Contribution from the Oak Ridge National Laboratory, Chemistry Division

ULTRACENTRIFUGAL MEASUREMENTS ON URANYL FLUORIDE SOLUTIONS

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Abstract

Activity coefficient ratios for UO$_2$F$_2$ were measured at 50° C by ultracentrifugation to equilibrium. The method was checked with CaI$_2$. The results for UO$_2$F$_2$ confirm the hypothesis of a monomer-dimer equilibrium which was used previously to interpret the freezing point depressions of UO$_2$F$_2$ solutions.

The dimerization constant at 50° C was found to be somewhat greater than at the freezing point. The proportionality constants for the dependence of the logarithm of the activity coefficients on molality were found to be essentially temperature independent. The heat and entropy of dimerization were estimated.

Experiments in the presence of an indifferent electrolyte (NaClO$_4$) support the assumption that dissociation into ions is slight. In potassium fluoride solutions, uranyl fluoride dimerizes more extensively than in water solutions.

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Activity coefficients of $\text{UO}_2\text{F}_2$, calculated from freezing point depressions of aqueous solutions, indicated that at concentrations above 0.1 molar ($m$), the solute exists primarily as an equilibrium mixture of monomer and dimer. It seemed of interest to confirm these results at higher temperatures and to obtain estimates of the temperature coefficients of the equilibrium constant for the dimerization reaction and of the activity coefficients of the monomer and dimer.

The activity coefficients of $\text{UO}_2\text{F}_2$ in water and in the presence of supporting electrolytes were measured by ultracentrifugation to equilibrium. This method has been used for inorganic salts by Pedersen and Drucker. In it, the concentration distribution of the solute is measured as a function of the radius of rotation ($\alpha$) at sedimentation equilibrium. The ratios of activity coefficients for different concentrations of the solute at different positions $\alpha$ and $\beta$ in the cell can be calculated from the equation

$$\ln \left( \frac{y_\beta}{y_\alpha} \right) = \frac{N (1 - \bar{v} \rho) \omega^2}{2 H} \left[ \frac{\phi^2_\beta}{\phi^2_\alpha} - 1 \right] - \ln \left( \frac{c_\beta}{c_\alpha} \right)$$

(1)

where $\bar{y}$ is the activity coefficient (molarity scale), $N$ is the molecular weight of the solute, $\bar{v}$ its partial specific volume, $\rho$ the density of the solution, $\omega$ the angular velocity of the centrifuge ($2\pi$ times the number of revolutions per second), $H$ the gas constant, $T$ the absolute temperature, and $c$ the molarity. The subscripts $\alpha$ and $\beta$.

If mean ionic activity coefficients, $y_*$, of a solute dissociated into ions are measured, the mean molecular weight $M/\Phi$ (where $\Phi$ is the number of moles of ions per mole of solute) appears in Equation (1) instead of $N$. 

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refer to different radii of rotation. From a knowledge of the activity coefficient at one
concentration and the ratios determined by Equation 1, one can calculate values of \( \gamma \) at
other concentrations.

In this work, the concentration interval from 0.15 \( H \) to saturated was studied for
uranyl fluoride-water solutions. In addition, a few centrifugation equilibrium experiments
of \( \text{UO}_2\text{F}_2 \) in \( \text{NaClO}_4 \) and HF solutions were carried out. In order to assess the precision
of this method, some experiments were also carried out with cadmium iodide, and the
observed activity coefficients compared with those obtained by other methods.

**EXPERIMENTAL**

The solutions were centrifuged in a Specialized Instrument Corporation ("Spinco")
Model Z Ultracentrifuge operated at speeds around 30,000 rpm. Average speeds (over

(6)


several hours) can be determined in this machine with a counter. These were constant to
better than \( \pm 20 \) rpm during an experiment.

The solutions were contained in cells with quartz windows which are standard with this
equipment. To avoid corrosion, the centerpieces were made of Kel-F plastic. With dilute
solutions, cells with 12 mm thickness (\( b \)) of solution in the direction of observation (perp-
endicular to plane of rotation) were used, and with the more concentrated solutions 3 mm
cells. The midpoint of the cells was 65 mm from the center of rotation.

The machine is equipped with a Philpot-Svensson optical system, which gives a

(7)


(photographic) plot of a distance (\( z \)) proportional to the gradient of the refractive
index (\( n \)) as a function of radius of rotation, \( x \), or \( dx/dx \). This distance (\( z \)) is the
displacement of the shadow of an inclined bar by the refractive index gradients in the
cell. The base line from which this displacement is measured is obtained in a "background"
equilibrium experiment, identical except for absence of the pertinent solute from the
solution in the cell.

The optical constants for the centrifuge are as follows: radial magnification of the cell at the photographic plate 2.04, magnification (ϕ) from the bar position by the cylindrical lens 4.47, and optical distance from the upper collimating lens to the bar (optical lever arm, L) 56.1 cm. Bar settings (θ) of 43° - 65° (angles complementary to the inclination of the bar to the axis of the cylindrical lens) were used. The optical constants allow conversion of $\frac{da}{dx}$ to $\frac{\Delta a}{\Delta x}$ by the equation:

$$\frac{da}{dx} = \frac{L \tan \theta}{\phi \cdot h}$$  \hspace{1cm} (2)

Refractive index measurements on UO$_3$F$_2$ solutions were carried out with an Abbé Refractometer.

The photographic plates on which the results are recorded were examined with a Geissler toolmaker's microscope or an equivalent comparator, both of which permitted measurements of distances to ±0.002 mm in directions perpendicular to each other. This is considerably better than the accuracy warranted considering the definition of the bar shadows in photographs.

The temperature of the solutions during equilibration could not accurately be controlled in this instrument. Measurements after the experiments indicated that equilibrium temperatures were $30 \pm 3^\circ$ C.

The time necessary to attain equilibrium varied from about three days for the more dilute solutions to approximately ten days for a saturated solution of urenyl fluoride. Equilibrium was considered attained when three photographs taken at least four hours apart indicated no significant change in the bar shadow displacement $Z$.

For the computations according to Equation 1, the densities of UO$_3$F$_2$ water solutions measured by Marshall, Gill and Secoy were used. The partial specific

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volume $\bar{y}$ of UO$_3$F$_2$ was calculated from these data and found to be 0.125 over almost
the whole concentration range, and this value was used throughout. Errors introduced by deviations from this value are probably small since \((1 - \frac{r}{\rho})\) is between \(0.75\) and \(0.88\).

The same uranyl fluoride preparations were used in these experiments as in the previous freezing point measurements. One was prepared by Harshaw and the other by the Chemistry Department of the Electromagnetic Plant at Y-12.

For the cadmium iodide experiments, Kiser and Amsud C. F. Cdl\(_2\) was used which, by titration, gave within \(0.1\%\) the theoretical percentage of iodine.

RESULTS AND DISCUSSION

(1) Cdl\(_2\) in Water. Cadmium iodide solutions with initial concentrations .3504 M and .5254 M were centrifuged to equilibrium at 35,500 rpm in 3 and 12 mm cells respectively. Temperatures at equilibrium were \(27.5 \pm .5^\circ\) C for both solutions. From the displacements of the bar shadow \(a\) (see Experimental Section), and the optical constants, the refractive index gradients \(dn/dx\) were obtained through Equation 2. Combining these values with the refractive index measurements of Getman and Gilroy, which indicated that \(a\) is a linear function of \(c\), the concentration gradient \(dc/dx\) was calculated as a function of \(x\), the distance from the center of rotation. From the concentration gradient \(dc/dx\), a concentration \(c\ vs. x\) diagram was constructed by normalizing to the known total quantity of solute in the cell, taking its wedge shape into consideration.

Combining these data with the density data of Gibson (from which \(\bar{v} = 0.182\))

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\(\bar{v} = 0.182\) was obtained ratios of the mean activity coefficients \(y_+\) (molarity scale) were calculated. As mentioned in Footnote 5, this involves the use of the mean molecular weight \(\bar{\nu}\), where \(\nu\) is the number of ions per mole of solute, was taken to be 3.

To permit ready comparison of these activity coefficients with the data in the literature,
the assignment \( \gamma^a = 0.0470 \) at \( c = 0.3529 \) was made for both solutions. This value was obtained from the data of Bates by converting his values of \( \gamma^a \) to \( \gamma^a \) and by interpo-

\[ \gamma^a = 0.0470 \text{ at } c = 0.3529 \]

(11)


The agreement between the activity coefficients calculated from the centrifuge data and those of Bates is satisfactory throughout the concentration range studied. At the highest concentration, the centrifuge data appear to be 1.1% lower than those of Bates, which appears to be within the experimental error of the method.

(2) UO$_2$F$_2$ in Water. A series of ultracentrifugal equilibrium experiments was carried out at 27,700 rpm on solutions of initial concentrations 0.254, 0.755, 1.57, 2.97 M and on saturated UO$_2$F$_2$. The solutions were in 5 mm cells except the most dilute one which was in a 12 mm cell. The series was selected in such a way that the concentration ranges of the various solutions at equilibrium overlapped with only moderate changes in concentration for each experiment. As in Section (1), a concentration vs. \( x \) diagram was constructed by normalizing to the known total quantity of solute in the cell. In the case of the saturated solution, the normalization was achieved by assuming that the uranyl fluoride was saturated (5.17 M) at the maximum value of \( x \).

Ratios of the activity coefficients were calculated for the concentration range 0.15 - 4.5 M by use of Equation 1 and setting \( \psi = 1 \), since this was the value used in the earlier freezing point measurements. From these ratios a set of activity coefficients \( \gamma^a \) (molarity scale) and \( \gamma^s \) (molality scale) was calculated where the asterisk indicates that the reference value is not \( y = y = 1 \) at infinite dilution. To make ready comparison with the activity coefficients \( \gamma^a \) determined from the freezing point depressions, the assignment \( c \gamma^s = \gamma^f_1 \) at \( c = 0.15 \) was made where \( \gamma^s = 0.890 \). The calculated activity coefficients, together with those obtained earlier from the freezing point measurements, are given in Table 1.
The precision of the measurements is somewhat difficult to estimate. The error in the measurements is probably greater than in the measurements with cadmium iodide, particularly at high concentrations of uranyl fluoride where the densities of the solutions become very high (larger than 2). Under these conditions, the cells are subjected to greater pressures which will cause deviations in the refractive index gradients of the water over those observed in the absence of solute and may also cause greater distortion of the quartz windows.

As can be seen from Table 1, the activity coefficients $\gamma^a$ of UO$_2$F$_2$ decrease from approximately 0.9 to 0.4 in the concentration range $15 < x < 5$. At the freezing point a similar, though smaller, decrease of $\gamma^a$ occurred, followed by a small rise at concentrations larger than $x = 2.5$. Although this rise is less pronounced in the activity coefficients at 50°C, it appears that the interpretation used for the explanation of the activity coefficients at the freezing point is applicable at the higher temperatures as well.

It was previously assumed that dissociation of UO$_2$F$_2$ into ions is small in the concentration range studied and that the downward trend of $\gamma^a$ is primarily due to dimerization of UO$_2$F$_2$ according to the equation:

$$Z = E - 7$$
The equilibrium constant for this reaction is

\[ K = \frac{a^2}{b^2} = \frac{\beta_1}{\beta_2 \gamma_1^2} \]

where \( a, b \) and \( \gamma \) are the activity, molality and activity coefficients and subscripts 1 and 2 refer to the monomer and dimer, respectively. It was assumed that the activity coefficients of the monomer and dimer follow the equations

\[
\begin{align*}
\log \gamma_1 &= b_1 \bar{m} \\
\log \gamma_2 &= b_2 \bar{m} \\
\text{and } 2 b_1 &= b_2
\end{align*}
\]

where \( b_1 \) and \( b_2 \) are constants and \( \bar{m} \) the molality of \( \text{UO}_2\text{F}_2^+ \). From these assumptions it was shown that the equation

\[
\log a^2 - \log \left( \frac{\delta}{K} \right) = b_1 \bar{m} - \log \beta
\]

should hold where \( a^2 = \gamma_2 \) and \( \beta a^2 = \gamma_1 \). Equation 6 should permit evaluation of \( K \) by a method of trial and error since for the proper choice of \( K \) the left side of Equation 6 plotted against \( \bar{m} \) should give a straight line with slope \( b_1 \).

The activity coefficients of \( 30^\circ \text{C} \) yielded best linearity for \( K \approx 4 \) and \( b_1 \approx 0.055 \). As shown in Figure 2, satisfactory agreement between the observed activity coefficients and those calculated according to the monomer-dimer hypothesis is obtained for \( K = 4 \) or 4.5 with \( b_1 = 0.055 \) and 0.056, respectively. The best values for the constants thus appear to be \( K = 4.25 \) and \( b_1 = 0.055 \). The agreement between theoretical and observed values is considerably closer than is warranted by the absolute precision of the data.

(3) Re-evaluation of Dimerization Constant at the Freezing Point -- Heat and Entropy of Dimerization. It appears of interest to estimate the heat and entropy of dimerization from the values of the constants at the freezing point and at \( 30^\circ \text{C} \) using the familiar equation

\[
\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}
\]
In order to do this satisfactorily, however, a re-evaluation of the freezing point data is necessary since they were applied at the freezing points which varied from 0 to -10° C. In the earlier interpretation, changes of $K$ with temperature had been ignored as well as possible changes of $b_1$ and $b_2$ and the values $K = 1.5$ and $b_1 = .070$ reported earlier at best would apply at the average temperature of the range.

From Equation 7 and the preliminary values of the constants, the heat of dimerisation was estimated and from it the change in $K$ in the freezing point range. Assuming in addition that $b_1$ is a linear function of the temperature, the freezing point data were fitted by successive approximations. The values $\Delta H = 5600 \text{ cal}, \frac{\Delta H}{\Delta T} = 2.6 \times 10^{-5}$ yield satisfactory fit of the data as shown in Figure 2. With these values, $K$ varies from 1.5 at -0.18° C to 1.07 at -9.5° C which may be compared with the earlier reported average value of 1.5. The constant $b_1$ is now found to be .056 and essentially independent of temperature, instead of the earlier reported value of .070.

With $K = 1.25$ at 30° C and $\Delta H = 5600 \text{ cal.}$, the entropy of dimerisation (Equation 3) is found to be 21 e. u.

(4) $\text{UO}_2\text{F}_2$ in $\text{NaClO}_4$ Solutions. Two ultracentrifugations to equilibrium were carried out with uranyl fluoride (initial concentration 0.153 M and 0.526 M) in 1 N $\text{NaClO}_4$ to test the assumption that uranyl fluoride is negligibly ionised at these concentrations. If dissociation into ions were pronounced, one would expect the activity coefficients of $\text{UO}_2\text{F}_2$ to vary differently with concentration for the $\text{UO}_2\text{F}_2$ - water and $\text{UO}_2\text{F}_2$ - supporting electrolyte systems. The results are shown in Figure 2 (dotted curves) with $\gamma^a$ in the $\text{NaClO}_4$ system matched at one concentration with $\gamma^a$ in the water system. Around .15 M $\text{UO}_2\text{F}_2$ the ratios of the activity coefficients are very close for the two systems, thus supporting the assumption of low ionisation. For the 0.5 N experiment, the ratios indicate a somewhat slower change of $\gamma^a$ with concentration for the $\text{NaClO}_4$ system than for the water system. In this case, however, the uranyl fluoride concentration across the cell at equilibrium varies from 0.3 to 0.8 N and is thus comparable with the sodium perchlorate concentration. It may, therefore, have modified the activity coefficients.
of the NaClO₄ in such a way that the background did not represent its distribution well.

(5) UO₃F₂ in KF Solutions. In order to determine the effect of the addition of a strong complexing ion on the degree of polymerization of uranyl fluoride, two ultracentrifugations to equilibrium were carried out in potassium fluoride solutions (0.04 M UO₃F₂ in .75 M KF and 0.2 M UO₃F₂ in 1 M KF). In these systems, in contrast to the studies of the UO₃F₂ - water and UO₃F₂ - perchlorate systems, the activity coefficients of UO₃F₂ were essentially constant throughout the cell.

It was shown by Pederson that if the activity coefficients of the substance under study are practically constant for the concentrations covered in an experiment, then

\[
\frac{\xi_3}{\xi_2} = \frac{(Z/2)\rho_2}{(Z/2)\rho_1}
\]

Thus by Equation 1, a plot of \(\log (Z/2)\rho_2\) vs. \(\xi_2\) should give a straight line, the slope of which multiplied by \(\frac{2 N}{(Z/2)(2.303)}\) gives the (apparent) molecular weight of the solute.

As shown in Figure 3, this plot indeed gives a straight line, indicating that the activity coefficients are essentially constant. The apparent molecular weights obtained are 612 and 578 for the 0.04 M UO₃F₂ and 0.2 M UO₃F₂ experiments respectively if \(\xi_2 = 0.15\) is assumed. The (theoretical) molecular weight of 300F₂ is 308.1. It thus appears that uranyl fluoride exists predominantly as a dimeric species in KF solutions at UO₃F₂ concentrations at which it would be only slightly dimerized in water alone. Since this dimer in KF solutions must contain more than four fluoride ions and hence carry a charge, the observed (apparent) molecular weights must be less than the actual molecular weights. These lower values stem from the incomplete suppression of the charge effect by the supporting electrolyte \(\text{(12)}\).

An estimate of the magnitude of this effect indicates that

\[\text{(12)}\]


the observed apparent molecular weights are consistent with the assumption of a dimer of
low negative charge, although the data are not sufficiently accurate to establish the magnitude of this charge conclusively.

(6) General Discussion. If one uses the crystallographic data on solid uranyl fluoride as a guide, one may postulate that the dimer of uranyl fluoride is held together by one or two fluoride bridges since the solid consists of a layer structure in which the uranyl groups are held together by fluoride ions. Using a section of such a layer, the proposed structure of the dimer of uranyl fluoride can be described by Figure 1. In this figure, the uranyl groups would stand perpendicular to the plane of the paper with one of the oxygens above and one below the plane of the paper. One of the fluoride ions of the bridge would probably also be above and one below the plane of the paper. Since the uranyl groups in the solid have a coordination number of 6, one might preserve this in the dimer by placing the remaining 2 fluoride ions and 6 water molecules in the remaining coordination positions.

One might attempt to explain the large positive entropy change of dimerisation (c. 10.5 e. u. per mole of uranium dimerizing) by considering the oriented water molecules which surround the uranyl group and the fluoride ions of the monomer. On dimerization some of these water molecules of hydration in the space between two monomers are removed, lose their orientation and give rise to a positive entropy change. This change in the entropy of hydration apparently is considerably larger than the negative entropy change which one might expect on producing a dimeric molecule from two monomeric species.

The increased stability of the dimer on addition of excess fluoride ions at first glance is very surprising since one might have expected that addition of fluoride ions would cause dissociation. Since increased association was observed, one may conclude that the uranyl group is not a sufficiently strong complexing agent with respect...
to fluoride ions to form $\text{UO}_2F_6^{4-}$ and that the repulsion between fluoride ions must be less than the added attraction gained by having the fluoride ions in the field of both uranium (VI) ions.
FIGURE I  ACTIVITY COEFFICIENTS OF CdI₂

- BATES
+ CENTRIFUGE, C₀ = 0.3504 M
□ CENTRIFUGE, C₀ = 0.5234 M
ACTIVITY COEFFICIENT $\gamma^*$

MOLALITY $\text{UO}_2\text{F}_2$

$K = 1.53$ to $1.07$
$b_1 = 0.056$

$K = 4.5$
$b_1 = 0.056$

$K = 3.5$
$b_1 = 0.054$

$K = 4$
$b_1 = 0.055$

$K = 5$
$b_1 = 0.056$
FIGURE 2  ACTIVITY COEFFICIENTS OF UO$_2$F$_2$

- FREEZING POINT DATA
- ULTRACENTRIFUGATION, UO$_2$F$_2$ - H$_2$O SYSTEM, 30°C
- ULTRACENTRIFUGATION, UO$_2$F$_2$ - NaClO$_4$ SYSTEM, 30°C
- CALCULATED CURVES

\[ \gamma = K^{-b} \]

<table>
<thead>
<tr>
<th>K</th>
<th>b$_1$</th>
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<tbody>
<tr>
<td>4.5</td>
<td>0.056</td>
</tr>
<tr>
<td>3.5</td>
<td>0.054</td>
</tr>
<tr>
<td>4</td>
<td>0.055</td>
</tr>
<tr>
<td>5</td>
<td>0.056</td>
</tr>
</tbody>
</table>

\[ K = 1.53 \text{ TO } 1.07 \]

\[ b_1 = 0.056 \]
A = 0.15 M $\text{UO}_2\text{F}_2$, 1 M KF
B = 0.04 M $\text{UO}_2\text{F}_2$, 0.7 M KF

FIGURE 3 EQUILIBRIUM DISTRIBUTION IN A CENTRIFUGAL FIELD
($\text{UO}_2\text{F}_2$ - KF SYSTEM)
FIGURE 4
SUGGESTED STRUCTURE
OF \{\text{UO}_2\text{F}_2\}_2
(BASED ON URANYL FLUORIDE STRUCTURE OF ZACHARIASEN)

- URANYL GROUPS, OXYGEN PERPENDICULAR TO PLANE
  OF PAPER (\pm 1.91 \text{ Å})
- FLUORIDE IONS
  (+) AND (−) INDICATE POSITIONS ABOVE AND BELOW
  PLANE OF PAPER (\pm 2.61 \text{ Å})
- WATER MOLECULES OF HYDRATION
- A, DISTANCE BETWEEN URANYL GROUPS (\approx 4.20 \text{ Å})