How to Use the R&D Capacity of the AKUFVE System in Rare Earth Projects.

The AKUFVE System – General Information

AKUFVE is a worldwide-recognised instrument for rapid and accurate measurement of partition factors in solvent extraction. The instrument is characterised as an idealised, one-stage mixer-(centrifugal)settler unit. It was developed about 40 years ago (some hundred units are on the market) to improve accuracy and rapidity in the measuring technique of solvent extraction distribution data.

In applied research the AKUFVE instrument considerably reduces the time and labour in the evaluation and optimisation of solvent extraction processes. Its application to basic research have included the determination of distribution and stability constants for various metal complexes, together with enthalpy and entropy values, obtained from temperature dependency measurements and the determination of reaction rates and activation energies. In general, the AKUFVE instrument offers great advantages over more conventional techniques.

Based on the mixer-(centrifugal)settler concept, some other instruments and systems are available. The ADMCS instrument is a smaller version of the AKUFVE instrument and the SMCS unit is the single-stage mixer-(centrifugal)settler unit, included in the SISAK system, a small-scale multi-stage processing unit for e.g. production of antibiotics and chemical separation of short-lived radioisotopes.

The heart of all these units is the continuous flow H-centrifuge. It is a unique centrifugal separator, developed to cover the requirement for rapid and absolute phase separation of a liquid mixture of two immiscible solvents (e.g. water and kerosene). The centrifuge, described in detail in the enclosed reprint, is characterised by a comparatively high speed of rotation (10-35,000 rpm), short hold-up time (0,05-2.5 sec), high liquid flow throughput (30-300 l/h) and extremely high phase separation efficiency, better than 99,9% in both phases.
The AKUFVE Instrument with Liquid Scintillator Detector System

This AKUFVE system, also called the AKUFVE-LISOL system, is used in the experiments described below. The results and figures are found in:

Yngve Albinsson, Solvent Extraction Studies of Lanthanide Acetylacetonates, Dissertation 1988
Example of Results - Promethium Complexes

Solvent extraction distribution data (log D) at different pH and calculated pAa (-log[Aa⁻]) in 1 M NaClO₄ at 25 °C.

These plots are typical for the case of Maₙ(HA)ₖ⁻ type complexes in that different and non-coinciding curves are obtained with the same limiting slope of −3 at increasing pAa (decreasing pH).
The figures above demonstrate the quality of experimental information for the determination of
- Equilibrium constants $\beta_n$ for the successive complex formation ($1 \leq n \leq 4$)
- Self-adduct constants $K_{\text{add}}$ for the formation of PmAa$_3$(HAa)$_i$ in the org phase
- Two-phase distribution constant $P_3$ for the uncharged PmAa$_3$ complex.

**Further Examples**

Solvent extraction distribution data ($\log D$) at different pAa ($-\log[Aa]$) from 1.0 M NaClO$_4$ to C$_6$H$_6$ containing 1.0 M and 3.0 M acetylacetone (HAa) respectively.
The experimental results may also be arranged as demonstrated in the figure below.

The figure shows the extraction of four lanthanides at constant pAa but at varying concentration of \((HAa)_{org}\), calculated using the function:

\[
Y = D \cdot \beta_3^{-1} \sum (\beta_n [Aa]^{-n^3}) = P_3 (1 + K_{add_1} [HAa]_{org} + K_{add_2} [HAa]_{org}^2 + \ldots)
\]

(Open symbols are values calculated from the extraction curves)

The distribution constant, \(P_3\), is obtained from the intercept and the adduct formation constant, \(K_{add_1}\), from the slope.

The complex formation of the lanthanides calculated from the measurements performed by the AKUFVE-LISOL system is shown below:

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Tb</th>
<th>Ho</th>
<th>Tm</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\log B_2)</td>
<td>7.54</td>
<td>8.87</td>
<td>9.20</td>
<td>9.30</td>
<td>9.79</td>
<td>10.00</td>
<td>9.93</td>
<td>10.43</td>
<td>10.58</td>
</tr>
<tr>
<td>(\log B_3)</td>
<td>10.10</td>
<td>11.87</td>
<td>12.22</td>
<td>12.57</td>
<td>13.12</td>
<td>13.34</td>
<td>13.30</td>
<td>13.82</td>
<td>13.91</td>
</tr>
<tr>
<td>(\log B_4)</td>
<td>11.21</td>
<td>13.57</td>
<td>14.06</td>
<td>14.29</td>
<td>14.97</td>
<td>15.26</td>
<td>15.23</td>
<td>15.66</td>
<td>15.70</td>
</tr>
</tbody>
</table>
The table shows the equilibrium constants for the weak complexes of lanthanides with acetylacetone (HAa) in the system 1 M NaClO₄ / C₆H₆ and CHCl₃.

The constants refer to the following reactions:

\[ B_n \quad M^{3+} + n \text{Aa}^- \leftrightarrow \text{MAa}_n^{3-n} \]

\[ P_3 \quad \text{MAa}_3 \text{(aq)} \leftrightarrow \text{MAa}_3 \text{(org)} \]

\[ K_{\text{add} i} \quad \text{MAa}_3 \text{(org)} + i \text{HAa} \text{(org)} \leftrightarrow \text{MAa}_3 \text{HAa}_i \text{(org)} \]

Please notice!

The measurements and calculations have been made at Chalmers University of Technology, Göteborg, Sweden, using the AKUFVE-LISOL system connected to on-line liquid scintillation detectors.