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PHYSICAL PROPERTIES OF URANIUM PROCESS SOLUTIONS

by

Robert S. Ondrejcin

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Approved by
H. M. Kelley, Research Manager
Analytical Chemistry Division

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ABSTRACT

Integral diffusion coefficients, viscosities, densities, and surface tensions were measured for the aqueous uranyl nitrate - nitric acid - aluminum nitrate system. The variation of the uranium diffusion coefficient was determined as a function of uranium concentration, nitric acid concentration, and temperature.

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PHYSICAL PROPERTIES OF URANIUM PROCESS SOLUTIONS

INTRODUCTION

The process of solvent extraction of uranium from an aqueous phase involves a diffusion mechanism. Data on the diffusion coefficients of uranium salts are limited in number and the concentrations reported^(1,2,3) are frequently lower than those of interest in the separations processes. For a given set of conditions, the diffusion coefficients quoted in the literature vary by as much as a factor of two. Since a rational interpretation of mass transfer in turbine contactors was desired, a more precise set of values had to be obtained over the concentration range of interest.

The work described here covers the measurement of diffusion coefficients of uranyl nitrate, nitric acid, and aluminum nitrate in the concentration range normally encountered in the separations processes for natural and enriched uranium. Measurements were made by means of a porous diaphragm cell with magnetic stirring^(4,5).

The variation of diffusion (D) as a function of solution viscosity is expressed in the Stokes-Einstein relationship and has been treated by others⁽⁶⁾; therefore, measurements of viscosity (μ) were made on all solutions prior to diffusion. Measurements of density (ρ) and surface tension were also made because the data would be useful in designing extraction equipment. With the available information the Schmidt group ($\mu/\rho D$) can be determined for use in calculations of fluid flow and mass transfer where the diffusion coefficient is seldom used alone.

SUMMARY

Measurements of the integral diffusion coefficients, viscosities, densities, and surface tensions were made on solutions of uranyl nitrate, nitric acid, and aluminum nitrate. The range of concentrations included those normally found in the separations processes for irradiated natural and enriched uranium.

Graphs are presented showing variations in the diffusion coefficient of uranium nitrate with changes in temperature and nitric acid concentration.

DISCUSSION

The diffusion coefficients that are published for uranium salts are based on two different types of measurements. The first type is the measurement of the self-diffusion or differential diffusion coefficient, normally based on the capillary tube technique first developed by Anderson and Saddington⁽⁷⁾. In this method radioisotopes are used and the diffusion of an isotope, in this case uranium^(1,2), is measured in the absence of a concentration gradient. The second type of measurement involves a concentration gradient. The value obtained is an average for the concentration studied and is known as the integral diffusion coefficient. The change in concentration is normally measured by light refraction or interference⁽⁸⁾, conductance, or chemical means after diffusion through a diaphragm⁽³⁾. The diaphragm cell is a closed glass tube separated into two compartments by a sintered glass frit. Diffusion occurs through the frit from a solution of high concentration to a solution of lower concentration. Most often the salts are diffused into some initially pure solvent.

The average length of the diffusion path is determined by the average pore size, the thickness of the frit, and the laminar layer formed on either side of the frit. Physical measurement of this path length is not practical; therefore, the cell is calibrated with a standard of known diffusion coefficient.

Much of the early work is unreliable because of the problem of providing adequate agitation in the cell. Early measurements were based on density stirring. The solution with the highest density was placed in the upper compartment and allowed to diffuse downward. Bulk streaming occurred if the frit had a few large pores, and the thickness of the laminar layer varied depending on the viscosities of the liquids in the compartments. In another method of stirring, solid bodies were used⁽⁹⁾ that sank as the cell was rotated. Several papers have appeared in which magnetic stirring was used^(10,11,12). With this system, one magnetized bar rests on the frit in the top compartment and another floats against the bottom of the frit in the bottom compartment. The bars are moved by a rotating magnetic field. This method eliminates the formation of laminar layers.

Diffusion coefficients of electrolytes in simple systems usually agree well with theory at concentrations below 0.01M⁽¹³⁾, but often depart radically at higher concentrations. In theoretical calculations the diffusion coefficient is a function of such quantities as transference numbers, conductivity, electrophoretic contributions, and concentration⁽¹⁴⁾. Consequently, integral diffusion coefficients must be measured at concentrations above 0.01M or when more than two components are present.

APPARATUS

A typical cell is shown in Figure 1. The cell compartments were made of "Pyrex" glass of 28-mm OD. The compartments were approximately 50 ml in volume and were separated by a frit 25 mm in diameter with a 4-5.5 micron nominal maximum pore size. The upper and lower compartments were closed with a 10/30 F stopper and a "Teflon" stopcock, respectively. The stirrers were "Teflon"-coated magnetic stirring bars attached to glass shafts by means of special "Teflon" collars. This arrangement prevented the stirrers from rubbing against the frit, as often occurs in this type of design^(10,11,12).

FIG. 1 DIFFUSION CELL

The solution was stirred by DC magnetization and demagnetization of four successive pairs of coils, which produced a rotating magnetic field. The field could be varied from 40 to 200 rpm by controlling the speed of the switching motor. The coils were mounted on a metal ring and were large enough to operate both the upper and lower stirrers. Each set of coils was encapsulated in "Kold-Weld"* resin, so that the coils could be immersed in a water bath regulated at 25, 40 and 55°C to $\pm 0.05^\circ\text{C}$.

Viscosities were measured at these temperatures with a series of Cannon-Fenske viscometers according to ASTM method D445-53T. A Christian Becker specific gravity balance, Model SG-1 and a Cenco-Du Noüy tensiometer with a 6-cm platinum ring were used to measure specific gravity and surface tension, respectively, in a special cell through which water from the water bath was circulated at the specified temperatures.

PROCEDURES

Prior to the preparation of multicomponent solutions, a solution of each component was standardized. Uranium solutions were prepared from uranyl nitrate and analyzed by titration against a standardized ceric solution. Nitric acid was analyzed by acid-base titration and the aluminum nitrate solution was analyzed by precipitation with 8-hydroxyquinoline. The analyzed solutions were then quantitatively combined and diluted to produce the desired final solutions.

After each diffusion experiment, uranium was analyzed by the same method that was used prior to diffusion. The total acidity of the samples containing uranium or aluminum was determined potentiometrically. Potassium fluoride was used as a complexing agent for uranium and aluminum in these samples. Aluminum was determined as previously described after it was separated from uranium by ion exchange⁽¹⁵⁾.

Before the diffusion cell was filled, all solutions were degassed and brought to the temperature of the water bath. Dissolved gases can form bubbles in the frit and partially block the pores during diffusion. Expansion or contraction of the solutions in the diffusion cell would cause bulk streaming through the frit.

The lower compartment was initially filled by partially evacuating the entire cell, opening the stopcock, and drawing in solution until the frit was filled. Some solution was allowed to enter the upper compartment to drive any entrapped gases from the pores of the frit. Excess solution on the frit was removed with a small polyethylene tube under vacuum. The upper compartment was then filled with a quantity of pure solvent equal to the volume of the lower compartment.

* Product of Precision Dental Mfg. Co.

After the filled cell was immersed in the water, a concentration gradient was allowed to develop in the frit⁽³⁾. This required about four hours. The cell was then removed, the solution in the upper compartment was emptied with a polyethylene tube under vacuum, and the compartment was rinsed and filled with new solvent. The solution in the lower compartment was withdrawn in the same manner and replaced with new standard solution. During these operations it was necessary to exercise care to prevent disturbing the concentration gradient in the frit. This procedure reduced uncertainties in the initial concentrations in the lower compartment and allowed a determination of the exact starting time.

An initial run was made to determine the length of time required for 20-25% of the solute molecules to diffuse. The runs used for measurement were then made, and the solute concentration was measured only at the end of the run. A diffusion run normally lasted from 72-240 hours.

RESULTS

INTEGRAL DIFFUSION COEFFICIENTS AND CELL CONSTANTS

The integral diffusion coefficient can be expressed by Equation (1)^(3,16).

$$\bar{D} = \frac{1}{\beta t} \ln \frac{\Delta c_t}{\Delta c_o} \quad (1)$$

where

Δc_o = concentration difference between compartments
at time 0

Δc_t = concentration difference between compartments
at time t

$\bar{D}$ = integral diffusion coefficient

t = time

β = a diffusion cell constant

In diffusion measurements all solutions must be analyzed accurately because small errors in concentration produce a large change in the value of $\ln \frac{\Delta c_t}{\Delta c_o}$. The limiting factor in the value of $\bar{D}$ is the accuracy of the determination of solute concentrations.

The value of $\bar{D}$ is well known for potassium chloride at 25°C when 25% of a 0.200M solution diffuses⁽¹²⁾. The diffusion cells were calibrated with this standard. The KCl solutions were analyzed by titration with standardized silver nitrate and dichlorofluorescein indicator.

It has been reported^(3,10) that the cell constant will vary with stirring speed until laminar layer formation is destroyed on both sides of the frit. Observations showed that the value of $\bar{D}$ for potassium chloride appeared to vary until a stirring speed of 70-90 rpm was reached. Variations in the speed necessary to reach a constant $\bar{D}$ were probably dependent upon slight variations in the surfaces of the frits. From the minimum stirring speed required for a constant $\bar{D}$ value to 150 rpm, there was no variation in the value of $\bar{D}$. Diffusions were made with stirrer speeds of 125-130 rpm.

Table I shows typical results from calibrations of cells with 0.200M potassium chloride.

TABLE I
Calibration of Diffusion Cells

Cell No.	B, Cell Constant, -cm^{-2}		
	Run I	Run II	Avg.
1	0.0395	0.0399	0.0397
2	0.0762	0.0758	0.0760
3	0.0640	0.0626	0.0633
4	0.0511	0.0506	0.0508

The diffusion coefficients quoted in Table II are for the multiple component systems and not for single components in a solvent unless specified as such.

The average coefficient of variation of uranium diffusion coefficients is 4.8%. The value of n varied from 2 to 4.

TABLE II
Integral Diffusion Coefficients and Viscosities

Uranyl Nitrate, M	Nitric Acid, M	Aluminum Nitrate, M	Temp., °C	Viscosity, millipoises	Diffusion Coefficient, cm^2/sec		
					Uranyl Nitrate	Nitric Acid	Aluminum Nitrate
0.0200	-	-	25.0	9.15	7.8×10^{-6}	-	-
0.200	-	-	25.0	10.1	8.3×10^{-6}	-	-
2.00	-	-	25.0	30.5	8.4×10^{-6}	-	-
0.200	0.100	-	25.0	10.2	6.1×10^{-6}	9.5×10^{-5}	-
0.200	1.00	-	25.0	10.3	4.6×10^{-6}	4.0×10^{-5}	-
0.200	3.00	-	25.0	11.3	4.4×10^{-6}	3.8×10^{-5}	-
0.200	-	0.500	25.0	14.6	9.6×10^{-6}	-	9.2×10^{-6}
0.200	-	1.00	25.0	22.2	10.2×10^{-6}	-	9.4×10^{-6}
0.200	1.00	0.500	25.0	15.0	8.9×10^{-6}	7.8×10^{-5}	4.8×10^{-6}
0.200	1.00	1.00	25.0	23.6	11.6×10^{-6}	9.9×10^{-5}	7.0×10^{-6}
0.200	3.00	0.500	25.0	16.7	8.9×10^{-6}	4.5×10^{-5}	4.4×10^{-6}
0.200	3.00	1.00	25.0	26.4	9.9×10^{-6}	5.2×10^{-5}	5.3×10^{-6}
0.0200	-	-	40.0	6.78	13.0×10^{-6}	-	-
0.200	-	-	40.0	7.43	13.6×10^{-6}	-	-
0.0200	-	-	55.0	5.21	13.8×10^{-6}	-	-
0.200	-	-	55.0	5.76	14.8×10^{-6}	-	-

The diffusion coefficients of uranium nitrate in the absence of aluminum nitrate decreased with increased nitric acid concentration, which indicates complex ion formation. Aluminum nitrate increased the diffusion coefficient of uranium in the absence of nitric acid. In the concentration ranges studied, the aluminum nitrate taken alone was more effective in increasing the diffusion coefficient of uranium than the nitric acid was in decreasing the diffusion coefficient of uranium. With the introduction of aluminum nitrate or nitric acid to the diffusion solutions, the diffusion coefficients did not continue to follow the original trends consistently.

Figure 2 shows the increase in diffusion coefficient at 0.0200 and 0.200M uranium nitrate with temperature. The relationship of the diffusion coefficient of 0.2M uranium nitrate and the concentration of nitric acid from 0.001 to 3M is shown in Figure 3. The small increases of the integral diffusion coefficient at 25°C with increasing uranium nitrate concentration over a range of 0.02 to 2M are shown in Table II.

FIG. 2 DIFFUSION COEFFICIENT OF URANYL NITRATE IN WATER VS. TEMPERATURE

FIG. 3 DIFFUSION COEFFICIENT OF 0.200M URANYL NITRATE VS. NITRIC ACID CONCENTRATION AT 25°C

VISCOSITIES, DENSITIES, AND SURFACE TENSIONS

The problem of correlation of diffusion coefficients with viscosities can be approached in two different manners. The classical method uses the Stokes-Einstein relationship, which assumes that the medium is continuous and the diffusing molecule is large. In an alternative approach that depends on the absolute reaction rate theory, diffusion and viscous flow are considered to be very similar. The assumption is made that the diffusing molecules and the medium have approximately the same dimensions. Theoretical treatment of these methods of approach is available in the literature⁽¹⁴⁾.

Table III shows the values of the density and surface tension for the solutions of uranyl nitrate, nitric acid, and aluminum nitrate.

TABLE III

Density and Surface Tension

<u>Uranyl Nitrate, M</u>	<u>Nitric Acid, M</u>	<u>Aluminum Nitrate, M</u>	<u>Temp., °C</u>	<u>Density, g/ml</u>	<u>Surface Tension, dynes/cm</u>
0.0200	-	-	25.0	1.004	73
0.200	-	-	25.0	1.062	73
2.00	-	-	25.0	1.641	77
0.200	0.100	-	25.0	1.067	70
0.200	1.00	-	25.0	1.096	70
0.200	3.00	-	25.0	1.162	70
0.200	-	0.500	25.0	1.143	75
0.200	-	1.00	25.0	1.218	74
0.200	1.00	0.500	25.0	1.175	45
0.200	1.00	1.00	25.0	1.254	45
0.200	3.00	0.500	25.0	1.238	48
0.200	3.00	1.00	25.0	1.313	49
0.0200	-	-	40.0	1.000	70
0.200	-	-	40.0	1.056	64
0.0200	-	-	55.0	0.993	67
0.200	-	-	55.0	1.051	60

These values will be useful for determining the dimensionless Schmidt number and the Reynolds number⁽¹⁷⁾. The Schmidt number is often used in calculations involving turbulent flow and the Reynolds number is used in approximations of fluid flow.

R. S. Ondrejcin

R. S. Ondrejcin
Analytical Chemistry Division

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