Adsorption of Fission Products on Alumina in Organic Solutions

Noboru Oi*

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Metal nitrates are readily adsorbed on alumina in organic solutions such as acetone and n-butylacetate. Adsorption isotherms for such compounds as uranyl nitrate, thorium nitrate and cerium nitrate (III) were examined, and the adsorption was found to have occurred monomolecularly on the surface of the alumina.

The weakest adsorption strength on alumina was found to be that of uranyl nitrate, and the adsorbed uranyl nitrate could be substituted very easily by other nitrates such as of fission products.

The logarithmic decrease of the \( K_d \) values of fission products on alumina with increase of uranyl nitrate concentration in n-butylacetate was found to correspond to the increase of the solubility of nitrates of fission products (Ce, Sr and Zr) with increase of uranyl nitrate concentration.

Separation of fission products from U in organic solution was described in previous papers\(^*\). Uranyl nitrate containing fission products dissolved in an organic solvent such as n-butylacetate or ethylether and the solution was then placed in contact with an adsorbent such as alumina or cellulose. Fission products were adsorbed by the adsorbent, leaving U in the solution.

In the present work, some experiments were carried out to elucidate the mechanism of separation. The experiments were done mainly by using alumina as adsorbent and n-butylacetate as organic solvent.

Firstly, the adsorption isotherms for various metal nitrates dissolved in an organic solvent were examined, and secondly, the adsorptive strengths of several metal nitrates on alumina were compared by using macroscopic amounts (not tracer amounts) of the salts. Thirdly, the relationship was determined between the distribution ratios of fission products on alumina and the solubilities of the nitrates in n-butylacetate solution.

**Experimental**

Alumina from Wako Pure Chem. Co., 200 ~300 mesh for chromatography, was used without pretreatment.

**Determination of the Amounts of Metal Nitrates Adsorbed on Alumina**

Metal nitrate was dissolved in an organic solvent such as n-butylacetate or acetone. The solution (if an aqueous layer also appeared, the organic layer) was poured into 20 ml graduated cylinder with stopper and 1 g of alumina was added. After letting it stand, with intermittent shaking, for 2 hr at \( 20^\circ \pm 2^\circ \)C (it was found that the equilibrium was complete within 20 min) the solution was centrifuged and pipetted out. The concentration of the solution before and after the adsorption was determined by EDTA titration (in the case of U, by conventional spectrophotometric method), and the amounts of metal nitrate adsorbed by the alumina were calculated.

**Determination of Solubility**

The values of solubility described in this paper (expressed in “amount of a salt (g) dissolved in a solvent/1 g of the saturated solution”) were all obtained at \( 20^\circ \)C.

A sufficient amount of metal nitrate was put into an organic solvent and kept overnight with intermittent shaking. One milliliter of the resulting solution was taken out and after weighing it, the amounts of dissolved metal nitrate were determined by conventional analytical methods. In determining very small solubilities, radioactive tracers such as \( ^{137}\text{Cs} \) and \( ^{89}\text{Sr} \) were used and the amounts of the metal nitrates in the resulting solutions were determined radiometrically.

Determination of the distribution ratios (\( K_d \) values) of fission products was described

* Central Research Laboratory, Tokyo Shibaura Electric Co., Ltd., Kawasaki-shi, Kanagawa-ken.
RESULTS AND DISCUSSION

1. Adsorption of Metal Nitrates on Alumina

It was confirmed by the following experiments that uranyl nitrate was adsorbed on alumina as molecules and not as uranyl ions in various organic solvents. Uranyl nitrate solution was passed through a column of alumina and the eluent was checked by alkali titration to ascertain that no hydrogen ion was detected so long as uranyl nitrate was being adsorbed by the alumina. And when U broke through the column, the mole ratio of U and nitric acid was found to be 1:1. Adsorption equilibrium curves for some nitrates in acetone are shown in Fig.1. The data obtained by using n-butylacetate were almost identical. It was found that the amount of adsorption reaches a saturation value over the extended ranges of nitrate concentration and the Langmuir plots also gave straight lines. All these points indicate that the adsorption is performed monomolecularly on the surface of the alumina. Nitrates of Ce, Th and other metals were chosen for the present experiments, since those of Cs, Sr, Zr and Ba, while they may more appropriately represent fission products, are almost insoluble in organic solvents. In the case of uranyl nitrate, the saturation values of adsorption by 1 g of alumina in acetone, n-butylacetate and isopropylether were respectively 60, 60 and 69 mg of U, which shows that the choice of organic solvents does not much affect the amount of adsorption. The saturation values of nitrates adsorbed by 1 g of alumina in acetone were 48 mg for Th, 36 mg for Ce and 48 mg for HNO₃, respectively. Here, it is possible to calculate the dimensions (Å²) of an adsorbed molecule if we divide the surface area of the alumina (obtained by the BET method and found to be 110 m²/g of alumina) by the number of molecules adsorbed. Similarly, it is possible to estimate the dimensions (Å²) of a metal nitrate hydrate from its density and molecular weight (molecular volume); in this case, the assumption is that the molecule is a cube. The values calculated from both adsorption data and molecular volume are shown in Table 1. The results show that the dimensions of adsorbed molecules are 1.6~1.9 times larger than that calculated from the molecular volume of hydrated nitrates. The cause of the difference may lie, firstly, in

Table 1 Dimensions of Adsorbed Molecules on Alumina in Acetone

<table>
<thead>
<tr>
<th>Nitrates</th>
<th>Molecular weight</th>
<th>Density</th>
<th>Saturated amounts of adsorbed nitrates (mg)†</th>
<th>Dimensions of adsorbed molecule (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>63.0</td>
<td>1.38</td>
<td>42</td>
<td>Calculated values‡‡</td>
</tr>
<tr>
<td>Cu(NO₃)₂·6H₂O</td>
<td>241.6</td>
<td>2.05</td>
<td>28</td>
<td>18</td>
</tr>
<tr>
<td>Ce(NO₃)₂·6H₂O</td>
<td>434.3</td>
<td>2.33</td>
<td>36</td>
<td>46</td>
</tr>
<tr>
<td>Th(NO₃)₄·4H₂O</td>
<td>552.3</td>
<td>2.72</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>UO₆(NO₃)₆·6H₂O</td>
<td>502.2</td>
<td>2.81</td>
<td>60</td>
<td>45</td>
</tr>
</tbody>
</table>

† mg of metal/g of alumina, except for HNO₃ for which adsorbed amount
‡‡ Calculated values from molecular volume
††† Calculated from the amount of adsorption and surface area of alumina
two or more sites being occupied by a metal nitrate whose size is larger than a nitrogen molecule which was used in the case of the BET method, and secondly in inadequate assumptions adopted for the adsorbed molecules: for example, the molecules could be hydrated to a greater degree. The above experiments indicate, however that the adsorptive capacity of alumina for fission products in organic solutions can be estimated from the molecular volumes of each fission products nitrate.

2. Comparison of Adsorptive Strengths of Various Nitrates

K\textsubscript{d} values of fission products on alumina were determined in a previous work\textsuperscript{10}. In the course of these experiments, it was noticed that alumina with surface completely covered with uranyl nitrate showed almost the same K\textsubscript{d} values for fission products as alumina not so treated. The reason is clear from the following experiment. Cerous nitrate solution in n-butylacetate was passed through a column of alumina on which uranyl nitrate had been adsorbed to saturation. In this case, uranyl nitrate was found to be eluted from the column while cerous nitrate was adsorbed (Fig. 2). This experiment means that the adsorptive strength of uranyl nitrate to alumina is weak and the adsorbed uranyl nitrate can be substituted easily by other nitrates. The same type of experiment was carried out on various nitrates to compare their adsorptive strength. The order of strength in n-butylacetate was passed through a column of alumina on which uranyl nitrate had been adsorbed to saturation. In this case, uranyl nitrate solution in n-butylacetate was passed through a column of alumina on which uranyl nitrate had been adsorbed. The order of strength in n-butylacetate was uranyl nitrate < thorium nitrate < cerous nitrate < manganese nitrate < cobaltous nitrate < cupric nitrate < nitric acid. Uranyl nitrate has the weakest adsorptive strength on alumina while nitric acid has the strongest. This is the reason why in the previous report it has emphasized that free nitric acid should be completely eliminated to achieve better separation of U and fission products. The order stated above seems to be dictated by the ionic charges of the cations. But the following fact shows that the solubilities of these nitrates in organic solvents also play an important role in determining this order. When acetone was used as solvent instead of n-butylacetate, the above order of Th and cerous nitrates was reversed. The solubilities of thorium nitrate tetrahydrate and cerous nitrate hexahydrate in acetone were respectively 458 and 605 g/g of saturated solution at 20\textdegree C, while in n-butylacetate, these were respectively 378 and 6.8. Solubility can be looked as a measure of the affinity between solute and solvent. On the other hand, adsorption is determined by the difference of the affinities between solute and alumina and solute and solvent. In acetone, thorium nitrate rather than cerous nitrate tends to stay in solution, while in n-butylacetate the situation is completely reversed.

Solvent: acetone; Column: 2 g of alumina adsorbing 220 mg U of uranyl nitrate; Eluent: cerous nitrate solution, 2 mg/ml

Fig. 2 Exchange of Uranyl Nitrate with Cerous Nitrate

3. Relation between the K\textsubscript{d} Values and the Solubilities of Fission Products

The K\textsubscript{d} values of fission products on alumina were found to decrease logarithmically with increase of uranyl nitrate concentration in n-butylacetate\textsuperscript{10}. It was found that the solubilities of some fission products also increase with the increase of uranyl nitrate concentration and the reciprocals of the solubilities have a linear relationship with the K\textsubscript{d} values, especially at lower U concentration. At higher uranyl nitrate concentration, the decrease of K\textsubscript{d} values can be also explained by the competition of uranyl nitrate with the fission products to the grain sites on the alumina. In Figs. 3 and 4 are shown examples obtained for Cs and Sr. However, the above relation holds true only if the solubilities of metal nitrates in n-butylacetate are very small; solubilities of cesium nitrate and strontium nitrate in n-butylacetate were
found to be respectively $2 \times 10^{-6}$ and $4 \times 10^{-7}$ g/g of saturated solution. Probably, the logarithmical increase of the solubilities of these nitrates will be due to the formation of complexes between metal nitrate and uranyl nitrate such as $\text{UO}_2\text{Cs(NO}_3)_3$ (this complex is known\(^{(3)}\)). On the other hand, in the case of cerous nitrate which has a considerable solubility in n-butylacetate ($1.4 \times 10^{-2}$ g/g of saturated solution), the solubility decreased with the increase of uranyl nitrate concentration as is shown in Fig. 5.

![Fig. 3 Kd values of $^{137}$Cs and the Solubility of Cesium Nitrate in n-butylacetate as a Function of U Concentration](image1)

![Fig. 4 Kd values of $^{89}$Sr and the Solubility of Strontium Nitrate in n-butylacetate as a Function of U Concentration](image2)

![Fig. 5 Kd Values of $^{144}$Ce and the Solubility of Ce(NO$_3$)$_3.6$H$_2$O in n-butylacetate as a Function of U Concentration](image3)

The same relation was noticed also for Y, La and Th nitrates which also have considerable solubility in n-butylacetate. These relations seem to be caused by the competition of uranyl nitrate and these nitrates for sites on n-butylacetate. This phenomenon was indiscernible in the former case when the salt concentration was very small and the affinity between nitrates and alumina was stronger.

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**REFERENCES**