Ion exchange and extraction chromatographic studies with homologs of seaborgium (element 106) in HNO_3-HF medium

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The experiments to understand the chemical behaviour of transactinides such as Rutherfordium (Element 104) and Seaborgium (Element 106) are of considerable interest from basic chemistry point of view. ^{261}Rf and ^{265}Sg have been produced by heavy ion reactions using intense beams of O-18 and Ne-22 on ^{248}Cm target, respectively [1]. Due to their short half lives ($t_{1/2}$ of ^{261}Rf and ^{265}Sg are about 78 s and 34 s, respectively) and limited availability of accelerator beam time for such exotic experiments, it is relevant to develop separation methods using their homologs such as Zr, Hf, (for Rf), Mo and W (for Sg) and pseudo-homologs viz. Th (for Rf) and U (for Sg) for utilization as a guide line for the actual experiment.

Rapid radiochemical separation methods involving Multi-Column Technique (MCT) have been used for the studies on the chemical properties of trans-actinides involving experiments in HNO_3 + HF medium using anion exchangers such as DOWEX 1x8. However, the K_d values of homologs like Mo and W were found to be too high when DOWEX 1x8 resin was used suggesting the need for weaker anion exchangers. The present work is an attempt in that direction where several other anion exchangers with different functional groups have been used along with an extraction chromatographic material made from Aliquat 336, a liquid anion exchanger, in chloroform.

As reported earlier, the contrasting K_d values obtained at 0.01 M HF and 0.1 M HNO_3 are made use of in a proposed scheme for the studies on the chemistry of Sg [2]. Table 1 lists the K_d values for Mo and W with three different anion exchange resins viz. DOWEX 1x8 (with – methyl group), HS 36 (with – ethyl group) and HB 36-I/92 (with – n-butyl group). The batch distribution data are obtained in the 0.1 M nitric acid as well as HCl in the presence of 0.01 M HF. As shown in the following table, the K_d values are significantly larger for the HCl medium as compared to the HNO_3 medium. This can be ascribed to two reasons, first, the chloro complexes are more easily formed than nitrate complex and second, the nitrate ion acts as a better counter anion. As shown in Table 1, the K_d values at 0.1M HNO_3 + 0.01M HF show a decreasing trend of Dowex 1x8 > HS 36 > HB 36-I/92 for Mo, while an opposite trend is observed for W. On the other hand, at 0.1M HCl + 0.01M HF, the trend for both Mo and W is Dowex 1x8 > HS 36 < HB 36-I/92. The results of the ARCA experiments carried out on-line with the accelerator produced ^{170}W have indicated reasonable agreement with those from the batch studies mentioned above.

Table 1. Effect of resin type on the Kd values of Mo and W

Conditions	Mo			W		
	DOWEX 1x8	HS 36	HB 36-I/92	DOWEX 1x8	HS 36	HB 36-I/92
0.1M HNO_3 + 0.01M HF	89	15	5.7	5.0	13	16
0.1M HCl + 0.01M HF	181	40	732	96	46	70

In spite of using three different functionalized ion-exchangers, it was not possible to obtain an experimental condition for which the K_d values of Mo and W fall in the range of 10-50. An extraction chromatographic material was prepared using Aliquat 336 (tri-caproyl methyl ammonium chloride) in chloroform sorbed onto chromosorb W. Figure 1 shows the results obtained with the extraction chromatographic studies carried out at varying concentration of HF at a fixed concentration (0.1M) of nitric acid using Mo and W tracers. It is interesting to note that the sorption of Mo and W onto the extraction chromatographic resin material is significantly high at lower HF concentration. It is attributed to the presence of anionic oxo complexes like MoO_4^{2-} and WO_4^{2-}. The decrease in the K_d values with increasing HF concentration in the case of Mo and W could be explained on the basis of the formation of neutral complexes such as MoO_2F_2 and WO_2F_2. On further increasing the HF concentration, the K_d values of W showed an upward trend while no such trend was seen with Mo. This is explained on the basis that though both the hexavalent Mo and W form anionic fluoride complexes, it is more favorably and readily formed for the latter [2]. The V-shape curve for W was observed earlier when DOWEX 1x8 was used as the ion exchanger [3]. The interesting aspect observed during these studies was that the K_d values are such that (Mo: 45 and W : 18 at the aqueous phase composition of 0.1M HNO_3 + 0.01M HF) experiments with ^{265}Sg can be carried out conveniently. These are much lower than the values obtained with DOWEX 1x8 suggesting that the Aliquat 336 loaded chromatographic material can be an ideal choice for the chemical studies involving ^{265}Sg.

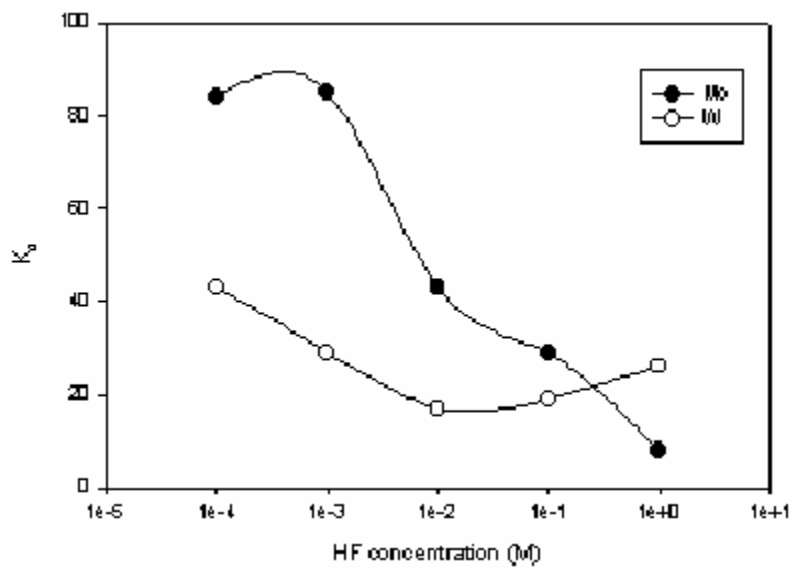

Figure 1. Distribution of Mo and W as a function of HF concentration at 0.1 M HNO_3. Resin: Aliquat 336 sorbed on chromosorb.

References

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