corresponding vanadate and tungstate exchanger. In both of the two cases, exchange capacities are monotonic function of atomic number and consequently of hydrated radious in inverse direction. Same conclusion is drawn for other two exchangers e.g. cerium(IV)iodo tungstate and

quinoline phosphor molybdate. The exceptional behavior of molybdate-based exchanger may be attributed to its anderson type structure and surely it is expected to behave somewhat differently in ion exchange character. An unusual variation of exchange capacity against radiation dose has been recorded with aluminium tungstate. For this material, sodium ion exchange capacity is 2.37 meq/g and follows an exponential reduction in capacity from 96 kGy to 1344 kGy i.e. even under such extreme high radiation level, it retains a parts of its capacity.

Capacity measurement results have been confirmed by pH metric study with a mixture of NaCl and NaOH. However in this case value for Na^+ capacity is found to be somewhat less than dynamic method of capacity determination using ion exchange column. Perhaps, the difference in approaches in two procedures makes the little difference in exchange capacity value although order of capacity value for a particular ion (e.g. Na) is same in two studies.

Radiochemical separations achieved over these polyoxometallates involve ^{137}Cs-^{137m} Ba, ^{90}Sr-^{90}Y, ^{115}Cd-^{115m}In and also ^{198}Au-^{110m}Ag. The latter pair is not genetically related but due to close chemical similarity, we picked up such pair to study the separation over aluminium vanadate. Au(III)was eluted with rhodamine-B reagent while Ag(I) was desorbed by thiourea solution. Both of the two reagents are known to form well known complexes with the respective metal ions and such idea is shown to be applicable even where the trace cation is present in no carrier added state.

The most interesting application of the sets of inorganic ion exchangers is their functioning as radionuclide generator. Such a generator, adsorpts parent and daughter is eluted by a suitable reagent. After a sufficient time of interval, when appreciable amount of daughter is grown through the parents decay, it may be further milked out of the exchanger applying same reagent. For ^{137m}Ba daughter, ascorbic acid was found to be suitable reagent, the concentration of which was different for different exchangers, perhaps due to different extent of binding with exchanger matrix. The experiment was repeated for 3-4 times for each of the exchangers and purity of the daughter was checked by γ-spectroscopy (photo peak at 667 keV appears having $T_{1/2}$ =2.61 min), However with the progress of milking, yields of daughter was found to decrease and it needed to be recharged after five cycles to get appreciable counts of daughter, for ^{115}Cd-^{115m}In system,

although ascorbic acid works good in aluminium molybdate but in the aluminium vanadate, we had to use 4.0 mol. L^{-1} HCl to get appreciable yield of daughter. Condition of adsorption of mixture was however same in two cases.

For ^{90}Sr-^{90}Y pair in cerium(IV)iodo tungstate exchanger , variation of distribution co-efficients for each of the tracer against the pH of the aqueous solution was the basis of separation. As ^{90}Sr is more firmly held than ^{90}Y within pH range 3 to 7 , the activity ^{90}Sr-^{90}Y was adsorbed on the column at pH 7, followed by elution with EDTA solution, concentration of which was restricted to a very low region so that stronger complex of Y(III) is only eluted out keeping parent unaffected. Here again, a generator concept was applied and at least two sets of milking were made possible. Only problem associated with this pair is the comparatively long $T_{1/2}$ value of ^{90}Y (than ^{137m}Ba) and it takes more time for the growth of daughter. Same idea was applied where ascorbic acid was used to elute the daughter and desorption of mixture was carried at pH 5.

VII.2. Conclusion

The chemistry of polyoxometallate has been reviewed in a number of publications. [1,2], C.B. Amphlett [3] dealt the subject in a comprehensive manner covering the ion exchange properties of these compounds and their applications. Perhaps, ammonium phospho molybdate [4] (AMP) is the most widely studied among this materials and it was found that one of the NH_4^+ in the molecule behave complete differently from the others and was not possible to replace. Subsequently macro and micro scale separation of alkali metal ions was replaced by Smit [5], showing it to be superior to the conventional organic ion exchangers. Preferential retention of Cs^+ ion on AMP was utilized for the large-scale recovery of Cs-137 from fission product waste solution. Later, extensive applications of AMP and similar sorts of polyoxometallates were reported in the field of immobilization of radioactive waste. Amorphous material supported on asbestos served the purpose very well. In the present desertation, our objective was to extrapolate the above behavior of AMP class material induced to explore new sorts of polyoxometallates and their applications in radiochemical separations.

Results of such experiments presented in Chapter II to Chapter VI and summarized in previous section, are very much encouraging with little violation in few limited cases.

Thus ion exchange capacities for alkali metalcations do obey inverse relation with their atomic number except in the case of ammonium molybdates. Similarly reported values of ion exchange capacity for Na^+ ion by column method differ, through small but significant, from pH metric titration. However appearance of single inflexion point in each case are very much in confirmation with the molecular composition, which was further supported by X-ray crystallographic data.

Ion exchange capacity for alkaline earth metal cations however, does not show any peculiarity and results are very much in accordance with their change in hydrated ionic radius. Again ion exchange capacity for each alkali cation exceeds that of its corresponding alkaline earth cation and in our separation experiments, we have utilized this result in order to achieve separation [IEC of Ba(II) < Cs(I)]. An interesting observation is the very high adsorption of NH_4^+ ion on each of the polyoxometallates. As a mater of fact it has highest value among all the cations studied in each of the ion exchange reported in present work.

The fact may be correlated with the behavior of AMP and exchange mechanism might be similar to that of AMP classes of exchanger, which in turn is attributed to its complex structure. However, kinetics of exchange process was not taken up in the present investigation.

Feasibility of these inorganic ion exchangers as radionuclide generator have been reported and summarized before. With the exception in few cases, all the systems provide reproducible data and may be strongly recommended for similar studies. This is particularly true when there is a large difference in decay rate between parent and daughter e.g. ^{137}Cs-^{137m}Ba. Elution of no carrier added pure daughter makes its possible to use them as radiopharmaceuticals. As effluent, we have used ascorbic acid or EDTA or HCl which were tested to have no effect on the exchanger composition by preliminary experiments, otherwise this could damage the exchanger and hamper the purpose of separation.

Success of these exchangers in radionuclear separation indicates that the behavior might be extrapolated to similar of the systems, not explored in our work. Particularly,

fission product separation could be a challenge to these sorts of exchangers as they are highly stable against high level of radiation. Secondly, high affinity for Cs(I) ion for these materials could be exploited to achieve immobilization of radioactive waste [7,8] in a manner of AMP. Again, the exponential decay of IEC against γ-dose for aluminium tungstate could be studied in terms of the effect ionizing radiation on solid matrix.

However, presented data on the separations of no carrier added daughter, having radionuclide purity as tasted by $T_{1/2}$ or $E\gamma$ or $E_{\beta-}$ (for ^{90}Y), from their parent with the aid of insoluble inorganic ion exchanger are very much encouraging. As such separation processes are practically harmless to the composition or properties of ion exchangers, methods are particularly valuable from economic point of view. Secondly the reported work is definitely a step forward to achieve green methods of separation as the carcinogenic organic solvents are totally avoided.

We are optimistic for advancing a few steps forward towards the progress of radio-chemical analysis.

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