

Anion-Exchange Behavior of Tungsten and Molybdenum as Homologues of Seaborgium (Element 106) in HNO₃/ HF-Solutions

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The first aqueous chemistry of Seaborgium (element 106, Sg) showed that it forms neutral or anionic oxyfluorides in 0.1 M HNO₃/5·10⁻⁴ M HF [1], but the experiment did not determine a distribution coefficient. In our future experiments with ²⁶⁵Sg, we plan to determine K_d-values on an anion exchanger in HF/0.1 M HNO₃ and pure HCl solutions using on-line chromatography with the multi-column technique [2]. In preparation of this experiment, we have measured the K_d-values of short-lived Hf [3] and W [4] using the multi-column technique and compared these with results obtained with ARCA.

Recently, prior to the studies with Seaborgium, we have investigated the chemical behavior of its homologs tungsten and molybdenum on cation and anion exchangers in HF/HNO₃ and pure HNO₃ and HCl solutions in batch experiments as well as with ARCA. We report here the results obtained from batch experiments with neutron activated ¹⁸⁷W and carrier free ⁹⁹Mo. These data are compared with those obtained with ARCA, involving 76-s ¹⁶⁵Hf and 2.4-min ¹⁷⁰W produced on-line by the reactions ¹⁵⁸Dy(¹²C, 5n) and ^{nat}Er(¹²C, xn), respectively, at the UNILAC at GSI.

Figure 1 shows the results from the batch experiments with ¹⁸⁷W and ⁹⁹Mo using varying concentrations of HF in 0.1 M HNO₃ (HCl). The situation is complex due to a competition between hydrolysis and fluoride complexation. In the case of tungsten, the minimum in the K_d-values at 0.01 M HF indicates that, for lower HF concentrations, high K_d-values due to the presence of anionic hydrolysis products are decreased with increasing HF concentration as a result of increasing charge neutralization by the addition of fluoride ligands. The increase of the K_d-values for >0.01 M HF is obviously due to the formation of anionic fluoride complexes. For Mo, the dependence of the K_d-values on HF concentration is less structured.

Figure 2 compares the K_d-values for Mo and W at 0.005 M HF as a function of the concentration of the counter ion NO₃⁻ which competes for the binding site on the anion exchanger. The lower slope for W is consistent with the presence of some neutral species along with anionic ones. At 0.1 M HF, slopes similar to that for Mo in Fig. 2 are observed for both Mo and W. The latter HF concentration is too high for a seaborgium experiment with the multi-column technique as the decay product Rf forms neutral or anionic fluoride complexes under these conditions which break through a cation-exchange filter [5].

Fig. 3 shows the K_d-values of Mo and W in the absence of HF in both HNO₃ and HCl. At low mineral acid concentrations, the sequence of the K_d-values, Mo>W, reflects the known fact that Mo is more hydrolysed than W [6]. The decrease of the K_d-values for >0.01 M HNO₃ or HCl is due to the action of the counter ions NO₃⁻ and Cl⁻ where NO₃⁻ competes more effectively for the binding sites than Cl⁻. By calculating the electronic structure and by applying her theoretical treatment of hydrolysis, V. Pershina predicts the sequence Mo>W>Sg in dilute mineral acids.

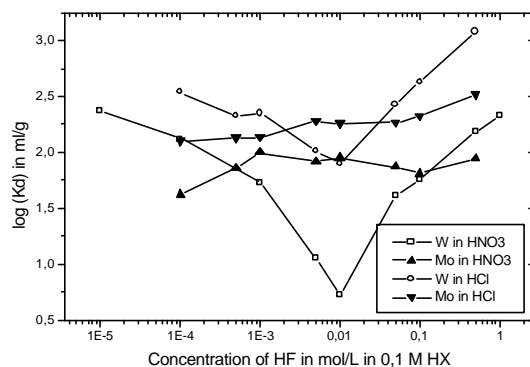


Fig. 1 K_d-values of W and Mo at variable HF-concentration and 0.1 mol/l HNO₃ or HCl on Dowex 1X8

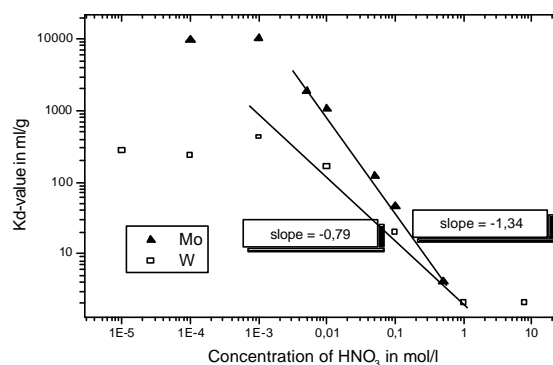


Fig. 2: Dependence of the K_d-values of Mo /W on varying HNO₃-concentration at 0.005 M HF on DOWEX 1X8

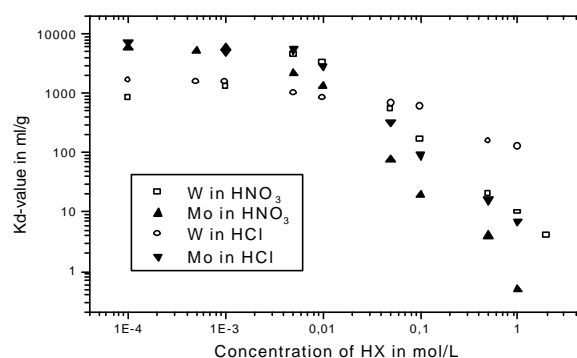


Fig. 3: Dependence of the K_d-values of Mo /W on varying HNO₃ / HCl concentration on DOWEX 1X86

References

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