A New Approach for Studying Complex-Ion Equilibria by Ion-exchange Method & Its Application to the Sulphate Complexes of U(IV) & U(VI)

S. K. SARPAL & A. R. GUPTA
Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085

Received 30 April 1977; accepted 5 July 1977

The ion-exchange method for the determination of stability constants of metal complexes has been extended to systems having non-linear isotherms on PSS type exchangers. Stability constants of the sulphate complexes of U(VI) and U(IV) have been determined using this approach and are found to be in good agreement with the literature values. The effect of chloride ions on the formation constants of mono- and bi-sulphato complexes of U(IV) has also been investigated.

Though $k_1$ is not affected, $k_2$ is found to be lower in the chloride medium than in perchlorate medium. This has been discussed in terms of the formation of mixed species like $[U(SO_4)Cl]^+$. Sorption of U(IV) and U(VI) species in the presence of sulphate ions at low acidities on Dowex-50W x 8 and the uranium isotope effects in this U(IV)-U(VI) exchange system have also been investigated.

Materials and Methods

All the chemicals used were of BDH Analar or E. Merck GR grade. The resin, Dowex-50W x 8 (30-50 mesh), was supplied by J. T. Baker Chemical Co., Phillipsburg, NJ, USA.

Uranium(IV) chloride solution was prepared by dissolving uranium metal in HCl. Uranium(VI) chloride solution was obtained by oxidation of this U(IV) solution by hydrogen peroxide. Uranium perchlorate solution was prepared by reacting uranyl perchlorate solution with HCl.

The resin Dowex-50W x 8 (30-50 mesh) was converted into H⁺-form and air-dried as usual after putting it through two Na⁺-H⁺ cycles. The capacities and the moisture contents of the two air-dried resin (ADR) samples used for these investigations were 3.520, 3.988 meq/g ADR; and 29.4, 21.6%, respectively.

The various exchange experiments were carried out by batch equilibrium method. ADR (1 g) and uranium solution (50 ml) of desired composition were equilibrated by shaking for 24 hr. Uranium solutions of varying initial concentrations (0-0.05M) were used for obtaining uranium(IV) and uranium(VI) sorption isotherms in the absence of sulphate ions.

The sorption of uranium by the resin in the presence of sulphate ions was studied by taking a solution of constant uranium concentration ({$\approx$}0.02M) and varying sulphate ion concentration (0-0.06M). The sulphate ions were added as sulphuric acid in the experiments in perchloric acid medium and as sodium sulphate in hydrochloric acid medium experiments. The starting free acid concentration
in all the batch experiments was maintained at 0.20M. After equilibration and adsorption of uranium on the resin, this increased to ~0.25M. The solution phase was analysed for its uranium content before and after equilibration and the composition of the resin phase was obtained by difference. In the case of experiments with uranium(IV), nitrogen atmosphere was maintained above the solution in the flask, to avoid any aerial oxidation.

Theoretical Considerations

The stability constants of complexes by the ion-exchange method are usually evaluated using Eq. (1a)

\[ \frac{1}{\varphi} = \frac{1}{l_0} + \frac{1}{l_0} \beta_1[\text{A}^+] + \frac{1}{l_0} \beta_2[\text{A}^{2+}] \] ...

where \( \varphi \) is the distribution coefficient defined by m llimoles of metal ions per g resin/mole of metal per litre of solution, \([\text{A}^+]\) is free ligand concentration, \( l_0 \) is distribution coefficient in the absence of ligand and \( \beta_1, \beta_2 \ldots \) are the stepwise formation constants of the complex ions.

Eq. (1b) is another form of the above equation generally used

\[ \left( \frac{l}{\varphi} - 1 \right) = \frac{1}{l_0} \beta_1[\text{A}^+] + \frac{1}{l_0} \beta_2[\text{A}^{2+}] \] ...

The coefficients of the ligand concentration terms and the stability constants are determined by numerically fitting the data to the plots of \( \frac{1}{\varphi} \) vs \([\text{A}^+]\) by the least square method.

The main assumptions in the derivation of the above equation are: (i) the sorption isotherms of free metal ions on the resin are linear, (ii) the complexed species are not absorbed by the resin and (iii) the ligand concentration is much greater than total metal ion concentration in the solution phase. The first assumption generally holds when the resin loading is low compared to the capacity of the resin and the second is also true because the complexed ionic species carry a lower positive charge than the free metal ions. These assumptions have restricted the application of the ion exchange method to those systems where the free metal ions are strongly absorbed by the resin nor form strong complexes.

In the derivation of the above equations the free metal ion concentration in the solution has been expressed in terms of the distribution coefficients of free metal ions on a specific resin. When the sorption isotherm is linear, the distribution coefficient is independent of resin loading or free metal ion concentration in the solution. However, even when the sorption isotherm is non-linear, a specific resin composition and metal ion concentration are in equilibrium. This implies that Eq. (1) is valid for any specific resin loading with the corresponding value of \( l_0 \) even when \( l_0 \) varies, i.e. when the sorption isotherm is non-linear. For such systems \( l_0 \) is treated as a function of resin composition in Eq. (1), i.e.

\[ \frac{1}{\varphi} = \frac{1}{l_0} + \frac{1}{l_0} \beta_1[\text{A}^+] + \frac{1}{l_0} \beta_2[\text{A}^{2+}] \] ...

or

\[ \left( \frac{l}{\varphi} - 1 \right) = \beta_1[\text{A}^+] + \beta_2[\text{A}^{2+}] \] ...

Now \( l \) and \( \varphi \) refer to a specific resin composition and \([\text{A}^+]\) is the free ligand concentration at that value of \( \varphi \). From the sorption isotherm of the metal on the resin, \( l \) can be determined for various \( \varphi \) values. The ion-exchange method can thus be extended to systems where the sorption isotherms are non-linear. However, it should be emphasized that this approach can be used only in the form of Eq. (2b) and not (2a), the counterpart of (1a).

Basically the ion-exchange method enables one to determine the free metal ion concentration in equilibrium with various complex species in the solution phase. With this information and the restriction that not more than two ligands are attached to the metal ion, an analytical solution to the problem is possible as discussed below with reference to U(IV) sulphate complexes.

Equations (A and B) describe the complexion of U\(^{IV}\) by sulphate ions,

\[ \text{U}^{IV} + \text{HSO}_4^- \xrightarrow{k_1} \text{USO}_4^{2+} + \text{H}^+ \] ... (A)

\[ C_{\text{USO}_4^{2+}} \ x = \left( \frac{C_{\text{USO}_4^{2+}}}{C_{\text{USO}_4^{2+}} + C_{\text{USO}_4^{+}} + C_{\text{USO}_4}} \right) \ x \] ...

From Eq. (A) \( k_1 \) can be written as shown in Eq. (3)

\[ k_1 = \frac{C_{\text{USO}_4^{2+}}}{C_{\text{USO}_4^{2+}} + C_{\text{USO}_4^{+}} + C_{\text{USO}_4}} \] ...

where \( C_{\text{USO}_4^{2+}} \) is the free uranium ion concentration, \( C_{\text{USO}_4^{2+}} \) is the total concentration of uranium present as complex, \( x \) is the concentration of bisulphate complex, \( C_{\text{HSO}_4^-} \) is equal to initial sulphate concentration (\( C_{\text{USO}_4^{2+}} \) minus \( C_{\text{USO}_4^{2+}} \)) and \( C_{\text{USO}_4} \) is the titre of the free sulphate ion concentration present in the solution.

Rearranging Eq. (3) one gets the expression (4) for \( x \),

\[ x = \frac{C_{\text{USO}_4^{2+}}}{C_{\text{USO}_4^{2+}} + C_{\text{USO}_4^{+}} + C_{\text{USO}_4}} \] ...

The quantities on the right hand side of Eq. (4) are obtained as follows: The free uncomplexed uranium concentration, \( C_{\text{U}^{1+}} \), is obtained from the uranium sorption isotherm in the absence of sulphate ions. The difference between the total uranium concentration (directly estimated in the solution and the \( C_{\text{USO}_4^{2+}} \) gives the complexed uranium concentration, \( C_{\text{USO}_4^{2+}} \). An approximate value of \( k_1 \) is obtained from the data at the lowest sulphate concentration (\( \approx 0.001 \text{M} \)), assuming that the bisulphate complex is not formed at this low sulphate concentration. This value of \( k_1 \) is used to compute \( x \) [using Eq. (4)] from the data at higher sulphate concentrations.
concentrations, $k_2$ can then be computed using Eq. (5)

$$k_2 = \frac{C_{\text{CuSO}_4}C_{\text{H}^+}}{C_{\text{CuSO}_4^{2-}}C_{\text{HSO}_4^-}} = \frac{x.C_{\text{H}^+}}{(C_{\text{Cu comp}}-x)(C_{\text{HSO}_4^-}-x)} \quad \text{(5)}$$

An average of $k_2$ values is used to back compute $k_1$. An iterative procedure is employed to get constant values of $k_1$ and $k_2$.

In the present study, the analytical approach has been used for the determination of the stability constants of the various complex species and Eq. (2b) has been verified using these data.

**Results and Discussion**

*Uranium(IV)-sulphate complexes* — Sorption isotherms (plots of the quantity of uranium(IV) sorbed per unit resin capacity versus equilibrium uranium concentration) for uranium(IV) in the absence of any sulphate ions in perchloric acid and hydrochloric acid media are given in Fig. 1. These isotherms are highly non-linear. The values of $k_{\text{app}}$ [obtained using Eq. (3)] and relevant data needed to compute them are given in Table 1. The variations in the computed values of $k_{\text{app}}$ show that complexes with more than one sulphate ligands are being formed.

The values of $k_1$ and $k_2$ [the stability constants for mono- and bi-sulphato complexes of uranium(IV)], computed as described above, are also given in Table 1. The stability constant values for mono- and bi-sulphato complexes of uranium(IV) in perchloric acid medium are in good agreement with the corresponding values of Sullivan and Hindman (Table 2) and of other workers. In hydrochloric acid medium, $k_1$ is nearly same as in the perchloric acid medium, the $k_2$ is almost half its value in perchloric acid medium. This lowering of $k_2$ value in the presence of chloride ligand could be due to the formation of species like UClSO$_4$ which hinders the formation of bi-sulphato complex.

![Fig. 1 — Sorption isotherms for U(IV)/H and U(VI)/H exchanges in the absence of sulphate on Dowex-50W × 8 resin (○) U(IV) in HClO$_4$ medium; (▲) U(IV) in HClO$_4$ medium; and (▼) U(VI) in HClO$_4$ medium](image)

**Table 1 — Uranium(IV)-sulphate complexes on H$^+$-form of Dowex-50W × 8**

<table>
<thead>
<tr>
<th>C$^{+}$HSO$_4$ (M)</th>
<th>U(IV) Cu$^{++}$ Cu$^{++}$</th>
<th>C$^{+}$HSO$_4$ (M)</th>
<th>C$^{+}$HSO$_4$ (M)</th>
<th>C$^{+}$HSO$_4$ (M)</th>
<th>C$^{+}$HSO$_4$ (M)</th>
<th>k$_{\text{app}}$ (litre/mole)</th>
<th>Final $A_1$ (litre/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In HClO$_4$ medium; $A_1$ = 292-0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00105</td>
<td>0.2461</td>
<td>0.00021</td>
<td>0.00020</td>
<td>0.00085</td>
<td>0.2675</td>
<td>304-4</td>
<td>19-1</td>
</tr>
<tr>
<td>0.00204</td>
<td>0.2326</td>
<td>0.00067</td>
<td>0.00017</td>
<td>0.00069</td>
<td>0.2576</td>
<td>297-7</td>
<td>17-1</td>
</tr>
<tr>
<td>0.02990</td>
<td>0.2161</td>
<td>0.00005</td>
<td>0.00005</td>
<td>0.00090</td>
<td>0.2357</td>
<td>428-8</td>
<td>17-1</td>
</tr>
<tr>
<td>In HCl medium; $A_1$ = 289-8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.000100</td>
<td>0.2211</td>
<td>0.00009</td>
<td>0.00093</td>
<td>0.000907</td>
<td>0.2613</td>
<td>297-7</td>
<td>9-3</td>
</tr>
<tr>
<td>0.002000</td>
<td>0.2199</td>
<td>0.000085</td>
<td>0.001812</td>
<td>0.001818</td>
<td>0.2500</td>
<td>306-2</td>
<td>9-1</td>
</tr>
<tr>
<td>0.000300</td>
<td>0.2188</td>
<td>0.00008</td>
<td>0.000267</td>
<td>0.002733</td>
<td>0.2586</td>
<td>315-8</td>
<td>9-5</td>
</tr>
<tr>
<td>Av. 9-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values in parentheses are $k_2$ (corr) values.

References [Division of Chemical Information, USAEC], 1964, 3.

24. RODDEN, C. J., in *Analysis of essential nuclear reactor materials* (Division of Chemical Information, USAEC), 1964, 95.
TABLE 2 — STABILITY CONSTANTS OF URANIUM(IV) AND URANIUM(VI) COMPLEXES (IONIC STRENGTH = 0.275 M)

<table>
<thead>
<tr>
<th>System</th>
<th>Medium</th>
<th>$k_1$ (litre/mole)</th>
<th>$k_2$ (litre/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(IV)-SO₄</td>
<td>HClO₄</td>
<td>292</td>
<td>19</td>
</tr>
<tr>
<td>U(IV)-Cl</td>
<td>HClO₄</td>
<td>257</td>
<td>21</td>
</tr>
<tr>
<td>(μ = 2 M)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U(IV)-SO₄</td>
<td>HCl</td>
<td>290</td>
<td>9.3</td>
</tr>
<tr>
<td>U(IV)-Cl</td>
<td>HClO₄</td>
<td>1.9</td>
<td>0.33</td>
</tr>
<tr>
<td>(μ = 2 M)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U(VI)-SO₄</td>
<td>HClO₄</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>

This situation can be analysed using the additional equilibria (C-E):

$$U^{4+} + Cl_2 \leftrightarrow UCICl$$  ... (C)

$$UCICl + SO_4^{2-} \leftrightarrow U(SO_4)Cl^+$$  ... (D)

$$U(SO_4)Cl^+ + Cl^- \leftrightarrow UCl^+$$  ... (E)

Assuming that $k_{Cl}$ and $k_{Cl}$ and $k_{SO_4}$ (defined by Eq. (A)) and $k_{Cl}$ are equal, the formation of bisulphato-complexes is given by Eqs. (F) and (G):

$$(UCICl, U^{4+}) + HSO_4^- \leftrightarrow [U(SO_4)Cl^+], USO_4^{2-} + H^+$$  ... (F)

$$(UCl^+, U^{4+}) + HSO_4^- \leftrightarrow [U(SO_4)Cl^+], Cl^+$$  ... (G)

The formation of species like $U(SO_4)Cl^+$ has been neglected. The lowering of $k_2$ is then entirely due to the presence of species like $U(SO_4)Cl^+$, i.e. actual concentration of $U(SO_4)Cl^+$ is less than the one used in the present calculations. On the basis of the above mentioned assumptions, the concentration of $U(SO_4)Cl^+$ species can be computed and the real concentration of $U(SO_4)Cl^+$ obtained. $k_2$ values computed on this basis are also listed in Table 1 as $k_{2	extrm{(corr)}}$. This $k_{2	extrm{(corr)}}$, though slightly lower than $k_2$, is in qualitative agreement with it.

This could be explained on the basis that any of the above mentioned assumptions may not be strictly valid. However, the $k_{2	extrm{(corr)}}$ values do show that the above analysis is on the right lines.

**Uranium(VI)-sulphate complexes** — The stability constants for uranium(VI)-sulphate species were also determined by this method. The sorption isotherm for uranium(VI) in perchloric acid medium in the absence of sulphate is given in Fig. 1. The stability constant and the relevant data needed to compute the same are given in Table 3. The constancy of $k_{app}$ at varying resin loading and ligand concentrations shows the formation of only monosulphato complex under these conditions. The value of the stability constant, $k_{Cl}$, obtained in this study is slightly lower than that reported in the literature (Table 2) by other workers.12-13, 15

**Sorption of U(IV) and U(VI) in presence of sulphate ions on Dowex-50W x 8** — Because of the interest in uranium isotope effects in U(IV)-U(VI) exchange system14,15 and the catalysis of this exchange by sulphate ions at low acidities16,17, the ion-exchange behaviour of U(IV)-U(VI) system in the presence of sulphate ions on Dowex-50 W x 8 resin was also investigated. The sorption studies of U(IV) and U(VI) by H⁺-form of Dowex-50 W x 8 resin from U(IV)-U(VI) 1:1 mixture solution (of 0.04 M) in 0.2 M HCl showed that the same amounts of U(IV) were taken up by the resin [U(VI), being completely excluded] at all the sulphate concentrations (up to 0.06 M) as in the absence of U(VI). The uranium isotope effects in these systems were investigated in a breakthrough experiment on a H⁺-form of Dowex-50(W x 8, 100-200 mesh resin column. The feed solution was made up of 0.02 M U(IV), 0.02 M U(VI), 0.1 M HCl and 0.02 M Na₂SO₄. Though sharp U(VI) and U(IV) fronts were formed, no fractionation of uranium isotopes was observed at the U(IV) front. It seems that even under these conditions the U(IV)-U(VI) exchange is not fast enough to be used on ion-exchange columns.

**Uranium(IV)-chloro complexes** — The formation of UCICl complex has been investigated in a narrow range of chloride concentration. The stability constant and the relevant data are given in Table 4. The constancy of the stability constant ($k_{app}$) indicates the formation of uranium complex with only one chloride ligand. This value of $k_1 (1.9$ litre/mole at 0.275 M ionic strength) is in reasonable agreement with the available data (Table 2), e.g. 0.33 litre/mole (μ = 2 M) by ion exchange method, 1.82 litre/mole (μ = 2 M) by distribution method, 2.0 litre/mole (μ = 1 M) by redox method, and 0.63 litre/mole (μ = 0.5 M) and 7.08 litre/mole (μ = 0) by spectrophotometric method.

---

**Table 3 — Uranium(VI)-sulphate complex on H⁺-form of Dowex-50W x 8**

<table>
<thead>
<tr>
<th>$C^+$/H₂SO₄ (M)</th>
<th>$C_{U(IV)}$ (M)</th>
<th>$C_{U(VI)}$ (M)</th>
<th>$C_{Cl⁻}$/H⁺</th>
<th>$C_{HSO_4^-}$/H⁺</th>
<th>$C_{HCl}$/H⁺</th>
<th>$k_{app}$/H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00222</td>
<td>0.2041</td>
<td>0.00458</td>
<td>0.00019</td>
<td>0.00203</td>
<td>0.2265</td>
<td>4.9</td>
</tr>
<tr>
<td>0.00478</td>
<td>0.1963</td>
<td>0.00492</td>
<td>0.00131</td>
<td>0.01347</td>
<td>0.128</td>
<td>3.5</td>
</tr>
<tr>
<td>0.00992</td>
<td>0.1946</td>
<td>0.00482</td>
<td>0.00152</td>
<td>0.01840</td>
<td>0.2075</td>
<td>3.6</td>
</tr>
<tr>
<td>0.002510</td>
<td>0.1902</td>
<td>0.00455</td>
<td>0.00210</td>
<td>0.02300</td>
<td>0.2017</td>
<td>4.1</td>
</tr>
<tr>
<td>0.00325</td>
<td>0.1866</td>
<td>0.00432</td>
<td>0.00258</td>
<td>0.02767</td>
<td>0.1960</td>
<td>4.2</td>
</tr>
<tr>
<td>0.00390</td>
<td>0.1836</td>
<td>0.00415</td>
<td>0.00296</td>
<td>0.03684</td>
<td>0.1870</td>
<td>3.6</td>
</tr>
<tr>
<td>0.00450</td>
<td>0.1802</td>
<td>0.00398</td>
<td>0.00337</td>
<td>0.04163</td>
<td>0.1814</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Av.  3.7
Application of Eq. (2) — The above equation has been tested using the data on the three systems investigated in the present study. As the third restriction in the conventional method, namely the initial ligand concentration equal to free ligand concentration, is not valid in the present series of experiments, the RHS of Eq. (2b) was computed for free ligand concentrations. In those cases where only mono complexes are formed, CHSO\(^{-}\) is a better approximation than CHSO\(^{-}\). Even in cases where higher complexes are formed, CHSO\(^{-}\) is a better approximation than CHSO\(^{-}\).

Plots of \((l/\phi-1)\) and the computed values of RHS of Eq. (2b) vs C\(_{\text{CHSO}^-}\) are given in Fig. 2. The good linear plots obtained for UO\(_2\)-SO\(_4\) and U(IV)-SO\(_4\) (HCl) systems, where only mono-sulphato complexes are formed and the good agreement between the observed and computed values of \((l/\phi-1)\) strongly support the present approach and emphasize its enhanced utility for the study of complexes. In the case of U(IV)-SO\(_4\) system, the computed values start deviating from the observed values at high ligand concentrations. However, in that case too, the agreement between observed and computed values of \((l/\phi-1)\) using CHSO\(^{-}\) is very good, again proving the validity of the present equations. Nevertheless, the applicability will be restricted to those systems where free ligand concentration is available independently or where assumption (iii) is valid. All the same, the present extension of Eq. (1), by removing the restriction of linear sorption isotherm, enhances the utility of the ion-exchange method for studying complex-ion equilibria.

Acknowledgement

The authors wish to express their sincere thanks to Dr M. D. Karkhanavala, Head, Chemistry Division, for his keen interest and encouragement during the course of this investigation.

References