THE UNIVERSITY OF MANITOBA

THE EXTRACTION OF URANYL NITRATE FROM AQUEOUS NITRATE SOLUTIONS BY OPEN-CELL POLYURETHANE FOAM SPONGE

BY

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TO

MY DEAR FATHER

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Abstract

The extraction of uranyl nitrate into open cell polyurethane foam sponge from aqueous solution, in the presence of salting out agents, has been examined. The extraction efficiency was observed to depend on the concentrations of uranyl and nitrate ions. Charge of the cations was also observed to influence the distribution ratio. The effect of the change in temperature and pH was also studied. The diffusion of uranyl nitrate and ammonium nitrate through the polyurethane membrane was observed to be a very slow process.

INTRODUCTION

Uranium(1)

The element uranium is ubiquitously distributed in nature. It was discovered by Klaproth in 1789. In 1841 E. Péligot succeeded in preparing the metal by the reduction of UCl_4 with potassium.

The mean content of uranium in the earth's crust is estimated to be 4×10^{-6} g per gram. Significant amounts have been reported in phoshate deposits in Russia, Algeria and Morocco. It is likely that all phosphate formations of marine origin contain uranium. In Florida, for example, only phosphate rock of marine origin (land pebble type) contains significant amounts of uranium. Its concentration in the ocean is 0.36×10^{-6} to 2.3×10^{-6} g per litre.

Uranium is a dense lustrous metal, which in appearance resembles iron. Even a polished surface of uranium tarnishes rapidly in air. Finely divided uranium reacts, even at room temperatures, with all components of the atmosphere except the noble gases. At elevated temperatures uranium reacts with most common refractories and metals.

The melting point of the metal has been accepted as 1133°C and boiling point obtained by extrapolation of vapour data is estimated to be 3818° C.

Electrical conductivity of uranium is about one-half that of iron and improves with purity. At slightly

above $1^{o}K$ uranium of high purity becomes super-conductive.

It exists in four oxidation states: +3, +4, +5 and +6, of which +4 and +6 are stable enough to be of practical importance. The alteration of +4 and +6 oxidation states of uranium is of importance in its metallurgy.

The general chemical character of uranium is that of a strong reducing agent, particularly in aqueous systems. Uranium forms non-stoichiometric compounds with oxygen. All of its oxides dissolve in HNO_3 to give UO_2^{2+} salts. Fusion of uranium oxides with alkali or alkaline earth carbonates gives rise to uranates,(2) generally of stoichiometry $M_2^{I}\ U_x\ O_{3x+2}$.

Uranium reacts readily with all the non-metallic elements to form semimetallic compounds (often non-stoichiometric). Some of them, for example, the silicides are chemically inert and the sulphides,(3) notably US, can be used as refractories.

All the uranium halides form halogeno complexes with metal halides (most commonly with alkali-metal halides), those with fluoride and chloride being the best known.

Aqueous solutions of uranium salts have an acid reaction due to hydrolysis which increases in the order $U^{3+} < UO_2^{2+} < U^{4+}$(4). The uranium (V) ion, UO_2^{+}, is extraordinary unstable towards disproportionation and has a transitory existence under most conditions.

Complex ions of uranium are formed with citrate

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and anions of other organic acids, thiocyanate and phosphates. The phosphates are important in view of the occurence of uranium in phosphate minerals.

The only common uranium salts are the uranyl salts. The most important one is nitrate which crystallizes with six, three or two molecules of water depending upon whether it is obtained from dilute, concentrated or fuming nitric acid.

The toxicity of uranium is in the order of that displayed by other heavy metals. Whether uranium bearing mineral is inhaled, ingested or injected, its ultimate destination is the kidney cortex. The pathologic damage depends upon the degree of exposure. Breathing dust containing radioactive uranium can be detrimental.

Uranium is important as a nuclear fuel; its chemical importance lies in its being the prototype for succeeding elements. Transuranium elements have found many useful roles in industry and medicine. Their industrial uses include radiography for non-destructive inspection of metals, thickness measurements, density gages, soil moisture, compaction measurements and many more.

Polyurethane Foams[5,6]

The polyurethanes are among the many commercially important classes of polymers. Polyurethanes include those polymers which contain significant number of urethane groups, regardless of what the rest of the molecule may be.

In 1849 Wurtz first synthesized aliphatic isocyanates and studied their reaction with alcohols and amines, the reactions which are of commercial importance today.

$$R_2SO_4 + 2KCNO \longrightarrow 2RNCO + K_2SO_4 \qquad \text{(i)}$$

$$R\text{-}N^{\delta-}=C^{\delta+}=O + H^{\delta+}\text{-}O^{\delta-}\text{-}R' \longrightarrow R\text{-}\underset{\underset{O}{\|}}{\overset{H}{N}}\text{-}C\text{-}OR' \qquad \text{(ii)}$$

Urethane

(R'=polyether)

In 1937, Prof. O. Bayer, who can justifiably be called "The father of polyurethanes", discovered the diisocyanate addition polymerization that resulted in the preparation of many different types of urethane polymers. These polymers have significant numbers of the urethane groups although not necessarily repeating in a regular order.

The most common commercial method of forming polyurethanes is by the reaction of di or poly-functional hydroxy compounds such as hydroxyl terminated polyesters or polyethers with di or poly-functional isocyanates.

The polymers obtained by reacting diisocyanates with glycols (such as 1, 4 - butylene glycol) possessed

interesting properties as plastics and fibres.

Toluene diisocyanate (TDI) is used almost exclusively for the preparation of flexible foams. Flexible foams based on polyesters and TDI are expensive and have poor resistance to hydrolysis.

In 1957, polyethers based on ethylene oxide and propylene oxide were introduced which lowered the cost and improved the resistance of the products to hydrolysis.

Two major reactions are important in urethane foam preparation: The urethane reaction (ii) and the formation of urea (iii)

$$R\text{-}N=C=O + H_2O \longrightarrow \underset{\text{carbamic acid (unstable)}}{R\text{-}NH\text{-}C(=O)\text{-}OH} \longrightarrow \underset{\text{amine}}{RNH_2} + CO_2$$

$$RNH_2 + R\text{-}N=C=O \longrightarrow \underset{\text{(substituted urea)}}{R\text{-}NH\text{-}C(=O)\text{-}NH\text{-}R} \qquad \text{(iii)}$$

In the one shot process urethane formation must be accelerated and kept in balance with the urea reaction to avoid foam collapse. Catalysts are used to control the rates of these reactions.

Long flexible polyether chains are introduced into the growing polymer by the urea reaction, also known as the chain extension reaction.

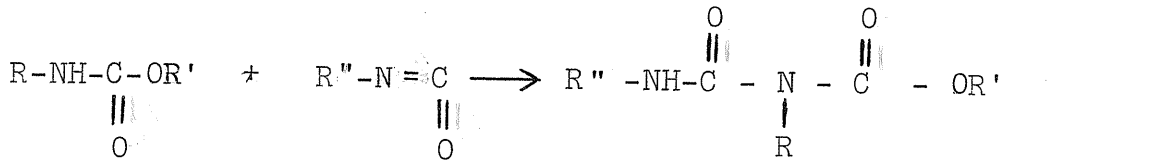
The degree of crosslinking in the final polymer and the resulting rigidity is determined by the nature of the

polyether.(7) For instance, the lower the functionality of the polyether and the higher its molecular weight, the lower will be the cross-linking density of the final polymer and the more flexible the foam.

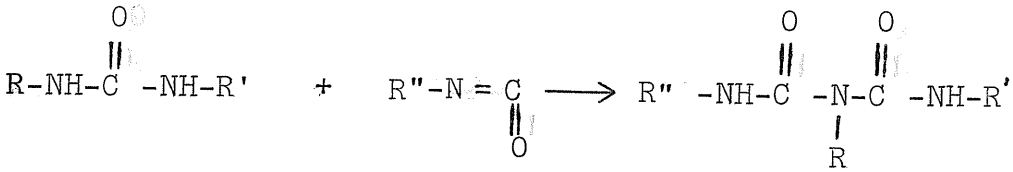
In flexible foams, the polyether chains are linear and only slightly branched, thus crosslinks are few and far between and the resulting polymer is a mass of entangled chains.

The urea reaction has two major functions to perform. The CO_2 gas released by the decomposition of the carbamic acid creates tiny bubbles in the polymerizing mass and gives the foam its cellular structure. The highly polar urea groups formed are capable of hydrogen bonding with each other to create additional crosslinking in the polymer. Low density foams require more water than high density foams.

Two minor reactions are allophanates (iv) and biurets formation (v):



urethane Isocyanate allophanate (iv)



Urea Biuret (v)

These are the main reactions which lead to branching and crosslinking and are much slower than the catalyzed

primary reactions. These reactions are reversible at the temperature at which foams are prepared.

The technology of the open-cell polyurethane foam sponge (OCPUFS) is quite complex. It requires a control of the rates of two primary reactions, so that the polymer growth is in step with gas evolution. Anything that effects either reaction or changes the polymer will have an effect on foam processing or its physical properties.

In addition to the principal raw material employed in the preparation of flexible foams such as diisocyanates, polyfunctional polyols, blowing agents, catalysts and surfactants; modifiers, fillers, plasticizers, flame retardants, colorants and stabilizers may also be used to impart special properties.

Three primary methods for the preparation of flexible foams are, the prepolymer, the semi or quasi-prepolymer and the one-shot process.(5,7) Generally the physical properties of the polyurethane foam depend mainly on the method by which the foam is prepared. The windows between the cells may or may not be ruptured in the final stages of expansion, depending upon the relative rate of molecular growth (gelation) and gas reaction, giving rise to flexible (open cell) or rigid (close cell) foam. The choice of the polyol has a major effect on the foam properties especially its rigidity and flexibility.(8) The chemical properties of polyurethane foams are also a function of the preparation process, for example, the solvent resistance of polyurethane structures

increases at higher crosslink densities, uneffected by the use of a large excess of iso-cyanate.

Bowen[9] examined the chemical resistance of some batches of commercial polyurethane foams and claimed that they are rather stable and inert. The foams degrade between 180°C and 220°C and slowly turn brown in UV light. They dissolve in concentrated H_2SO_4 and are destroyed in conc. HNO_3. They are mostly unaltered, apart from reversible swelling, by water, HCl up to 6M, H_2SO_4 up to 2M, glacial acetic acid, 2M ammonia, 2M sodium hydroxide as well as by solvents such as light petroleum, benzene, CCl_4, $CHCl_3$, diethyl ether, diisopropyl ether, acetone, isobutyl-methyl-ketone, ethyl-acetate, iso-pentylacetate and alcohols. The change in weight after shaking with these reagents for 5 min. and subsequent drying was less than 0.7%. Polyurethane foams can be dissolved in hot arsenic (III) chloride solution.(9)

Extraction by OCPUFS[6,10]

During the experiments to test polyurethane foams loaded with diethyl-ether as extractants, it was noticed that the foams themselves extracted a number of substances from aqueous solutions.[9] The simplicity of the apparatus required and the specificity of the extractions makes foam extraction useful in analytical laboratories as well as as in technical processes. Bowen[9] showed that most of the substances extracted by the foam from aqueous solutions were those which were extractable by use of liquid diethyl ether. The process has been shown to be absorption rather than adsorption. In a subsequent communication Bowen[11] recommended the application of OCPUFS for collection of gold (III) from mineral waste waters. Gold at ppm levels has been collected quantitatively from aqueous solutions in batch experiments by Schiller & Cook.[12] Braun and Farag[13] also investigated the recovery of $[Au(thiourea)_2^+]$ complex from acidic perchlorate solution by polyurethane (Polyether and Polyester types) foams. The uptake of the gold-thiourea complex by different samples of the polyether foam was observed to decrease with a decrease in the cell size. The absorption capacities of the polyether type foams were found to be greater than those of the polyester type.[13] Sukiman[14] quantitatively collected gold (III) at trace concentration (0.02-25 ppm) from aqueous solutions by percolating the solution through a short foam column at relatively high flow rates (10-13 ml cm^{-2} min^{-1}).

In the course of some work on the extraction and recovery of gallium from tantalum tailings, Gesser et al.(15) found polyurethane foam with polyether backbone useful for the extraction and recovery of gallium from acid chloride solutions. Gallium was not extracted by OCPUFS from sulfuric acid solutions. However, the addition of hydrochloric acid or sodium chloride to the sulphuric acid solution of gallium renders it extractable by OCPUFS. Iron absorbed in the foam decreases its efficiency for the extraction of gallium, whereas, aluminum even at concentrations 1000 times more than gallium is not absorbed by the foam.

The thermodyanamic properties of open-cell polyurethane foam as a solvent extractor for gallium from acidic chloride solution have been described in terms of acid, chloride and gallium concentrations.(16) The capacity of the foam (up to 10% Ga by wt.) has been found to be much greater than that due to surface adsorption and the diffusion of gallium through the polyurethane membrane has been found to be consistent with the solubility of $HGaCl_4$ in polyurethane.

Gesser et al.(17) were the first to study the possibility of using OCPUFS columns for the extraction and concentration of organic contaminants from water. Polychlorinated biphenyls (PCB) at various concentration levels (2-20 ppb) have been collected by passing the aqueous solution through the foam column at high flow rates ($\simeq$ 80 ml. cm^{-2} min^{-1}). Polyurethane foam columns have also been shown to be useful in monitoring organic matter in drinking water.(18)

Musty and Nickless[19] examined the recovery of PCB and OCI (organochlorine insecticides) from water at the ppb level, using six foams of different surface areas and bulk densities. It was observed that the higher the amount of methylene blue adsorbed on a foam, the higher was the efficiency of the foam material for recovering insecticides from water.

Bidleman and Olney[20,21] used polyurethane foam for the collection of PCB vapours from atmospheric samples by drawing air into the sampling systems at the rates of 0.4-0.8 m^3/min.[20] Concentrations of PCB, DDT and chlordane at the levels of 10^{1}-10^{-3} ng/m^3 were measured.

Open-cell polyurethane foam (mainly ether type) has been utilized for the concentration of trace amounts of polynuclear aromatic hydrocarbons (PAH) from water.[22,23] Saxena et al.[23] observed an increase in recovery of PAH with an increase in temperature.

Polyurethane foam has been observed to be a highly efficient trapping medium for pesticide vapours in air.[24] The trapping efficiency was found to be independent of the vapour concentration of six pesticides examined. The pesticide (300 μg) was retained on the foam even when pesticide free air was drawn through the exposed plug for an additional 18 hours.

Lewis et al.[25] recently used polyurethane foam in a high-volume air sampler for the collection of a broad spectrum of pesticides, polychlorinated biphenyls and

polychlorinated naphthalenes. Up to 360m^3 of air can be sampled in a 24h period at controlled flow rates of 25-100 l min^{-1}.

Porous polyurethane foam has been successfully used to remove some phthalate esters from water at ppm level.(26) Coating of the foam is observed to increase the efficiency of extraction.

The general applications of the foamed polyurethanes have been increased by using polyurethane foams impregnated with certain organic reagents. The separation of gold (III) from thiourea perchloric acid systems on tributylphosphate (TBP) loaded polyurethane foam have been investigated by batch and column techniques.(27,28) The rate of extraction of gold as a (Au (thiourea)-ClO_4-4TBP) complex was found to be quite high and was not effected by the presence of various possible interfering elements, eg. Zn (II), Fe (III) or Bi (III). Gold can be recovered by dissolving the foam in hot concentrated HNO_3.(27)

The TBP-loaded foam columns have also been found suitable for separation of ^{58}Co and ^{59}Fe isotopes.(29) The distribution of Co (II), Cu (II) and Fe (III) chlorides has been investigated in a TBP foam-HCl reversed phase chromatography system.(29) The analytical use of tri-n-octylamine loaded polyurethane foam has also been examined for the separation of cobalt from nickel in HCl medium under a wide range of relative concentrations.(30)

A study on the separation of palladium from bis-

muth and nickel in a thiourea perchloric acid system has been done by Braun and Farag using TBP-loaded foam columns.(31) A polyether foam was shown to have much superior hydrodynamic properties and much more power to absorb and retain TBP than "voltalef powder" did, resulting in a higher capacity and a faster extraction rate for palladium-thiourea complex by polyether foam.(31)

The separation of Pd (II) and Ni (II) from a perchloric acid solution containing thiourea was achieved by Braun and Farag(32) using TBP loaded foam. Palladium (II) chloride formed a complex with the thiourea and was retained by the foam while nickel (II) chloride passed through without any measurable retention.

Musty and Nickless(19) observed quantitative recoveries of OCI and PCB over a pH range of 6-9. Higher recoveries were obtained with uncoated foams than with foams coated with chromatographic greases except at very high flow rates (250 ml/min).

Polyurethane coated with DC-200 was found to be very effective in removing pesticides from water by Uthe, Reinke and Gesser.(33) Dow Corning Silicone Oil (DC-200) gave better than 90% recovery of all pesticides studied.

Gough and Gesser(26) tried several experiments with foam plugs coated with Dow-200 silicone oil. The extraction of phthalates was observed to differ little from that with untreated foams.

The plasticized reagent foams loaded with chelating

agents have been found to play an important role in separation and preconcentration of metal ions from aqueous solutions. Plasticizers,[34] essentially non-volatile liquids used to modify synthetic resins, do not chemically react with the resins but modify them through the reduction of van der Waals forces.

Chelating agents on, or in, the solid support are generally considered to have an advantage over liquid-liquid extraction especially when elements of small destribution ratios are collected.[35] Plasticized zinc-dithizonate foam has been used by Braun and Farag[35] for the collection of traces of silver from aqueous solutions. The collection rate of 0.1 g of silver in 10 ml of aqueous solution with 0.1 g of loaded plasticized-foam material was observed to be much faster than with unplasticized foam. Rapid attainment of equilibrium between silver and TBP-plasticized zinc dithizonate foam allowed the application of relatively high flow rates (50-60 ml min^{-1}) without effecting the efficiency of the operation.

The collection and preconcentration of traces of Hg (II) was done by using zinc-dithizonate foam.[36] As in the case of silver,[35] the collection rates of mercury (II) with the plasticized foam materials are generally higher than with the unplasticized foam.

The possibility of using TBP-plasticized zinc diethyl-dithiocarbamate foam (ZnDDTC foam) for the collection of Hg (II) from aqueous solution (pH $\simeq$ 6) was also in-

vestigated.(36) It is claimed that cobalt (III) can be completely and rapidly collected from aqueous solutions using 1-nitroso-2 naphthol and diethylammonium diethyl-dithiocarbamate foams.(37)

Plasticized polyurethane foams have also been employed for immobilizing various hydrophobic reagent solutions for isotope exchange separations.(38) Almost complete exchange was obtained with carrier free ^{131}I. High mobility of iodide in the plasticized foam material is useful in the separation of radio-iodide at relatively high flow rates without affecting the column efficiency.

Braun and Farag(39) used OCPUFS for immobilizing a finely divided silver sulphide precipitate for isotope exchange separation of radio-silver. For 0.1 g of Ag_2S-foam shaken with 10 ml of aqueous silver solution (0.01 mg *Ag+), the exchange yield obtained was equal to or higher than 99% from acid solutions up to 2M HNO_3. Radio-silver was also found to exchange from acid solutions (pH< 2) on foam material containing the primary silver-dithizonate complex.(38)

Polyurethane foam treated with hydrogen sulphide in an electric discharge to incorporate sulphhydryl groups in foam was shown to remove mercury (II) chloride very efficiently from aqueous solutions over the concentration range 4.0-0.0004 ppm mercury.(40)

The sulphhydryl foam was also shown to remove methyl mercury (II) chloride from aqueous solution over con-

centration range 2.0-0.0004 ppm methylmercury, but somewhat less effectively. Chow and Buksak[41] obtained quantitative extraction of methyl-mercury (II) and mercury (II) chloride from dilute solutions down to 10 ppm at slower flow rates (1-3 ml min^{-1})by dithizone treated foams. The faster flow rates gave more variable and less quantitative results.

Valente and Bowen[42] used both batch as well as column methods for the separation of antimony (III) and antimony (V) in solutions. In batch experiments adsorption of $Sb(DDC)_3$ (antimony tris-di-ethyl dithiocarbamate) complex was observed to be 80.6% effective at pH 9.5 after shaking with Na-DDC and polyurethane foam for 5 minutes and 100% after 15 minutes. In column experiments, on the other hand, the solution was passed through a column of foam previously treated with 5% solution (m/v) of NaDDC in CCl_4.

The method was also used for concentration of antimony from natural waters[43], using polyurethane foam loaded with 1% solution of 1-2 ethanedithiol in benzene. Absorption of antimony was 50% complete in one minute and 95% in 3 minutes. and was independent of the type of water used.

Benzoylacetone treated foams have been used for the separation of copper and cadmium by utilizing the pH dependent nature of the extraction curves.[44]

Flexible OCPUFS impregnated with dimethylglyoxime finds its use for quantitative and selective separation of Ni from aqueous solutions down to very dilute concentrations (10^{-5} M) in the pH range 8-10.[45] Fe (II),

Fe (III), Cu (II), Cd (II), Zn (II) and Co (II) do not interfere with the adsorption of nickel.

Braun et al.[46] obtained quantitative reduction of Ce (IV), V (V) and Fe (III) with foam filled columns. A pulsed technique[47] for effecting reduction of Ce (IV), V (V) and Fe (III) depends on packing the foam, containing the immobilized chloranil in a finely divided state as in chlorobenzene, in a syringe (pulsed column).

Silicone rubber foam treated with tri-n-octylamine has been used for the separation of rhodium and iridium from solution in hydrochloric acid containing free chlorine by batch or column adsorption.[48] Under suitable conditions more than 99% of rhodium remains in the aqueous phase while 98.5 ± 0.9% of iridium is retained by the foam.

Gregoire and Chow[49] achieved separation of platinum and palladium in solutions containing as little as 1.0 ppm using silicone-rubber foam treated with dimethylglyoxime.

A method of using OCPUFS loaded with various organic reagents as a media for the detection of very low amounts of metal was developed by Braun and Farag.[50] The "chromofoams" prepared by physical immobilization of hydrophobic organic solvents (especially plasticizers) containing different insoluble chromogenic organic reagents in the thin membranes and strands forming the foam material were used for the detection and semiquantitative determination of metal ions in ppb range after passage of one litre of

solution at a fast rate.

Since the presentation of the original work on the use of porous polymers as gas chromatographic supports by Hollis in 1965, these polymeric materials have proved invaluable as supports in chromatographic separations. Ross and Jefferson(51) were the first to prepare in situ formed open-pore polyurethane columns. The urethane support material was evaluated for gas solid, gas liquid and liquid-liquid chromatographic separations.(51) Good separations of several classes of compounds,(51,52) for example, alcohols, metal chelates, aliphatic and aromatic hydrocarbons, were obtained.

Schnecko and Bieber(53) described the preparation of columns for gas-solid chromatography filled with various types of elastomaric and thermoplastic foams and preferred pre-ground materials for packing columns rather than in situ production.

Lynn and Coworkers(54) employed in situ prepared open pore polyurethane (OPP) columns for high-resolution-low pressure liquid chromatography. The packing used was polyol (LA475) and polyisocyanate (Mondur MR). Good separations of dichloroanilines with symmetrical peaks have been achieved by using excess OH/NCO ratios (2.0:1.0).

Owing to the high capacity and extremely high permeabilities of OPP, spherical particle shape, narrow particle size distribution and openness of gross packing structure, high speed analytical separation have been

performed on milligram quantities (up to 50 mg) in less than 1 hour.(55)

The use of polyurethane-varion KS heterogeneous cation exchange foam for rapid separations in aqueous and alcoholic solutions has been investigated by Braun & Farag.(56) The cation exchange distribution coefficients of cadmium (II), zinc (II), iron (II) and calcium (II) were determined for foam material and convention bead exchanger. The selectivity of both was about the same.

OCPUFS has also been used in the form of pads for supporting immobilized cholinesterase to prolong its activity and monitoring air and water for the presence of cholinesterase inhibitors.(57,58,59)

Evans et al.(60) described the use of OCPUFS coupled with specific antibody as a matrix for immunologic binding of erythrocytes.

More recent applications of polyurethane foams include the extraction of iron (III) as a function of acid chloride and iron concentration in the aqueous phase,(64) antimony (III) and antimony (V) from hydrochloric acid medium in the presence of LiCl,(61) iridium and platinum from organic solvents, for example, ethyl acetate and acetone(62) and quantitative recovery of cobalt from aqueous thiocyanate solutions.(63)

The probable extractable species being $FeCl_3$ and $HFeCl_4$, $HSb(III)Cl_4$ and $HSb(V)Cl_6$,(61) $NaIr(IV)Cl_6$, $NaPt(IV)Cl_6$(62) and $Na_2\,Co(NCS)_4^{2-}$.(63) The results of

J. J. Oren[64] indicate the dissociation of extracted $HFeCl_4$ species in the foam.

Srikameswaran and Gesser[65] used polyester type foams loaded with PAN (1-(2-pyridylazo-2)-naphtol) for extraction of copper, zinc and mercury from large volumes of water.

Extraction of Uranium in Organic Solvents

The property of uranyl nitrate in being organic-solvent extractable from aqueous nitrate solutions is quite remarkable. Since most metal ions are not extracted under similar conditions, solvent partition provides a most convenient procedure for the separation of uranium from most other metals. Péligot first discovered the solubility of uranyl nitrate dihydrate in diethyl ether in 1842. Actinide elements, particularly neptunium and plutonium, are also organic-solvent extractable. Solvent extraction is very useful for separating uranium, neptunium and plutonium from each other and from accompanying fission product elements during the reprocessing of nuclear fuels.

Warner[66] has studied the uranyl nitrate-water-organic solvent systems for a large number of organic solvents. In a given homologous series of organic solvents, the solubility of uranyl nitrate decreases with increasing molecular weight of the organic compound. Solvents of lower molecular weight with sterically unhindered oxygen atoms are the most favourable solvents.

Uranyl nitrate is not extracted by most organic solvents in the absence of high concentrations of nitrate ion. Uranyl nitrate in sufficiently high concentration can serve as its own salting-out agent when solid uranyl nitrate hexahydrate is the starting material.[67] The effectiveness of various nitrates, including lithium, calcium, magnesium, zinc, copper (II), aluminium, iron (III), cerium (III) and

thorium nitrates as salting-out agents has been studied.[68] Nitrates of metals which form well-defined hydrates are found to be better salting agents than those which do not. In general, the order of efficiency is $M^{+3} > M^{+2} > M^{+1}$. It would appear that the addition of a salting agent reduces the amount of water available for the hydration of UO_2^{++} as well as decreases the water activity, favouring the distribution coefficient for extraction. With respect to salting out power, the higher the activity coefficient of the pure metal nitrate in aqueous solution, the better is its salting-out power.[69]

Kaplan et al.[70] observed that the extraction of uranyl nitrate from aqueous nitric acid into methyl isobutyl ketone was greatly increased in the presence of hydrazine. The reason for this was established to be the formation of ketazine which is present as its nitrate salt.

The addition of relatively small amounts of an organic-soluble nitrate, compared to that of nitric acid, was shown to increase the uranium extraction markedly due to the formation of trinitrato-uranyl complex, $RUO_2(NO_3)_3$.[70]

There are solvents, however, which are highly effective extractants for uranium even in the absence of salting agents. Of these probably the most important is TBP.[71] In TBP the uranyl nitrate is unhydrated, unionized and apparently unable to form a trinitratouranyl complex.[67] A solid complex $UO_2(NO_3)_2 \cdot 2TBP$ has been isolated from uranyl nitrate-TBP solutions. Although not essential,

neutral inorganic salts do increase the distribution ratio provided a certain minimum of nitric acid is present.[67] Uranium also extracts into TBP, with a high extraction coefficient, from moderately concentrated hydrochloric acid solution.[67]

Krishen and Freiser[72] used acetylacetone as a chelating and extracting solvent for the extraction of uranium from an aqueous solution (pH 4~6). Later Tabushi[73] studied the extraction of uranyl acetylacetonate from an aqueous solution with chloroform as well as 1% acetylacetone-chloroform solution. The extraction yield of uranyl acetonate was observed to increase in the presence of sodium chloride (maximum extraction yield of 92% was obtained at pH 7-7.5 from 50 ml of solution containing 5 g of sodium chloride with one ml of 10% EDTA). Ethylene-diamine tetra-acetate (EDTA) was used as a masking agent to study the separation of uranium from the mixed fission products and from thorium.

The solvent extraction of uranium (VI) by bis-(di-n-hexyl phosphinyl)-alkanes was studied by Mrochek and Banks.[74] The distribution ratio of uranium (VI) was observed to decrease with an increase in nitric acid concentration in solution. On the other hand, a rapid increase in the extraction was observed with an increase in the concentration of hydrochloric acid in solution. The maximum distribution ratios were observed with 5M HCl. The extraction from perchloric acid solution was also

studied.[74]

The influence of fatty acids on the extraction of uranium (VI) with solutions of trioctylphosphine oxide (TOPO) in different diluents has been studied.[75] The highest distribution coefficients of uranium were obtained in the extraction with benzene as diluent.

Patil and coworkers[76] studied the effect of temperature on the TBP extraction (xylene used as a diluent) of actinides and calculated the thermodynamic changes associated with the extraction of their nitrates. Influence of temperature on distribution coefficients of nitrates of uranium and other actinides in TBP (employing n-dodecane and Shellsol-T as diluents) has also been studied by several other authors.[77,78,79] The distribution coefficient of uranyl nitrate is observed to decrease with an increase in temperature indicating that the process of extraction is exothermic in nature. The values of ΔH^{o} and ΔS^{o} determined by Filippov and coworkers[78] and Siddal[79] are in good agreement.

Mojski and Poitrenaud[80] used TOPO in cyclohexane and chloroform to study the extraction of HBr and UO_2Br_2, with and without added NaBr.

A study of the extraction of uranium (VI) from mineral acid solutions by 4-(5-nonyl) pyridine oxide (NPyOX) and trioctylamine oxide (TOAO) was done by Ejaz and Carswell.[81] With NPyOX, the extraction from HCl, as well as from H_2SO_4 solution, was observed to decrease

with an increase in acid concentration. The decrease was more pronounced in the presence of H_2SO_4. In the presence of HNO_3, on the other hand, the extraction of uranium (VI) was observed to attain a maximum in the 0.1-0.5M HNO_3 range before decreasing again at higher acid concentrations. With TOAO the extraction of uranium attains a minimum at 0.25-0.5M HNO_3 and 0.25M HCl before increasing again at higher acidities. From H_2SO_4 solutions the extraction behaviour is similar to, though less sharp than, that with NPyOX. Xylene was found to be a favourable diluent for both of the amine oxides.(82) The transfer of uranyl nitrate and uranyl chloride in both of the amine oxides is increased in the presence of $NaNO_3$ and NaCl respectively at comparatively high ($\sim$ 0.25M) acidity where hydrolysis does not occur. NPyOX was found to be a better extractant than TOAO or TBP for extracting uranium at low acid concentrations (0.1-1M).

The extraction of U (VI) and Th (IV) with bis-paraoctylphenyl phosporic acid (HDOØP) in benzene diluent decreases with an increase in H^+ concentration at a constant Cl^- and NO_3^- strength, whereas it increases with an increase in HDOØP concentration under similar conditions.(83)

A number of other organic solvents, for example, tri-isooctylammonium acetate in CCl_4, C_6H_6, $C_6H_5CH_3$; TOPO and benzoic acid in CCl_4;(85) tetraphenyl-arsonium chloride,(87) benzoyl, paranitrobenzol and 3,5-dinitro derivatives of 2, 4-dihydro 5-methyl 2-phenyl 3H-pyrazol 3-ones;(88) bis-(2-ethyl hexyl) phosphoric acid(89) have been used for the

extraction of uranium.

But the use of liquid organic solvents is associated with problems including fire and health hazards due to the volatility of the solvents and effluent clean-up because of the solubility of the organic substances in water. Solvent losses also add to the cost of the process.

It is thus of interest to develop methods using solid phases as the extractants in order to circumvent the difficulties encountered with liquid organic solvents. Dai and Wu[90] used a mixture of aluminum hydroxide, ferric hydroxide and activated carbon in the weight ratio 1:3:4 for the extraction of uranium from dilute aqueous solutions. The mixture was shown to possess high adsorbability for uranium with a maximum at pH 4.0-5.5. The capacity of the adsorbent decreased with an increase in temperature. Of the number of eluting solutions tested for recovery of uranium, $(NH_4)_2CO_3$ was found to be most successful eluting solution.

Hydrous titanium oxide (TiO_2, 60%; H_2O, 35%; Na, 5%) shows a high capacity ($\sim$ 550 mg uranium per g titanium) for absorbing uranium from sea water.[91] In excess of 80% of the dissolved uranium was separated in less than five minutes by an adsorbing colloid floatation method.[92] The method utilizes a collector-surfactant-air system.

Micro-organisms possess selectivity for binding uranium from sea water,[93] e.g. cultured unicellular green algae have been used for this purpose. Experiments showed

that even high concentrations of uranium were not poisonous to the mutants. Another method for the extraction of uranium from natural water is by sorption of the uranyl thiocyanide complex on an anion exchange resin.(94) The preconcentration step is largely independent of water quality.

In the present work polyurethane foam is used as an organic phase, ie. a viscous organic ether solvent, for the extraction of uranium from aqueous nitrate solutions.

EXPERIMENTAL

Apparatus and Reagents

Beckman DU-Quartz Spectrophotometer.

Unicam Spectrophotometer SP500 Series 2.

Accumet Digital pH/ion meter, Model 520.

Conductivity Meter type CDM 2d, No. 50073
Radiometer Copenhagen NV.

Temperature Regulator, Haake E12, Germany;

Stir Kool Model SK 12 Thermoelectrics, Unltd Inc.

Fisher Scientific Certified Buffer Solutions.

Uranyl Nitrate Hexahydrate, Baker Analyzed Reagent,
J. T. Baker Chemical Co.

Uranyl Acetate Dihydrate, Analar, The British Drug Houses Ltd.

Stannous Chloride Dihydrate, Certified Reagent,
Fisher Scientific Co.

Hydroxalamine Hydrochloride, Certified Reagent,
Fisher Scientific Co.

Ammonium Thiocyanate, Certified Reagent,
Fisher Scientific Co.

Ammonium Nitrate, Certified Reagent,
Fisher Scientific Co.

Calcium Nitrate Tetrahydrate, Certified Reagent,
Fisher Scientific Co.

Aluminum Nitrate Nona hydrate, Certified Reagent,
Fisher Scientific Co.

Hydrochloric Acid, Nitric Acid and Acetone, Certified Reagents, Fisher Scientific Co.

Polyurethane Foams:

Union Carbide type "A" (surface area 0.081 m^2/g by B.E.T. Method using krypton) Dr. C. G. Seefried, Union Carbide Corp., Chemicals and Plastics, P. O. Box 8361, South Charleston, W. Virginia, U. S. A., 25303.

D-2931-A (Phosphate type Foam) prepared with exceedingly high level of flame retardant, tris-(2,3-dibromopropyl) phosphate (approx. 14% by weight of the foam polymer.

Polyurethane Film, 0.127 mm., MP1880 Natural
J. P. Stevens and Co., Inc.,
Elastomeric and Plastic Products Dept., Easthampton, Mass. 01027.

Pyrex batch Extractor (Fig. 1).

Pyrex diffusion cells (Fig. 12).

General Procedure

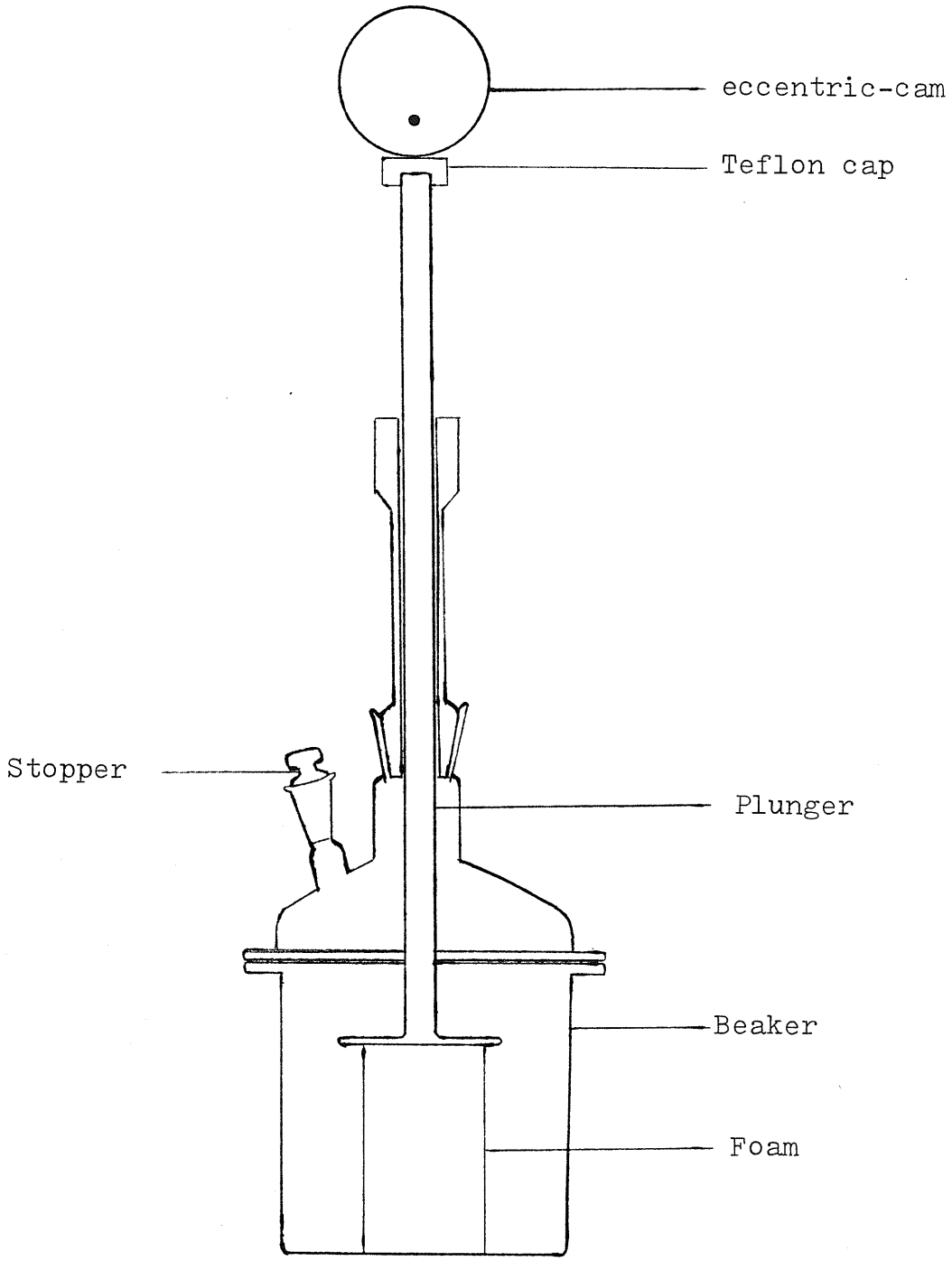
Washing of the Foam

Cylindrical plugs (4.0 cm in diameter and 4.7 cm in length with an average weight of 2.00 ± 0.17 g) were cut from sheets of polyurethane foam. Each plug, prior to use, was squeezed in 2MHCl in a batch extractor (Fig. 1) for one hour, washed with distilled water until free from HCl (tested with blue litmus paper) and squeezed dry. The foam plug was then rinsed with acetone, squeezed and air-dried overnight.

The phosphate type foam was observed to lose weight, (~14%) on first washing with 2M HCl solution with acetone. The weight loss decreased on successive washings. After three washings the weight of the foam stayed constant. This loss in weight is due to dissolution of the flame retardent, tris-(2,3, dibromopropyl) phosphate in acetone. This was indicated by the comparison of the NMR spectrum of the foam extract and the literature spectrum of (2,3-dibromo-1-propanol) phosphate.[106]

Figure 1

Batch Extraction Apparatus


eccentric-cam
Teflon cap
Stopper
Plunger
Beaker
Foam

Preparation of Standard and Sample Solutions

A stock solution, 5000 ppm in uranium was prepared by dissolving 10.5470 g of $UO_2(NO_3).6H_2O$ in water to give 1.00 litre of solution. A stock solution of ammonium nitrate (11M) was prepared by dissolving 880 g of ammonium nitrate to give 1.00 litre of the solution.

Sample solutions were prepared by diluting the above solutions to give the required concentrations.

For the sample solutions of high uranium concentrations and 11M NH_4NO_3, A stock solution of uranium, 20000 ppm in concentration was prepared. Sample solutions were then prepared by dissolving solid ammonium nitrate and an appropriate volume of stock solution of uranium together in water.

Distilled deionized water was used for all purposes.

Method of Uranium Analysis

The thiocyanate method for the spectrophotometric determination of uranium was employed. This method was developed by Currah and Beamish[95] for rapid estimation of small quantities of uranium (VI). The thiocyanate method has also been described by Dyck and Boase.[96] The determination is based on the estimation of the color produced by the uranyl thiocyanate complex. The method used in the present work is similar to the above referred methods except that the appropriate volumes of 10% (w/v) solution of hydorxylamine hydrochloride were used instead of 10% (w/v) solution of stannous chloride in order to supress the interference from iron (III) by its reduction to iron (II). Optical density measurements at 355 nm showed that Beer's law is obeyed and linearity of the data is obtained up to 30 ppm uranium. The intensity of the color was observed to be a function of the amount of uranium as well as of thiocyanate present in the solution.

A standard curve of uranium concentration plotted against absorbance was prepared, for the analysis of uranium content in the samples (Fig. 2). For analyzing sample solutions of higher concentrations ($\geqslant$ 200 ppm), standard solutions of concentrations between 5 ppm and 30 ppm (final volume = 10.0 ml) were prepared and cells of 1.00 cm path length were used. For dilute samples ($<$200

Figure 2

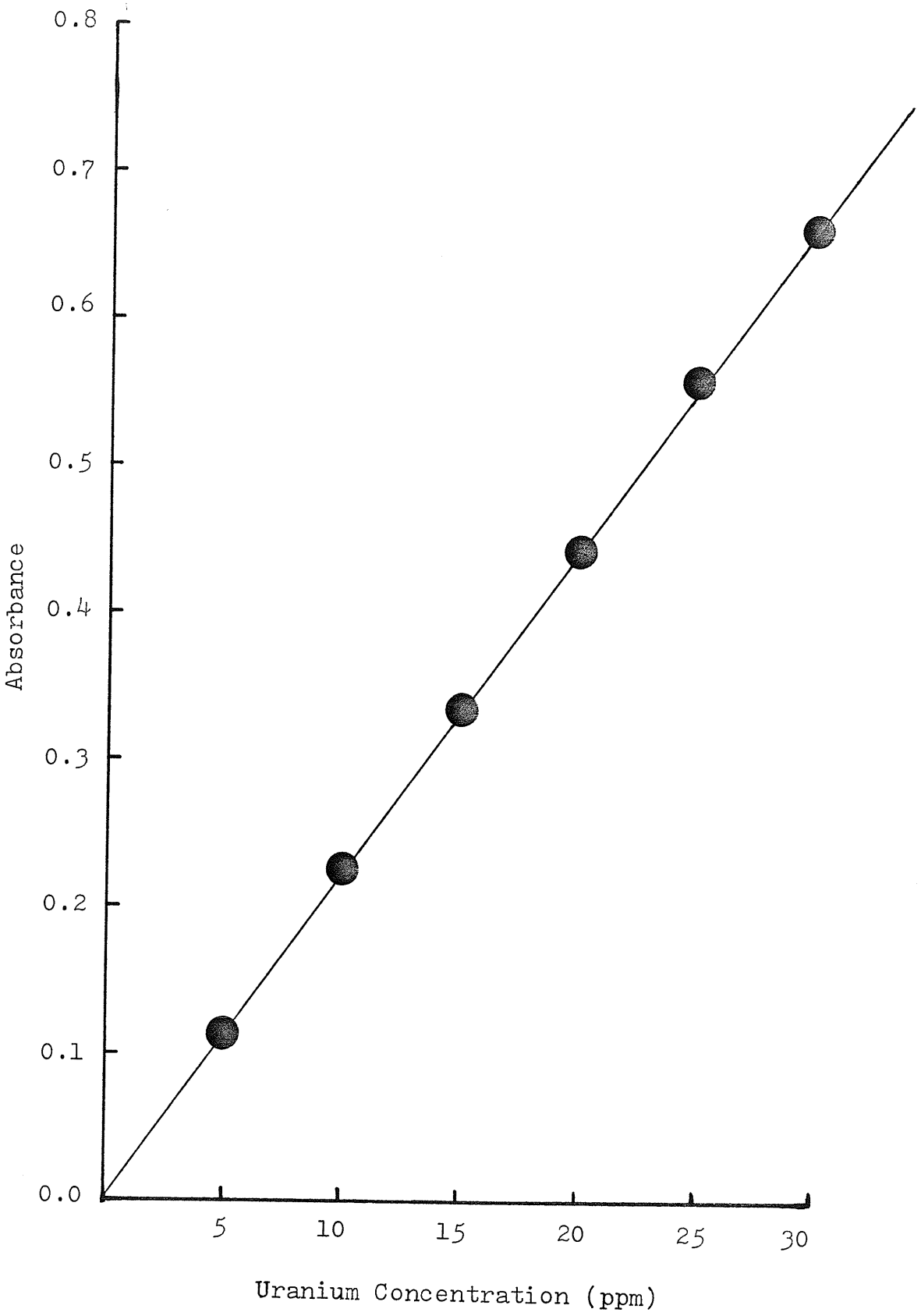
Absorbance of Uranyl Thiocyanate Complex as a Function of Uranium Concentration (Appendix C, Table C-1).
Initial Conditions:

Volume of 50% (w/v) NH_4SCN = 4.00 ml

Volume of 10% (w/v) $NH_2OH.HCl$ = 1.00 ml

Total Volume = 10.0 ml
Cell = Quartz
Path length = 1.00 cm

Wave length = 355 nm.


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Absorbance
5
10
15
20
25
30
Uranium Concentration (ppm)

ppm concentration), standard solutions of concentrations up to 5 ppm (final volume = 25.0ml) were prepared and cells of 10.0 cm path length were used. Volumes of 1.00 ml of 10% (w/v) $NH_2OH.HCl$ solution and 4.00 ml of 50% (w/v) NH_4SCN solution were added in each solution and the final volume adjusted with water. Precision of the method was $\pm$ 5%.

Extraction Procedure

Experiments were performed, by placing a dry, weighed foam plug in the batch extractor containing 150 ml. of solution, as shown in Fig. 1. The foam plug was first squeezed manually with the plunger to remove the air bubbles trapped in the foam. An eccentric-cam driven by a slow speed electric motor (which converts rotary motion of the electric motor into linear motion) was used to move the glass plunger up and down to squeeze the foam plug periodically in the test solution. The plunger moved a distance of 2.25 cm at a rate of $7\frac{1}{2}$ strokes min^{-1}.

The concentration of uranium in the solution before and after extraction was determined by interpolation from the calibration curve. The percentage extraction (% E) was calculated by use of the equation:

$$\% \text{ Extraction} = \frac{\text{Conc. of Metal before Ext.} - \text{Conc. of Metal after Ext.}}{\text{Conc. of Metal before Ext.}} \times 100$$

From the value of % extraction and weight of the foam plug used, the value of the distribution coefficient (D) was calculated by the equation (appendix A):

$$D = \frac{\sum [U]_f}{\sum [U]_{aq}} = \frac{\text{volume solution (ml)}}{\text{weight of foam (g)}} \left(\frac{100}{\%E} - 1 \right)$$

All experiments were performed at $25 \pm 0.5^{\circ}C$, unless otherwise stated.

RESULTS

Part 1. Extraction of Uranyl Nitrate

Section 1. Foam Studies

A. Preliminary Experiments

Introduction

It has already been shown by Bowen[9] that uranium as the nitrate complex is absorbed by OCPUFS. Preliminary experiments were performed by Weitzel[101] to confirm Bowen's results that uranyl nitrate in excess nitrate is absorbed by OCPUFS.

The experiments were first performed to determine the time required to reach equilibrium. Desorption of uranium from the foam was studied to recover the uranium extracted by the foam, so that the foams could be reused. Experiments were also done to study the effect of reusing the foam plugs.

1. Type "A" foam:

Experimental:

Several experiments were performed by squeezing the foam plug in 150 ml of 500 ppm uranium solution at

different ammonium nitrate concentrations (5M, 6M, 7M, 11M) (Fig. 3). The samples were taken out at 15 minutes intervals and analyzed for uranium, until equilibrium was achieved. A correction was applied for the change in the volume due to the samples taken out (Appendix A.2).

To study the recovery of uranium, the foam plug loaded with uranium from the sample solution (500 ppm in uranium and 11 M in ammonium nitrate), was squeezed dry between the folds of the filter paper and then squeezed continuously in 150 ml of distilled deionized water. Aliquots of sample solution were taken out at 15 minutes intervals and analyzed for uranium, until equilibrium was achieved (Fig. 4). A correction was applied for the volume of solution trapped in the foam plug. The same foam plug, after washing and drying, was used for the extraction of uranium from solutions to examine the effect of reusing the foam plugs.

Results and Discussion

The extraction curves in Fig. 3 indicate that equilibrium is achieved within 150 minutes.

The curve in Fig. 4 shows the back-extraction of uranium in distilled deionized water. Comparison of the extraction (Fig. 3) and back-extraction curves (Fig. 4) indicates that the recovery of uranium is more rapid than extraction. During back-extraction the plateau is attained within 60 minutes. Almost complete recovery ($\sim$99% of uranium in a single aliquot (150 ml) of water proves that water is an efficient eluant of uranium from foam. The foam

Figure 3

Extraction of $UO_2(NO_3)_2$ as a Function of Time at Different Nitrate Concentrations (Appendix C, Table C-2).

Initial Conditions:

$[U]$ = 500 ppm

Salting out agent = NH_4NO_3

Volume of Solution = 150 ml
Weight of foam ≃ 2 g

○: 5.0 M $[NO_3^-]$ ◇: 7.0 M $[NO_3^-]$
⬡: 6.0 M $[NO_3^-]$ ⬡: 11.0 M $[NO_3^-]$

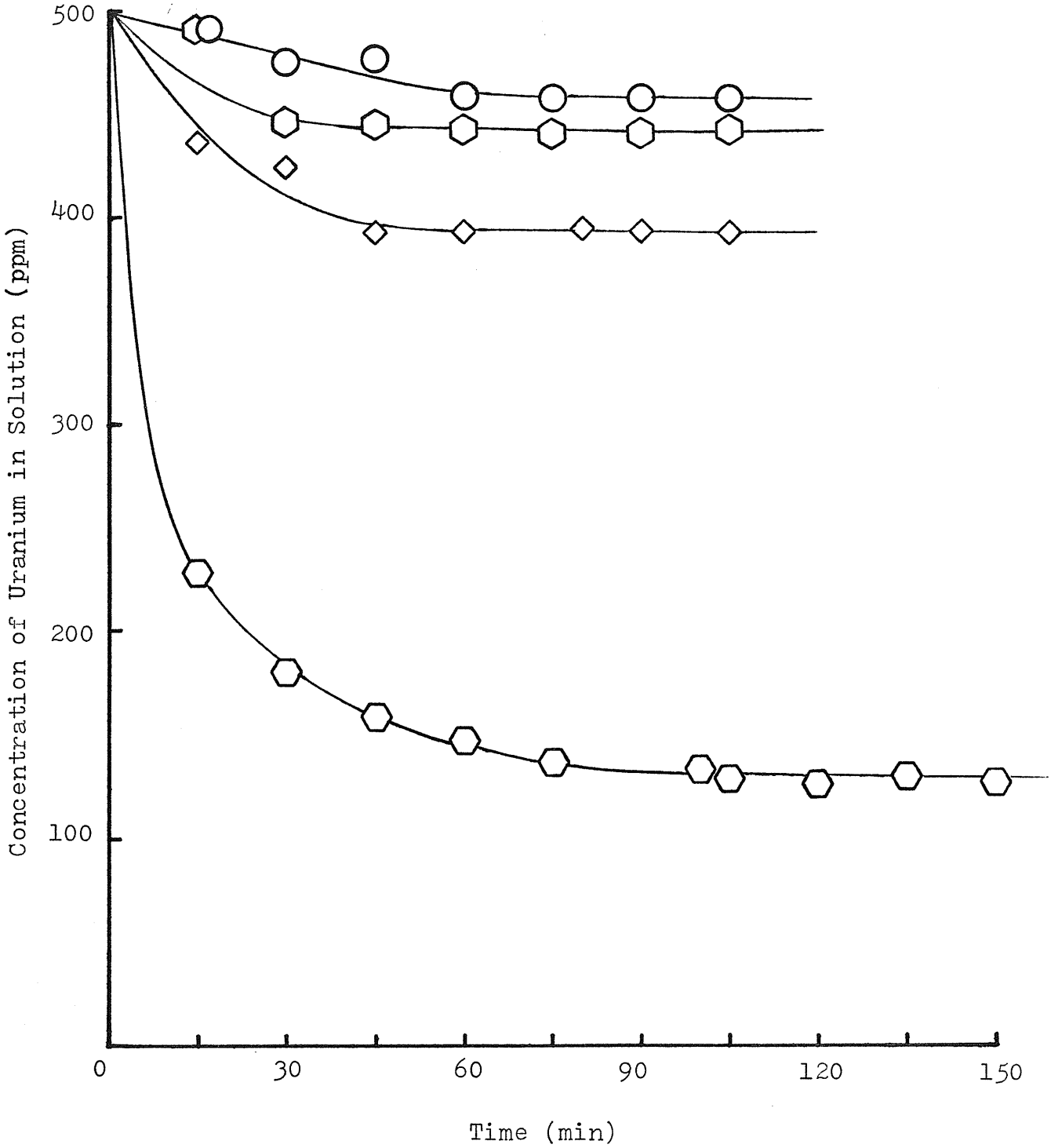
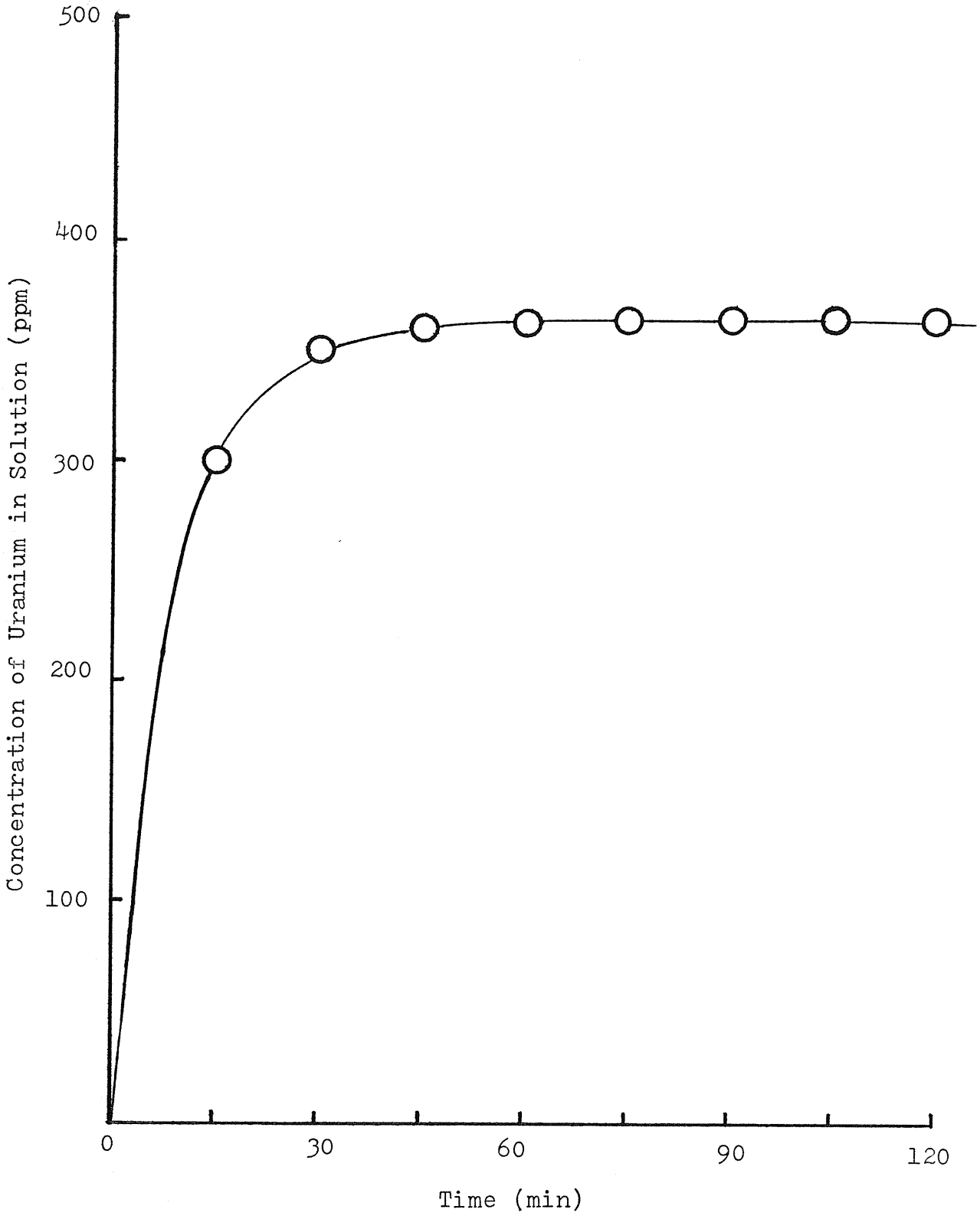

500
400
300
200
100
Concentration of Uranium in Solution (ppm)
0
30
60
90
120
150
Time (min)

Figure 4

Recovery of $UO_2(NO_3)_2$ from Loaded OCPUFS into 150 ml of Water as a Function of Time (Appendix C, Table C-3).


500
400
300
200
100
Concentration of Uranium in Solution (ppm)
0
30
60
90
120
Time (min)

was squeezed in another aliquot (150 ml) of water. Even after 150 minutes, no detectable amount of uranium was observed in the solution.

Extraction of uranium, from 150 ml of solution, 500 ppm in uranium and 11 M in ammonium nitrate was determined three times with the same foam plug. The foam plug was washed and dried before each experiment. Constant percentage of uranium extracted (~75%) (Table 1) indicated no difference in the extraction behaviour of unused and used foam. In all three experiments almost complete recovery of uranium was observed with water as an eluant. This study, thus, indicated that the foams could be reused without affecting the extraction efficiency.

Thus after each experiment, the foam plug was manually compressed and allowed to expand in water using a glass plunger, while distilled water was continuously run into the beaker. After several washings the foam plug was squeezed dry between the folds of the filter paper, rinsed with acetone and left overnight for drying.

2. "Phosphate" type foam

Experimental

An equilibration experiment was also performed with phosphate type foam. The foam plug was squeezed in 150 ml of uranium solution (500 ppm in uranium and 11 M in NH_4NO_3). The sample solution was analyzed every 15 minutes to determine the time of attainment of equilibrium.

Table 1

Variation of extraction efficiency for uranyl nitrate using same polyurethane foam cleaned between successive experiments

Initial Conditions: 150 mls., 11 M $[NH_4 NO_3]$, 500 ppm [U], $pH_{initial} = 2.5$

Experiment no.	weight of foam (g)	% Extracted	D	pH_{final}
1	2.048	74.7	216	2.7
2	2.140	74.9	209	2.9
3	2.032	73.6	205	3.0

Results

The equilibrium was not achieved even after 210 min (Fig. 5). The extraction of uranyl nitrate after 90 minutes was quite slow. The percent extraction by the phosphate type foam was observed to be greater ($\sim$ 82% E) than that with a type "A" foam ($\sim$ 75% E) of comparable weight, from a similar sample solution.

The phosphate type foam was not used in subsequent experiments because it was desired to compare the extraction efficiency of the ether type foam (without phosphate group) with that of liquid ether.

Figure 5

Extraction of $UO_2(NO_3)_2$ by "Phosphate" Type Foam as a Function of Time (Appendix C, Table C-4)

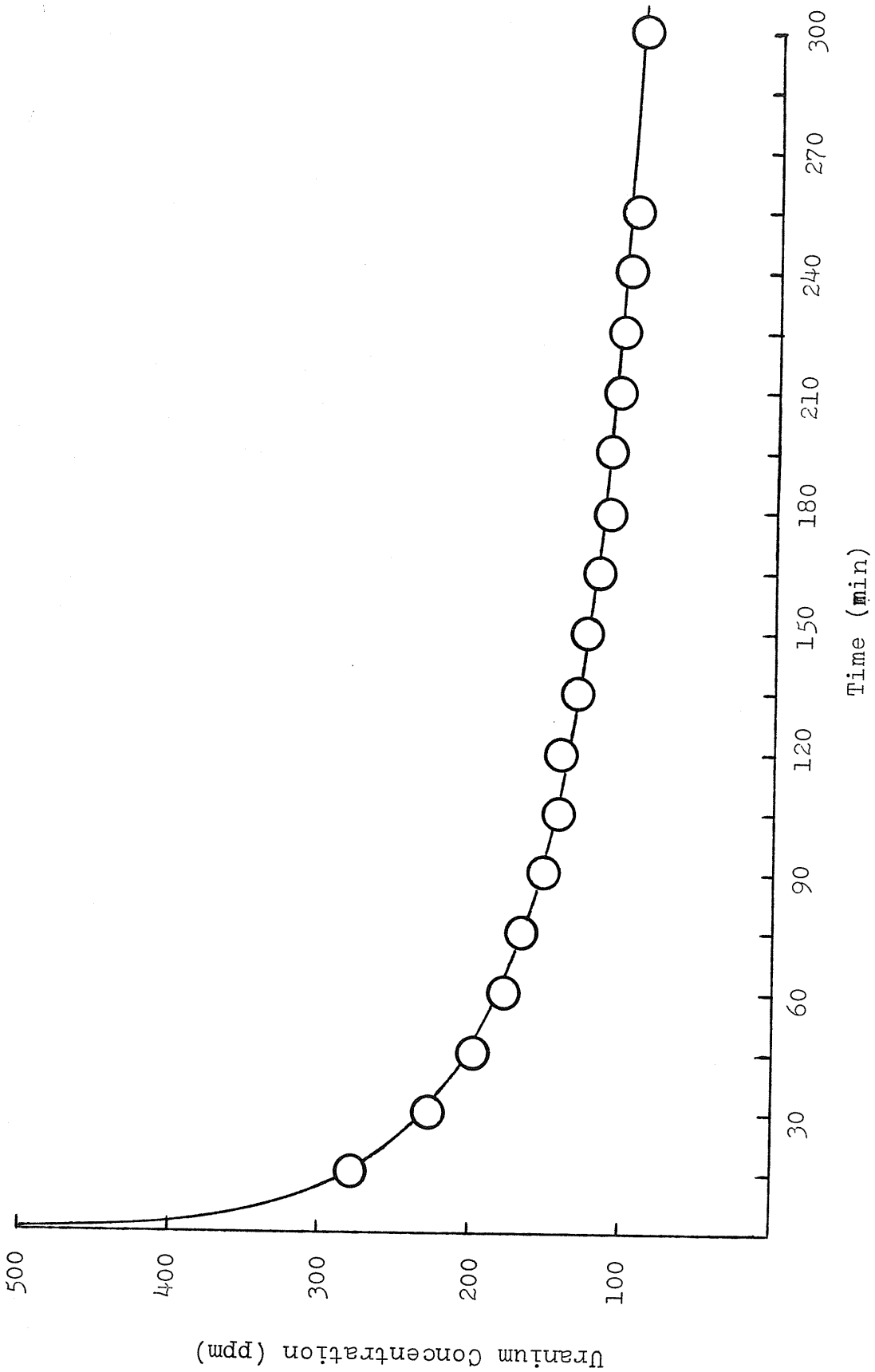
Initial Conditions:

$[U]$ = 500 ppm

$[NH_4NO_3]$ = 11 M

Volume of Solution = 150 ml
Weight of Foam $\simeq$ 2 g

Temperature = 25°C


Uranium Concentration (ppm)
500
400
300
200
100
30
60
90
120
150
180
210
240
270
300
Time (min)

B. Effect of Uranium Concentration

Introduction

The effect of uranium concentration on the distribution coefficient was studied at a constant ammonium nitrate concentration. Two sets of experiments were done at 25±0.5°C, at 7 M and 11 M ammonium nitrate. Another set of experiments was studied at 10± 0.5°C keeping ammonium nitrate concentration constant at 7 M.

Experimental

A foam plug was equilibrated with a solution of a given initial uranium concentration in the presence of ammonium nitrate. Several experiments were done at a constant ammonium nitrate concentration, varying the initial concentration of uranium in the solution. The foam plug was washed and dried before reusing it in successive experiments. The log of distribution coefficient was plotted as a function of the log of equilibrium uranium concentration in the solution (Fig. 6).

Results and Discussion

A decrease in the distribution coefficient of uranyl nitrate is observed with an increase in the equilibrium concentration of uranium in the aqueous phase at a constant concentration of the salting out agent (Fig. 6).

The shape of the curves obtained could not be

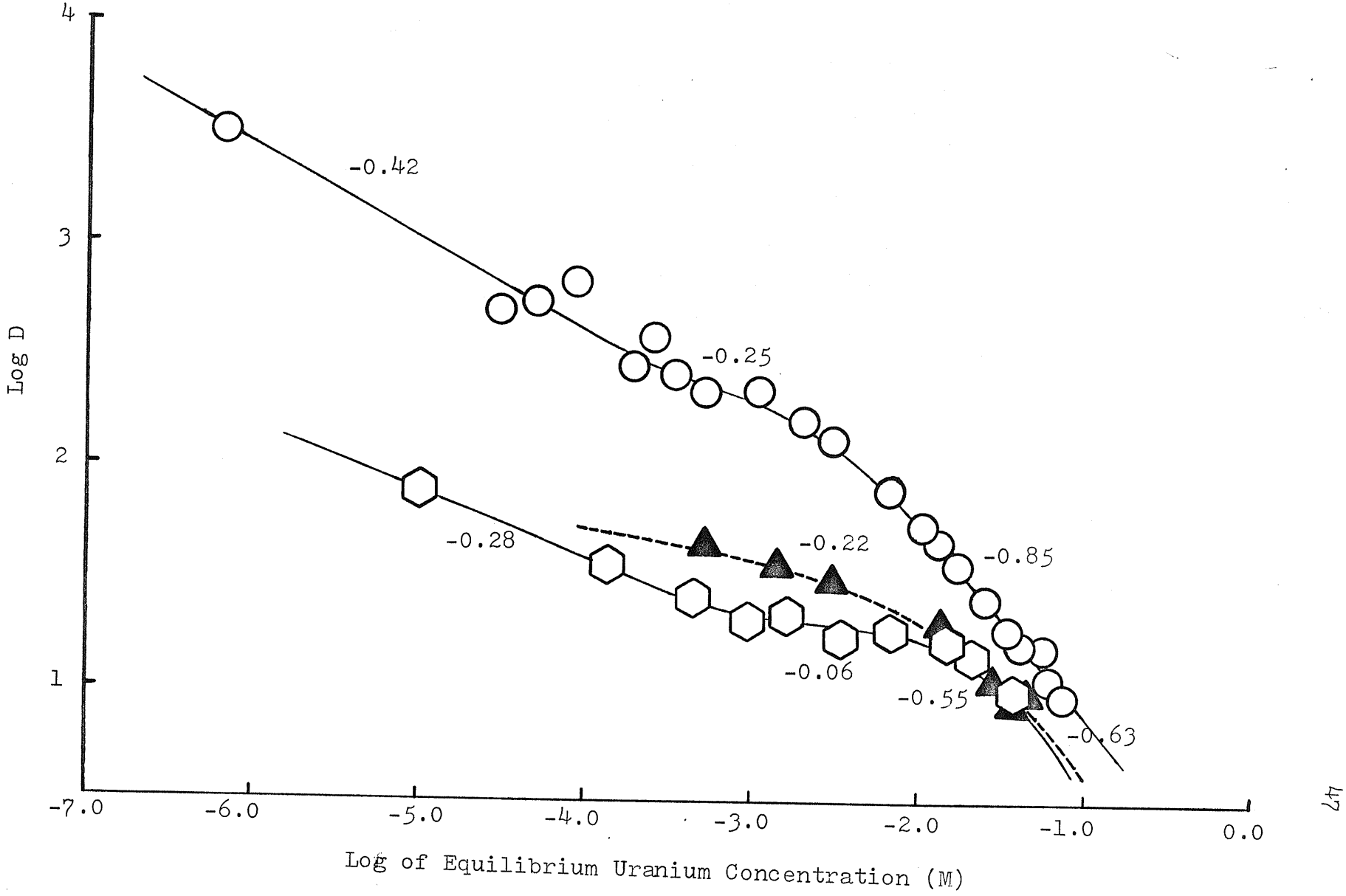
Figure 6

Variation of Log of Distribution Coefficients as a Function of Log of Equilibrium Uranium Concentration in Aqueous Phase Under Different Conditions of Temperature and $[NH_4NO_3]$ (Appendix C, Table C-5).

○ : 11 M $[NH_4NO_3]$, 25 ± 0.5°C

▲ : 7 M $[NH_4NO_3]$, 10 ± 0.5°C

⬡ : 7 M $[NH_4NO_3]$, 25 ± 0.5°C


4
3
2
1
Log D
-0.42
-0.25
-0.85
-0.28
-0.22
-0.06
-0.55
-0.63
-7.0
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
0.0
Log of Equilibrium Uranium Concentration (M)

explained by either of the equations developed for our system, considering ionization (Appendix B, Part 1) or dimer formation (Appendix B, Part II) of the extracted complex in the foam.

The experiments on the diffusion of uranyl nitrate and ammonium nitrate through polyurethane membrane indicate that ammonium nitrate dissolves to some extent in the foam (See section 2). Thus it would seem reasonable to assume that ammonium nitrate dissolves in the polyurethane foam and along with uranyl nitrate ionizes in the organic phase.

Thus an equation is derived, taking into account the extraction of uranyl nitrate as well as ammonium nitrate and their subsequent ionization in the foam.

The hydrolysis of the uranyl ion under the conditions of the experiment (ie. pH <3 and high nitrate concentration) is insignificant.[97a] Thus the possible species present in the aqueous phase are:

$$UO_2^{++},\ UO_2NO_3^{+} \text{ and } UO_2(NO_3)_2$$

The formation of $UO_2NO_3^{+}$ and $UO_2(NO_3)_2$ in the aqueous phase can be represented by the equations

$$UO_2^{++} + NO_3^{-} \overset{K_1}{\rightleftharpoons} (UO_2NO_3)^{+} \qquad \ldots\ldots (1)$$

$$\text{or } \underbrace{K_1}_{\beta_1} \left[UO_2^{++}\right] \left[NO_3^{-}\right] = \left[UO_2NO_3^{+}\right] \qquad \ldots\ldots (1a)$$

$$UO_2NO_3^+ + NO_3^- \xrightleftharpoons{K_2} UO_2(NO_3)_2 \quad \ldots\ldots (2)$$

$$\text{or } K_2 \left[UO_2NO_3^+\right]\left[NO_3^-\right] = \left[UO_2(NO_3)_2\right] \quad \ldots\ldots (2a)$$

$$\text{or } \underbrace{K_1K_2}_{\beta_2} \left[UO_2^{++}\right]\left[NO_3^-\right]^2 = \left[UO_2(NO_3)_2\right] \ldots\ldots (2b)$$

The extraction equilibrium of uranyl nitrate is represented by

$$(UO_2(NO_3)_2)_{aq} \xrightleftharpoons{K_D} (UO_2(NO_3)_2)_f \quad \ldots\ldots (3)$$

(The subscript "f" represents the species in foam, the species in aqueous phase are, as usually, written with no subscript).

$$\therefore K_D = \frac{\left[UO_2(NO_3)_2\right]_f}{\left[UO_2(NO_3)_2\right]_{aq}} \quad \ldots\ldots (3a)$$

Assuming dissociation of the extracted complex in the foam, the following equations can be written:

$$(UO_2^{++})_f + (NO_3^-)_f \xrightleftharpoons{F_1} (UO_2NO_3^+)_f \quad \ldots\ldots (4)$$

$$\therefore F_1 \left[UO_2^{++}\right]_f \left[NO_3^-\right]_f = \left[UO_2NO_3^+\right]_f \quad \ldots\ldots (4a)$$

$$(UO_2NO_3^+)_f + (NO_3^-)_f \xrightleftharpoons{F_2} (UO_2(NO_3)_2)_f \ldots\ldots (5)$$

$$\therefore F_2 \left[UO_2NO_3^+\right]_f \left[NO_3^-\right]_f = \left[UO_2(NO_3)_2\right]_f \quad \ldots\ldots (5a)$$

$$\text{or } F_1F_2 \left[UO_2^{++}\right]_f \left[NO_3^-\right]_f^2 = \left[UO_2(NO_3)_2\right]_f \quad \ldots\ldots (5b)$$

The distribution ratio, D, may be defined as

$$D = \frac{\text{Total uranium concentration in organic phase}}{\text{Total uranium concentration in aqueous phase}}$$

$$\text{ie. } D = \frac{\sum[U]_f}{\sum[U]_{aq}} = \frac{[UO_2(NO_3)_2]_f + [UO_2NO_3^+]_f + [UO_2^{++}]_f}{[UO_2(NO_3)_2] + [UO_2NO_3^+] + [UO_2^{++}]} \quad \ldots\ldots (6)$$

From equations (1a),(2b)and (4) to (6)

$$D = \frac{[UO_2(NO_3)_2]_f + \frac{[UO_2(NO_3)_2]_f}{F_2[NO_3^-]_f} + \frac{[UO_2(NO_3)_2]_f}{F_1F_2[NO_3^-]_f^2}}{K_1K_2[UO_2^{++}][NO_3^-]^2 + K_1[UO_2^{++}][NO_3^-] + [UO_2^{++}]} \quad \ldots\ldots(7)$$

$$D = \frac{[UO_2(NO_3)_2]_f \left[1 + \frac{1}{F_2[NO_3^-]_f} + \frac{1}{F_1F_2[NO_3^-]_f^2}\right]}{[UO_2^{++}]\left[K_1K_2[NO_3^-]^2 + K_1[NO_3^-] + 1\right]} \quad \ldots\ldots(8)$$

From equations (2b),(3a)and (8)

$$D = \frac{K_1K_2K_D[UO_2^{++}][NO_3^-]^2 \left[1 + \frac{1}{F_2[NO_3^-]_f} + \frac{1}{F_1F_2[NO_3^-]_f^2}\right]}{[UO_2^{++}]\left[K_1K_2[NO_3^-]^2 + K_1[NO_3^-] + 1\right]} \quad \ldots\ldots (9)$$

Substituting $K_1K_2[NO_3^-]^2 + K_1[NO_3^-] + 1 = Y$

$$DY = K_1K_2K_D[NO_3^-]^2 \left[1 + \frac{1}{F_2[NO_3^-]_f} + \frac{1}{F_1F_2[NO_3^-]_f^2}\right] \quad \ldots\ldots(10)$$

Assuming extraction of ammonium nitrate by the foam and its subsequent ionization, we may write the equilibria in the foam as:

$$(NH_4^{++}) + (NO_3^-) \xrightleftharpoons{K_A} (NH_4NO_3)_f \quad \ldots\ldots(11)$$

$$(NH_4NO_3)_f \xrightleftharpoons{K_{dA}} (NH_4^+)_f + (NO_3^-)_f \quad \ldots\ldots(12)$$

The electroneutrality in the foam is represented as:

$$[NO_3^-]_f = [NH_4^+]_f + [UO_2NO_3^+]_f + 2[UO_2^{++}]_f \quad \ldots\ldots(13)$$

Assuming incomplete dissociation[98] of the extracted complex, the concentrations of the species in the foam can be written as:

$$[UO_2(NO_3)_2]_f \gg [UO_2NO_3^+]_f \gg [UO_2^{++}]_f$$

Thus, $[UO_2^{++}]_f$ may be neglected in the electroneutrality equation (13).

ie. $$[NO_3^-]_f \simeq [NH_4^+]_f + [UO_2NO_3^+]_f \quad \ldots\ldots(14)$$

From equations(11) and (12)

$$[NH_4^+]_f = K_{dA}\frac{[NH_4NO_3]_f}{[NO_3^-]_f} = \frac{K_{dA}K_A[NH_4^+][NO_3^-]}{[NO_3^-]_f} \quad \ldots\ldots(15)$$

From equations (2b), (3a), (5a), (14) and (15), we may write:

$$[NO_3^-]_f = \frac{K_{dA}K_A[NH_4^+][NO_3^-]}{[NO_3^-]_f} + \frac{[UO_2(NO_3)_2]_f}{F_2[NO_3^-]_f}$$

$$= \frac{K_{dA}K_A \left[NH_4^+\right]\left[NO_3^-\right]}{\left[NO_3^-\right]_f} + \frac{K_DK_1K_2 \left[UO_2^{++}\right]\left[NO_3^-\right]^2}{F_2 \left[NO_3^-\right]_f}$$

ie.

$$\left[NO_3^-\right]_f^2 = K_{dA}K_A \left[NH_4^+\right]\left[NO_3^-\right] + \frac{K_DK_1K_2 \left[UO_2^{++}\right]\left[NO_3^-\right]^2}{F_2} \quad .....(16)$$

Substituting the value of $\left[NO_3^-\right]_f$ into equation (10), we get:

$$DY = K_1K_2K_D \left[NO_3^-\right]^2 + \frac{K_1K_2K_D \left[NO_3^-\right]^2 (F_2)^{\frac{1}{2}}}{F_2\left[K_{dA}K_AF_2 \left[NH_4^+\right]\left[NO_3^-\right] + K_DK_1K_2\left[UO_2^{++}\right]\left[NO_3^-\right]^2\right]^{\frac{1}{2}}}$$

$$+ \frac{K_1K_2K_D \left[NO_3^-\right]^2 F_2}{F_1F_2\left[K_{dA}K_AF_2 \left[NH_4^+\right]\left[NO_3^-\right] + K_DK_1K_2 \left[UO_2^{++}\right]\left[NO_3^-\right]^2\right]}$$

$$= K_1K_2K_D \left[NO_3^-\right]^2 + \frac{K_1K_2K_D \left[NO_3^-\right]^{3/2}}{\left[K_{dA}K_AF_2^{\,2} \left[NH_4^+\right] + K_DK_1K_2F_2 \left[UO_2^{++}\right]\left[NO_3^-\right]\right]^{\frac{1}{2}}}$$

$$+ \frac{K_1K_2K_D \left[NO_3^-\right]}{K_{dA}K_AF_1F_2 \left[NH_4^+\right] + K_DK_1K_2F_1 \left[UO_2^{++}\right]\left[NO_3^-\right]} \quad .....(17)$$

Log DY = Log D + Log Y =

$$\text{Log}\left\{K_1K_2K_D \left[NO_3^-\right]^2 + \frac{K_1K_2K_D \left[NO_3^-\right]^{3/2}}{\left[K_{dA}K_AF_2^{\,2} \left[NH_4^+\right] + F_2K_DK_1K_2\left[UO_2^{++}\right]\left[NO_3^-\right]\right]^{\frac{1}{2}}}\right.$$

$$\left. + \frac{K_1K_2K_D \left[NO_3^-\right]}{K_{dA}K_AF_1F_2 \left[NH_4^+\right] + K_DK_1K_2F_1 \left[UO_2^{++}\right]\left[NO_3^-\right]}\right\} \quad .....(18)$$

Presumably $F_1 > F_2$

At a constant ammonium nitrate concentration, the slope of the curves in the different regions of uranium concentration may be explained as follows:

At very low concentration of uranium, the second terms in the denominators of the second and the third terms may be neglected, since

$$K_{dA}K_A F_2^2 [NH_4^+] \gg F_2 K_D K_1 K_2 [UO_2^{++}][NO_3^-]$$

and $$K_{dA}K_A F_1 F_2 [NH_4^+] \gg K_D K_1 K_2 F_1 [UO_2^{++}][NO_3^-]$$

Therefore $$\frac{d \log D}{d \log [UO_2^{++}]} = 0$$

At higher concentrations of uranium, the second terms in the denominators of the second and the third term become important, but since $F_1 > F_2$, the third term on the whole is negligible compared to the second term. Thus the slope of the curve of log D vs log $[UO_2^{++}]$ in that region is

$$\frac{d \log D}{d \log [UO_2^{++}]} = -\frac{1}{2}$$

At very high concentrations, the foam is saturated with uranium ie.

$$\log D = \log \underbrace{\sum [U]_f}_{\text{(constant)}} - \log \sum [U]_{aq}$$

$$\therefore \frac{d \log D}{d \log [UO_2^{++}]} = -1$$

Extraction at very low concentrations of uranium has not been examined. The initial part of the curve obtained at 11 M ammonium nitrate shows a slope of about -0.42, a value closer to that obtained theoretically(-0.50). As the equilibrium uranium concentration increases, the slope of the curve is observed to increase (-0.85) approaching -1.0 as the saturation point is reached. The curves obtained at lower ammonium nitrate concentrations (7 M) follow the same general shape, though the values of the slopes do not agree well with theoretical values. The change in the ionic strength (μ) of the solution at the highest concentration of uranium (20000 ppm) studied in our system is small (about 0.25). Thus the change in the ionic strength of the solution with the change in the concentration of the uranium at lower concentrations of ammonium nitrate (7 M) in solutions may affect the slopes of the curves to some extent.

Thus it is obvious that the use of a salting out agent, which dissolves in the foam to a greater extent than ammonium nitrate and which may result in a constant nitrate concentration in the foam (eg. perhaps $(CH_3)_4$ N NO_3), would prevent the fall off and would show a slope of zero for the log D v/s log $[UO_2^{++}]$ curve.

C. Effect of Nitrate Concentration

Introduction

The effect of increasing nitrate concentration on the extraction of uranyl nitrate into foam was examined in the presence of different cations eg. NH_4^+, Ca^{2+} and Al^{3+} in order to make a comparison between the foam and diethyl ether[68] as extractants for uranyl nitrate.

Experimental

An amount of nitrate salt along with an appropriate aliquot of stock solution of uranium was dissolved in water to give a solution of required uranium and nitrate concentrations. The foam was equilibrated with the solution in the batch extractor. The sample solutions were analyzed at 15 minutes interval until the achievement of equilibrium. The foam plug was cleaned and dried before using it in an experiment.

Results and Discussion

The curves in Fig. 3 and 7 show that the extraction of uranyl nitrate increases with an increase in the nitrate concentration. The increase in the concentration of nitrate ion in the aqueous solution shifts the equilibrium between uranyl ion and the nitrate complex towards the formation of the latter, and thus facilitates the extraction of uranyl nitrate.

In Fig. 8, at the same molar nitrate concentration

Figure 7

Extraction of $UO_2(NO_3)_2$ as a Function of Time at Different Nitrate Concentrations.

Initial Conditions:

$[U]$ = 500 ppm
Salting out agent = $Ca(NO_3)_2.4H_2O$
Volume of solution = 150 ml

Weight of foam $\backsim$ 2 g
Temperature = 25°C

○: 5.0 M $[NO_3^-]$ ⬡: 10.4 $[NO_3^-]$

□: 7.0 M $[NO_3^-]$

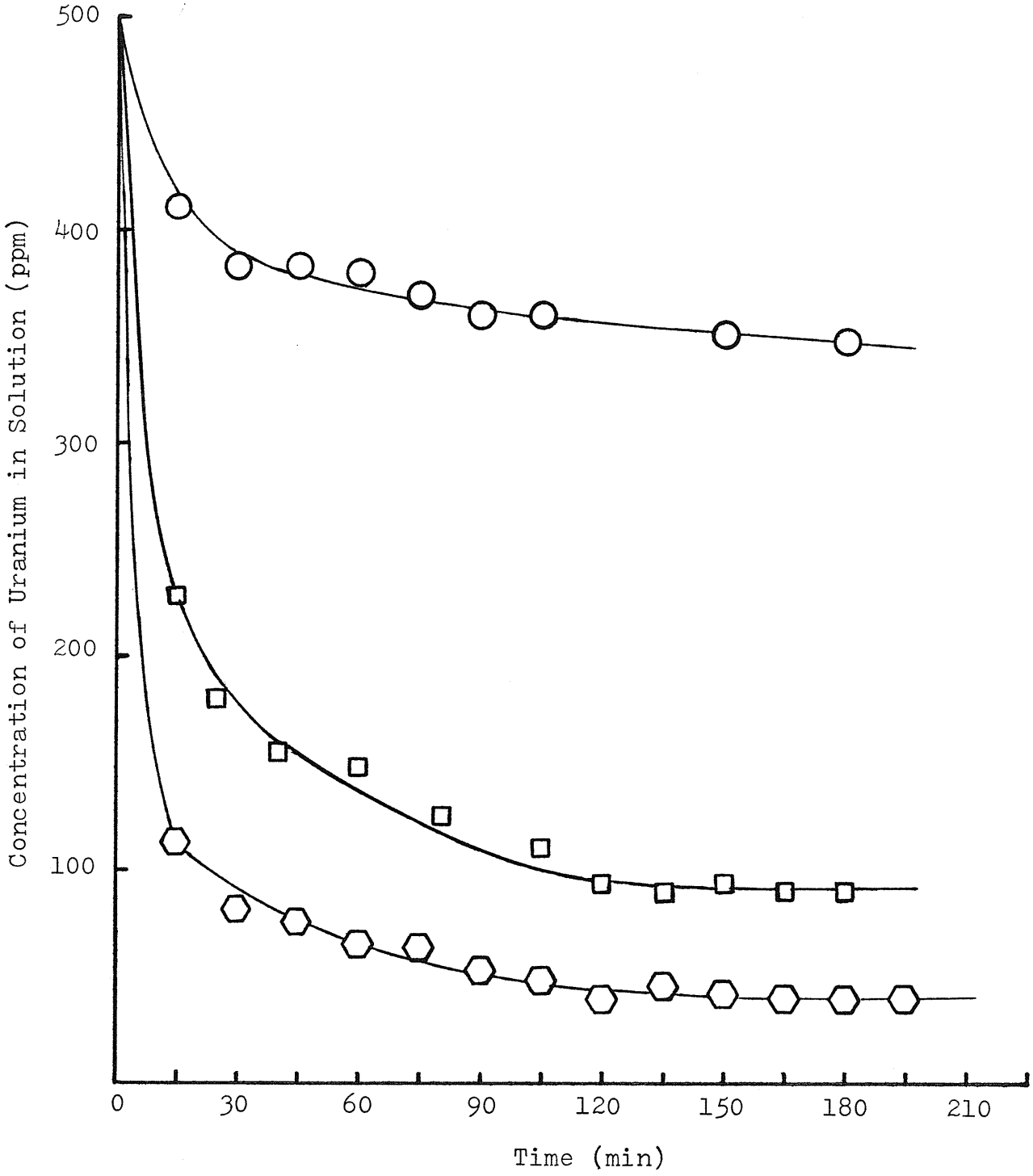

500
400
300
200
100
Concentration of Uranium in Solution (ppm)
0
30
60
90
120
150
180
210
Time (min)

Figure 8

A Comparison between OCPUFS and Diethyl Ether for Variation of Log of Distribution Coefficient as a Function of Log of Nitrate Concentration (M) for Different Salting out agents. (Appendix C - Table C-6. Log D v/s Log $[NO_3^-]$ for OCPUFS)

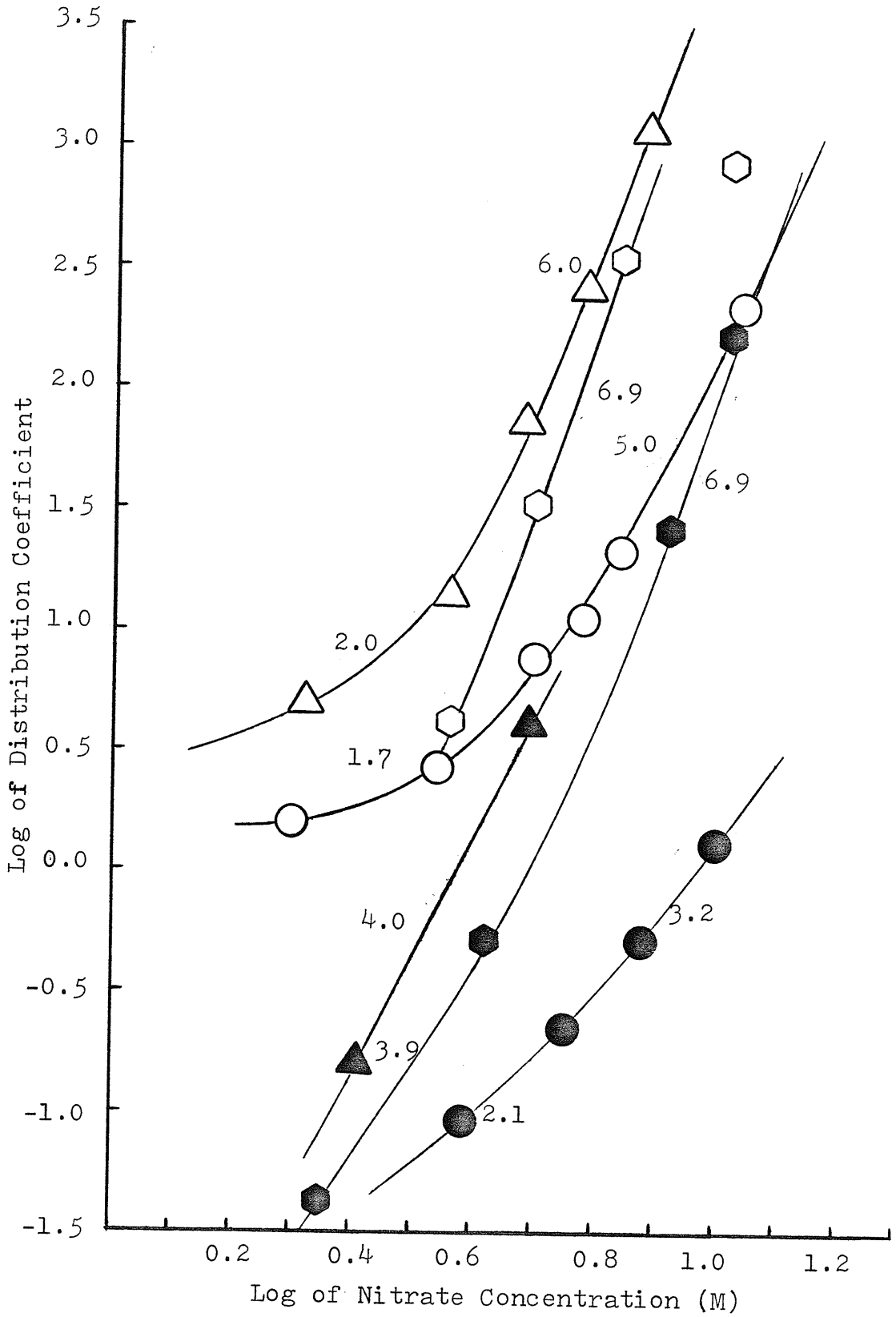
Triangles : $Al(NO_3)_3.9H_2O$

Hexagons: $Ca(NO_3)_2.4H_2O$

Circles: NH_4NO_3

Open Symbols: Ext. into Foam

Filled Symbols: Ext. into Diethylether.[68]


3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
Log of Distribution Coefficient
0.2
0.4
0.6
0.8
1.0
1.2
Log of Nitrate Concentration (M)
6.0
6.9
5.0
6.9
2.0
1.7
4.0
3.2
3.9
2.1

in the solution, the extraction efficiency of the salting out agent is observed to increase in the order NH_4NO_3 < $Ca(NO_3)_2$ < $Al(NO)_3$. The order is similar to that observed by Furman and Coworkers[68] for the extraction of uranyl nitrate into diethyl ether in presence of the salting out agents. This reflects that relatively high distribution coefficients are observed with the nitrates of the ions which form well defined hydrates. The addition of the salting out agent reduces the amount of water available for the hydration of uranyl ion.[68,69] The hydration number increases with an increase in the charge and a decrease in the radius of the cations. Thus the nitrates of the multivalent cations prove to be better salting out agents.

The ionic strength of the solution also changes with the change in the nature of the salting agent (Table 2), i.e. μ is higher for the nitrates of multivalent cations for the same molar concentration of nitrate in the solution. This factor also adds to the higher distribution ratio obtained with nitrates of multivalent cations used as salting out agents (resulting in an increased slope: 5 for ammonium nitrate, 7 for calcium nitrate and 6 for aluminum nitrate).

In Fig. 8 the distribution coefficient of uranyl nitrate into OCPUFS is compared to that observed by Furman and coworkers[68] into diethyl ether. The extraction into OCPUFS is about 10 to 100 times greater than into diethyl ether under comparable conditions. The maximum difference (about 100 times at all concentrations of salting out

Table 2

Ionic strengths of the solution of same molar nitrate concentrations

Salting out agent	$[NO_3^-]_{(M)}$	Ionic Strength: μ
NH_4NO_3	5.0	5.0
$Ca(NO_3)_2.4H_2O$	5.0	7.5
NH_4NO_3	7.0	7.0
$Ca(NO_3)_2.4H_2O$	7.0	10.5
NH_4NO_3	6.0	6.0
$Al(NO_3)_3.9H_2O$	6.0	12.0
$Ca(NO_3)_2.4H_2O$	3.6	5.4
$Al(NO_3)_3.9H_2O$	3.6	7.2

agent) is observed with ammonium nitrate. The high extraction efficiency of OCPUFS compared to that in liquid ethers is obtained for the extraction of gallium[16] and iron.[64] This effect is probably due to a high chain length of the polyether and a higher oxygen to carbon ratio than that for diethyl ether.

D. Capacity of the Foam

Introduction

Various factors, for example, concentrations of HCl, chloride ion and gallium, were observed to affect the capacity of OCPUFS to absorb gallium (16).

Thus an attempt to determine the capacity of the foam to absorb uranium under different experimental conditions was also made. The effect of changes in ammonium nitrate concentration and temperature on the capacity of OCPUFS was determined.

Experimental

No new experiments were performed. The data from section 1. B. was used to calculate the amount of uranium in mg per g of foam and in mg per ml of aqueous solution at equilibrium, under different experimental conditions.

Results and Discussion

A plot of the amount of uranium loaded on foam (mg g^{-1}) as a function of the amount of uranium in aqueous solution at equilibrium (mg ml^{-1}) is shown in Fig. 9. The amount of uranium absorbed in the foam increases with an increase in the equilibrium uranium concentration in solution until a point is reached beyond which the amount of uranium absorbed on foam remains constant as the concentration of uranium in the solution is further increased.

This maximum amount of uranium loaded on foam may be taken as the foam capacity.

In Fig. 9 the dashed and the dotted curves represent such a study at 7 M ammonium nitrate, whereas, the solid curve represents that at 11 M ammonium nitrate.

As mentioned before the extraction process may be represented by the equation:

$$\beta_2 \left[UO_2^{++}\right]_{aq} \left[NO_3^-\right]_{aq}^2 = \left[UO_2(NO_3)_2\right]_{aq} \overset{K_D}{\rightleftharpoons} \left[UO_2(NO_3)_2\right]_f$$

At a constant nitrate concentration (eg. 7M), with an increase in the uranium concentration the equilibrium will be shifted towards the right by the mass action effect. On equilibration with the foam the extractable complex distributes itself between the foam and aqueous phase. This will shift the equilibria in the aqueous phase until distribution equilibrium of uranyl nitrate species is established between the foam and the aqueous phase. The ionization of the extracted complex in the foam adds to this equilibrium resulting in a higher distribution ratio. A point is reached, however, where the foam cannot dissolve any more uranyl nitrate under these conditions. This certain amount of uranium per g of foam is defined as the capacity of the foam under specified conditions.

As the nitrate concentration is increased again by the mass action effect as well as due to the decrease in activity and dielectric constant of water, the equilibrium will be shifted towards the right, in turn increasing

Figure 9

Amount of Uranium loaded on foam (mg g^{-1}) as a Function of Equilibrium Uranium Concentration (mg ml^{-1}) in Aqueous Phase under Different Conditions of Temperature and $[NH_4NO_3]$ (Appendix C, Table C-7.)

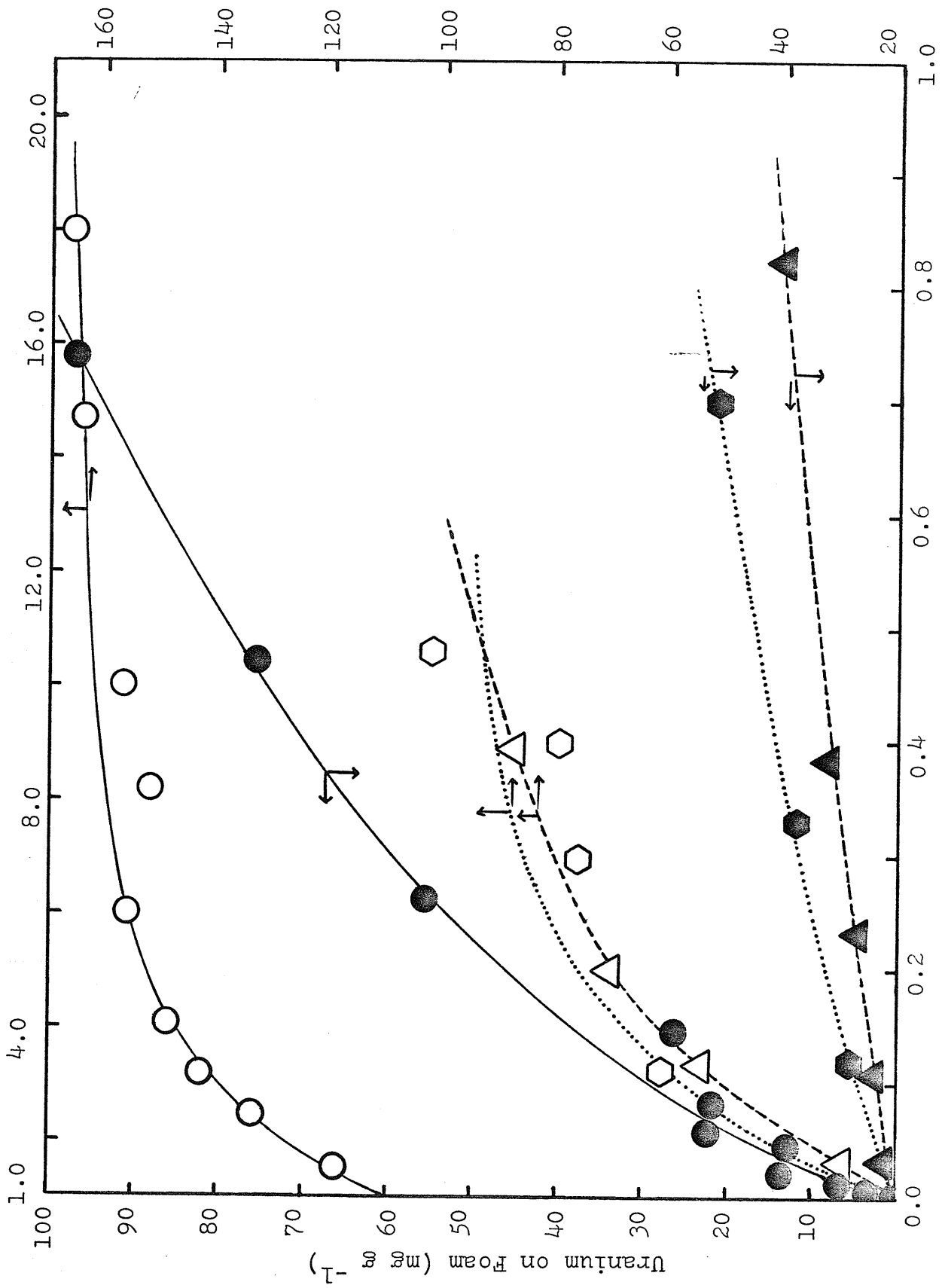
Circles: 11 M $[NH_4NO_3]$, 25 ± 0.5°C

Triangles: 7 M $[NH_4NO_3]$, 25 ± 0.5°C

Hexagons: 7 M $[NH_4NO_3]$, 10 ± 0.5°C

Filled Symbols: Left ordinate and lower abscissa

Open Symbols: Right ordinate and upper abscissa


Uranium on Foam (mg g^{-1})
Equilibrium Uranium Concentration (mg ml^{-1})
100
90
80
70
60
50
40
30
20
10
0.0
4.0
8.0
12.0
16.0
20.0
160
140
120
100
80
60
40
20
1.0
0.2
0.4
0.6
0.8
1.0

the amount of uranium in the foam. Thus the capacity of the foam is higher at higher nitrate concentrations.

Since a decrease in the temperature increases the distribution ratio, this should result in a higher capacity of the foam at lower temperature than at higher temperature (at same ammonium nitrate concentration in the solution).

A study at different temperatures (10 $\pm$ 0.5°C and 25 $\pm$ 0.5°C) has been done in solutions, 7 M in ammonium nitrate. As expected, at both temperatures, the capacity of the foam seems to be low compared to that observed at 11 M ammonium nitrate in the solution (which is about 16% by weight of foam). The achievement of the saturation point is observed to be rather slow. The extraction efficiency, as a function of the equilibrium uranium concentration in the aqueous phase, is observed to be greater at 10$\pm$ 0.5°C than at 25 $\pm$ 0.5°C at lower equilibrium concentrations. This increase in the extraction efficiency with a decrease in temperature is understood to be due to the lowering of water activity. But at higher equilibrium uranium concentrations in solution, similar distribution ratios are observed. This may be explained by assuming that at high uranyl nitrate concentrations in the solutions, the association and the dissociation constants of uranyl species in the aqueous phase and in the foam have changed with a change in temperature resulting in a change in the importance of the second terms in the denominators of the second and the third terms in the equation (18) (section 1.B) relative to the uranyl free terms.

E. Effect of Temperature

Introduction

The thermodyanamic quantities, ΔH, ΔG and ΔS of a whole series of extraction processes have been determined by several authors[76-79] from the temperature dependence of the partition coefficients of uranyl nitrate as well as nitrates of other actinides between aqueous nitric acid solutions and solutions of organo-phosphorous compounds in different diluents. The values of ΔH^{o} and ΔS^{o} determined by Filippov and coworkers[79] and by Siddal[78] are in good agreement.

The effect of temperature on the present system of the extraction of uranyl nitrate in to the foam from aqueous solution was also studied. An increase in the D value with a decrease in temperature was observed. An attempt to calculate ΔH and ΔS values was made.

Experimental

Since the increase in the D value was expected with a decrease in the temperature, a system with a low extraction efficiency was selected. A 500 ppm uranium solution (150 ml), 7 M in ammonium nitrate shows about 23% extraction efficiency at 26°C. The foam plug was equilibrated with such a solution at different temperatures (0°, 11°, 15°, 26° and 46°C). To study the experiments at low temperatures (below 25°C), the batch extractor was

placed in a water bath maintained at the desired temperature by placing it on a "stir kool". A temperature regulator in a water bath was used for higher temperatures.

Results and Discussion

A decrease in the distribution ratio with an increase in the temperature indicates that the extraction process is exothermic. Thus the experimental data can be employed to calculate the enthalpy and the entropy change associated with the extraction of uranyl nitrate into the foam. According to the following equations,

$$\Delta G = -RT \ln D$$

$$\Delta H - T \Delta S = -RT \ln D$$

$$\ln D = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\text{Log } D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R}$$

A plot of Log D as a function of 1/T should be a straight line with a slope of $-\Delta H/2.303R$ and a Y intercept equal to $\Delta S/2.303R$, if ΔH and ΔS are independent of temperature.

The experimental values (Fig. 10) of the slope and the intercept in our system were found to be 901 $\pm$ 109 and -1.7 $\pm$ 0.38 respectively. These in turn give a value of -4.1 $\pm$ 0.5 k cal $mole^{-1}$ for ΔH and -7.8 $\pm$ 1.7 cal $^{o}K^{-1}$ $mole^{-1}$ for ΔS for the foam extraction of uranyl nitrate. In the literature ΔH and ΔS values, for various uranyl nitrate extraction systems, vary from about

Figure 10

Variation of Log of Distribution Coefficient as a Function of $1/T$ (Appendix C, Table C-8).

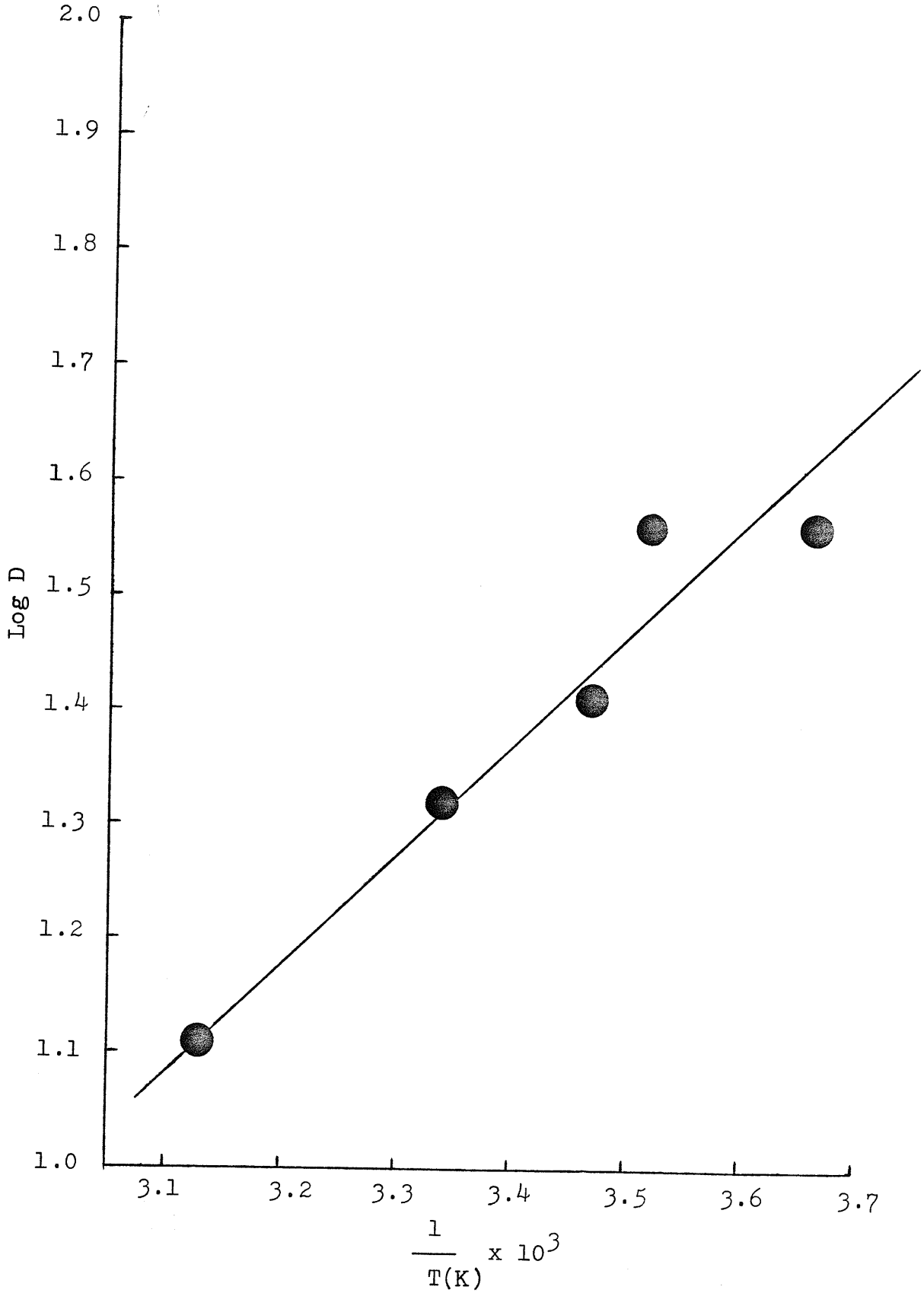
Initial Conditions:

$[U] = 500$ ppm

$[NH_4NO_3] = 7$ M

Volume of solution = 150 ml

Weight of Foam $\simeq$ 2 g


2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
Log D
3.1
3.2
3.3
3.4
3.5
3.6
3.7
1/T(K) x 10^3

-3 to -8 k cal $mole^{-1}$(76-79) and about -7 to -16 cal $^{o}K^{-1}$ $mole^{-1}$(77-79) respectively (Table 3). A value of -2.6 cal $^{o}K^{-1}$ $mole^{-1}$ has been reported by Patil and coworkers(76) for the extraction of uranyl ion into 30% TBP from a 3.0 M HNO_3 solution.

In the present system the study has not been done over a wide range of temperature, which lowers the reliability of ΔH and ΔS values.

In the above equations D (distribution coefficient) has been used instead of K_D (equilibrium constant). From equation 17 (section 1.B), D is proportional to K_D. The ΔH value is determined from the slope of Log D v/s $\frac{1}{T}$ and the constants involved in the proportionality constant do not effect the value of slope. Thus the use of D instead of K_D does not effect the value of ΔH. On the other hand the constants involved in the proportionality constant, change the value of intercept and since ΔS value is obtained from the value of intercept, some doubt exists concerning the process for which this value applies.

Table 3

Enthalpy and entropy change associated with extraction of uranyl nitrate into different organic solvents

Extractant	$\Delta H \pm \delta$ (kcal. $mole^{-1}$)	$\Delta S \pm \delta$ (cal $^{o}K^{-1} mole^{-1}$)	Ref.
TBP (Tri-n-butylphosphate)	-6.1 ± 0.7	-11.5 ± 2.3	(79)
TIBP (Tri-iso-butyl phosphate)	-5.2 ± 0.7	-10.4 ± 2.1	(79)
TSBP (Tri-sec-butyl phosphate	-6.5 ± 0.5	-13.2 ± 1.5	(79)
TBP	-6.3 ± 0.13	-15.0 ± 0.45	(78)
TIBP	-6.6 ± 0.13	-16.2 ± 0.49	(78)
TSBP	-6.9 ± 0.14	-15.6 ± 0.31	(78)
TBP	-5.0 ± 0.5	-7.9	(77)
TBP	-2.85	-2.6	(76)
Diethyl ether	-9.8*	-40.2*	(104)

* Calculated from the distribution coefficients obtained at two temperatures ($2^{o}C$ and $20^{o}C$) and at very high initial uranium concentration (90590 ppm, uranyl nitrate acts as a self salting out agent). Warner has also studied the temperature effect at still higher initial uranium concentrations. The calculated ΔH and ΔS values are observed to first increase and then decrease with an increase in the uranium concentration. Thus the ΔH and ΔS values for the extraction into diethyl ether are expected to be lower at the uranium concentration (500 ppm) used in our experiments and agree with those obtained for our system.

F. Effect of pH

Introduction

Nitrates of organic bases enhance the extraction of uranyl nitrate into ketonic solvents by the formation of a trinitratouranyl complex.[70] A similar complex is produced by the addition of nitric acid to a solution of uranyl nitrate in methyl iso-butyl ketone.[97b] The following equilibrium has been suggested:

$$UO_2(NO_3)_2 + HNO_3 \overset{K}{\rightleftharpoons} HUO_2(NO_3)_3$$

If this is the extractable complex formed in the present system, the extraction efficiency should increase with a decrease in pH. The effect of high pH cannot be studied because of hydrolysis of uranyl ion to polyuranyl complexes.[97a] In perchlorate solution (ClO_4^- has the least tendency for complexing), the hydrolysis of uranyl ions starts at pH > 2.[97a] Thus a set of experiments was designed to study the effect of pH on the extraction of uranyl nitrate by foam.

Experimental

A stock solution 600 ppm in uranium and 8.4 M in ammonium nitrate was prepared. A volume of 125 ml of solution was taken for each experiment. Nitric acid and ammonium hydroxide were used to vary the pH of the solutions and the final volume of each solution was adjusted to 150

ml with distilled deionized water to give a solution 7 M in ammonium nitrate and 500 ppm inuranium. Final pH of each solution was noted. Extraction into foam was studied in the usual way.

Results and Discussion

Since nitrate has a higher tendency of complexing with uranyl ions, the hydrolysis is expected at higher pH than when perchlorate is present as the anion. Log D as a function of the initial pH of the solutions is shown in Fig. 11. The extraction efficiency is observed to be constant at pH $\leqslant$ 3.2. A sharp decrease in extraction is observed beyond this value.

The results of the experiments thus indicate that no protons are associated with the extractable complex in the pH range 0 to 3. Extraction of species of type $HUO_2(NO_3)_3$ is not likely in our system.

The sharp decrease in the extraction efficiency is probably due to the start of formation of polyuranyl complexes (non-extractable) at pH$>$ 3.2.

Figure 11

Variation of Log of Distribution Coefficient as a Function of pH at Room Temperature. (Appendix C, Table C-9).

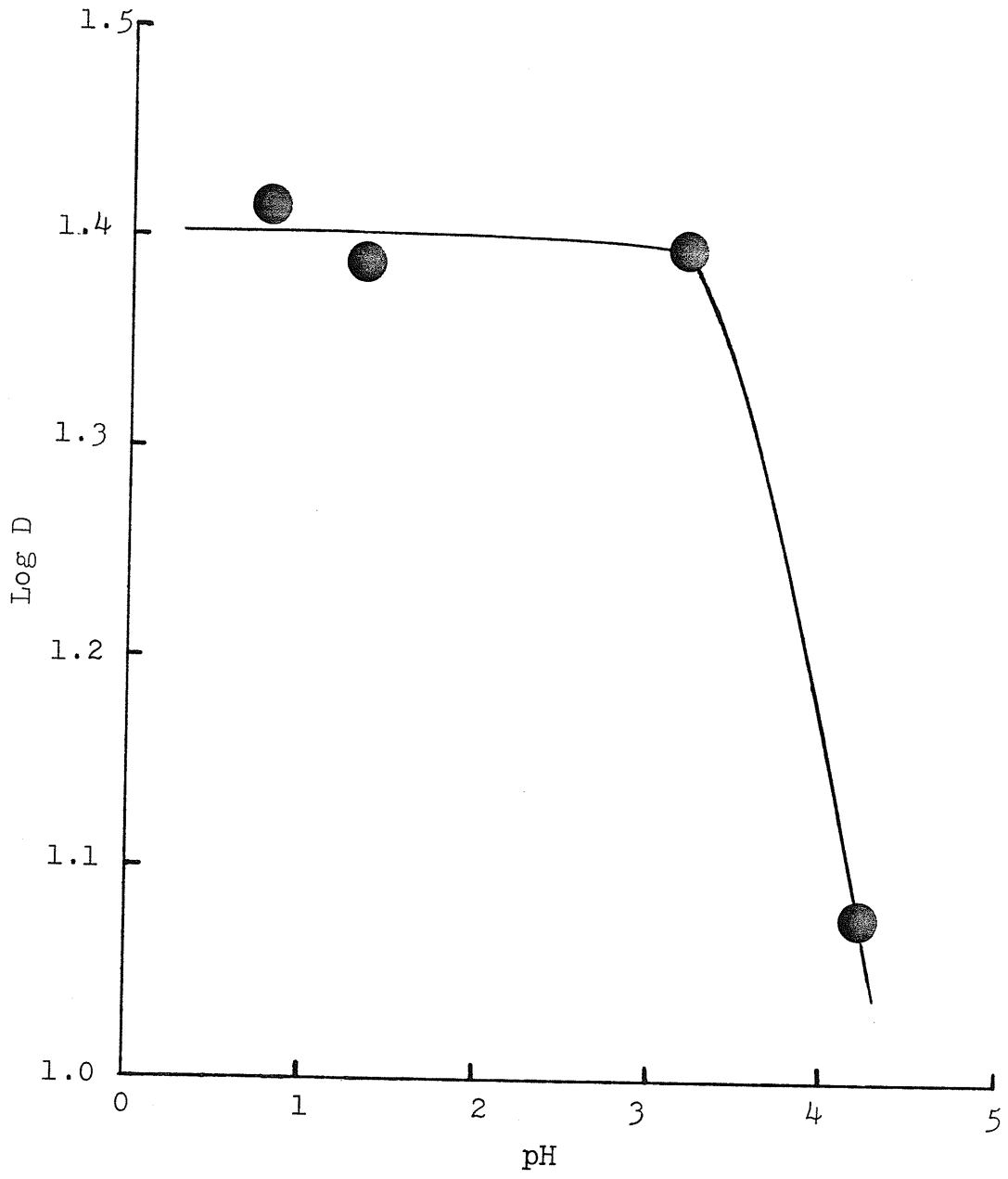
Initial Conditions:

$[U] = 500$ ppm

$[NH_4NO_3] = 11$ M

Volume of Solution = 150 ml

Weight of foam $\simeq$ 2 g


1.5
1.4
1.3
1.2
1.1
1.0
Log D
0
1
2
3
4
5
pH

Section 2. Membrane studies

Introduction

It has been concluded[102] that "solvent membranes" are not just another way of carrying out a solvent extraction process. Separations by means of membranes are obtained because of kinetic factors involved in the permeation process. The same separations may or may not be achieved by equilibrium extraction using the same active ingredients.

Previous work in this laboratory shows that gallium and iron (III) can be extracted by polyurethane foam as well as transported[105] through the polyurethane membrane film.

Thus it was desired to study the diffusion of uranyl nitrate through polyurethane film in the presence of ammonium nitrate.

Studies on permeation of uranyl ion through polymeric membranes have already been done by several authors. Ketzinel and coworkers[103] devised a continuous decontamination process, for separating uranium from its fission products and from aluminum solutions, based on selective permeation of uranyl ions through solvent polymeric membranes. A highly selective separation of uranyl nitrate was obtained from an acid feed solution containing uranyl, iron, aluminum and nitrate ions using polymeric membrane containing alkyl phosphoric ester.

Experimental

A circular membrane, about $5\frac{1}{2}$ inches in diameter was cut from a sheet of 0.127 mm thick polyurethane film. The membrane was sealed between two cells (A) by means of Dow Corning High vacuum silicone grease to prevent leakage (Fig. 12). One of the cells (A_s) was filled with 675 ml of 500 ppm uranium solution 11 M in ammonium nitrate concentration. The other cell (A_w) was filled with only 650 ml of distilled deionized water. Thus the level of the solutions in both cells was the same.

A similar apparatus (B), with an 11 M ammonium nitrate solution (725 ml) in one cell (B_s) and distilled deionized water (815 ml) in other cell (B_w) was set up at the same time.

The solutions in the cells were stirred continuously by means of a magnetic stirrer in each and kept at 25 $\pm$ 0.5°C in a water bath.

The conductivity* of the water sides of the cells (A_w and B_w) was measured using a Radiometer-conductivity meter.* The samples of the water side of the cell (A_w) containing uranyl nitrate and ammonium nitrate solution were analyzed for uranium to determine the amount of uranyl nitrate transferred through the membrane.

---

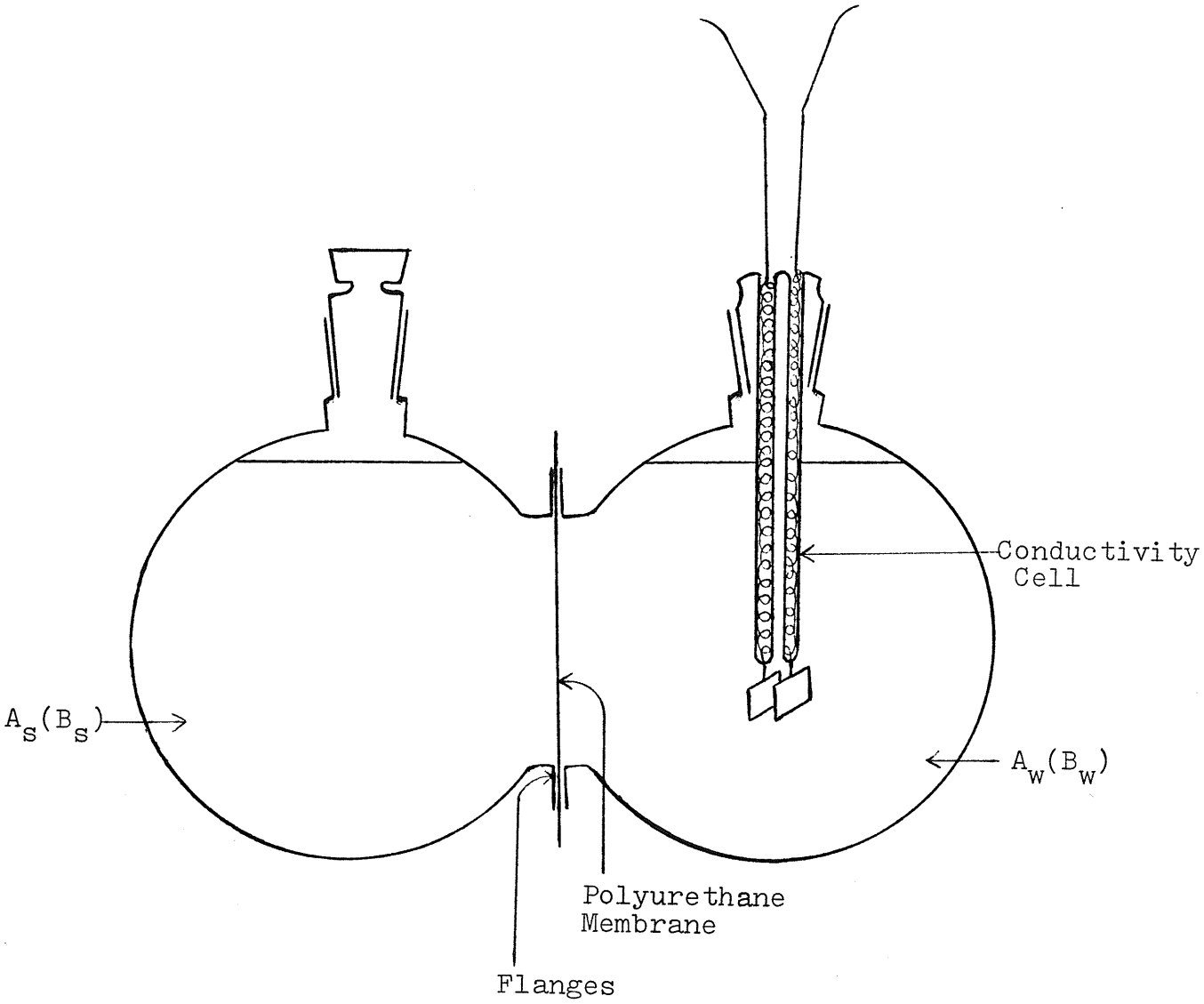
* Cell constant of
Cell in A_w = 0.2771 cm^{-1}

Cell in B_w = 0.2960 cm^{-1}

Note: Exposed area of membrane in Cell A $\simeq$ 7 sq. in.
Cell B $\simeq$ 9 sq. in.

Figure 12

Diffusion Cell


Conductivity
Cell
$A_S(B_S)$
$A_W(B_W)$
Polyurethane
Membrane
Flanges

Results and Discussion

A plot of specific conductance in A_w and B_w and uranium concentration in A_w as a function of time is shown in Fig. 13. The conductance was observed to increase in both. But the rate of increase in conductance of the water side of cell A was higher than that of the water side of cell B indicating that both uranyl nitrate as well as ammonium nitrate diffuse through the membrane.

The volumes of the solutions in the sample sides (A_s and B_s) of both the cells were observed to increase due to osmosis. The changes in the volumes of the solutions in A_s and B_s are given in the Table . 4 . In the experiments on gallium diffusion through polyurethane membrane(16) the osmotic transfer of water was observed to occur only after complete transfer of gallium to the water side of the cell. Gallium diffusion was thought to "condition" the membrane to allow solvent transfer to occur. This is not true in uranyl nitrate system since an osmotic effect was observed even in the cell containing only ammonium nitrate. The conductivity of B_w was still increasing which indicates that complete diffusion of even ammonium nitrate had not occured before the observation of the osmotic effect.

The water side of cell A was analyzed for uranium. The curves for the increase in conductivity and uranium concentration in A_w followed the same general shape. Thus

Table 4

Change in the Volumes of the solutions in the sample sides of the cells.

	Volume of solution at the beginning of expt. (ml)	Volume of solution at the termination of the expt. (ml)	Increase in volume (ml)
A_S*	675	787	112
B_S**	725	830	105

Change in the volumes of the solutions in the water sides of the cells.

	Volume of solution at the beginning of expt. (ml)	Volume of solution at the termination of the expt. (ml)	Decrease in volume (ml)
A_W*	650	515	135
B_W**	815	690	125

* 11M $[NH_4NO_3]$ + 500 ppm [U]

** 11M $[NH_4NO_3]$

Note: The lack of the volume balance is probably due to the evaporation of the solution creeping out of the ammonium nitrate precipitated on the sides of the stoppers of the sample sides of the cells.

Figure 13

Diffusion of Uranyl Nitrate and Ammonium Nitrate through Polyurethane Membrane and Variation of Specific Conductance of A_w* and B_w** as a Function of Time. (Appendix C, Tables C-10 and C-11).

Circles: sp. cond. in A_w

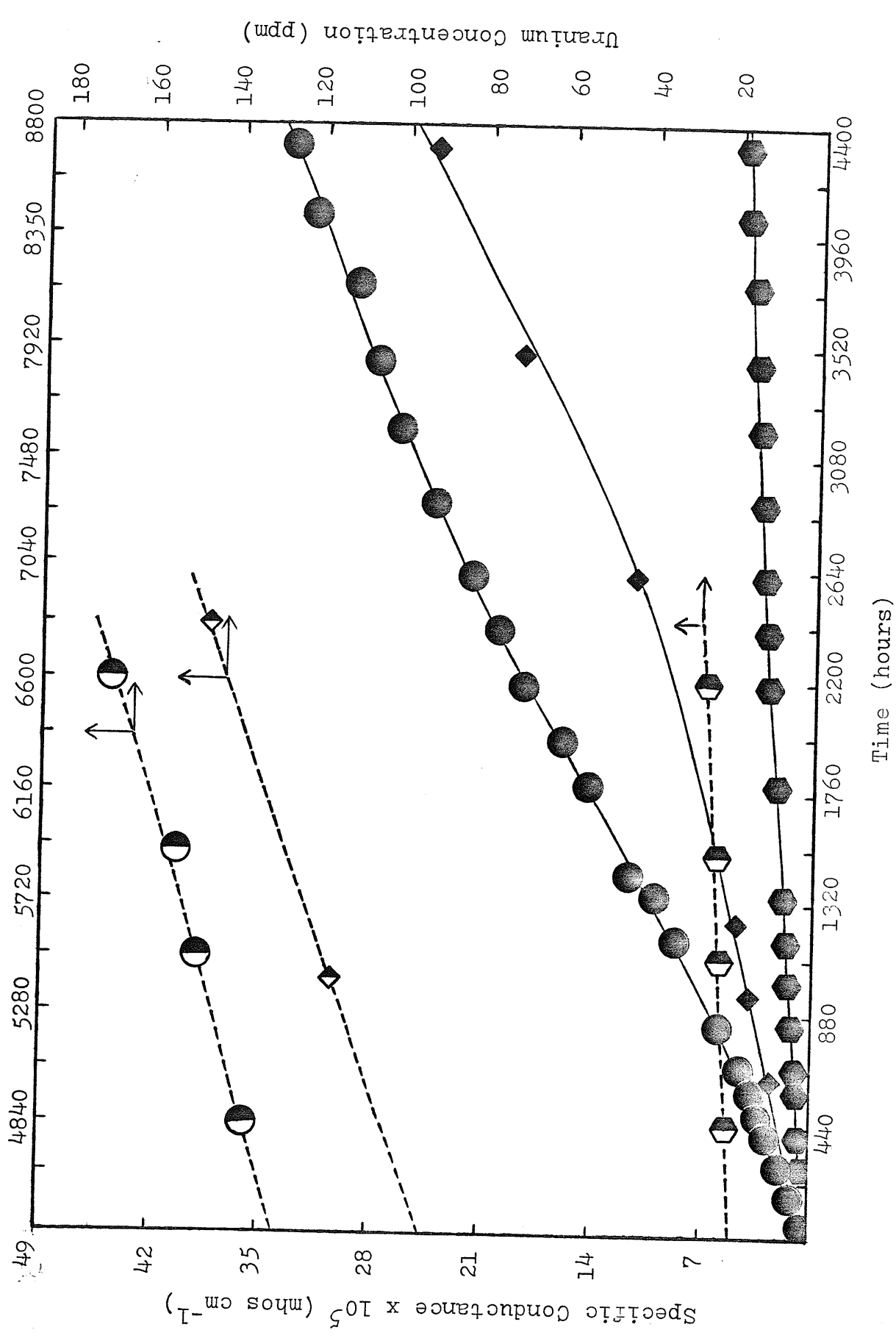
Hexagons: sp. cond. in B_w

Diamonds: Uranium Conc.

---------- Upper Abscissa
_____ Lower Abscissa

* Water side of the cell containing 500 ppm Uranium solution 11 M in amm. nitrate

** Water side of the cell containing 11 M amm. nitrate solution.


Uranium Concentration (ppm)
180
160
140
120
100
80
60
40
20
Specific Conductance x 10^5 (mhos cm^{-1})
49
42
35
28
21
14
7
Time (hours)
440
880
1320
1760
2200
2640
3080
3520
3960
4400
4840
5280
5720
6160
6600
7040
7480
7920
8350
8800

the higher rate of increase of conductivity can be said to be due to diffusion of uranyl nitrate through the membrane. The experiment did not prove to be an efficient one. It was terminated after about 10 months but the uranium concentration in the water side of cell A was observed to increase only up to 146 ppm. A lower uranium concentration would have been observed if no water would have transferred to the other side.

On termination of the experiment, the uranium concentration in the sample side of cell A was observed to be 286 ppm. It would have been observed to be higher if an osmotic effect had not occured.

The transfer of gallium through membrane[16] had taken place against concentration gradient and the phenomenon was said to be "active transport". Since no steady state had arrived in our experiment, nothing can be said about the type of transport taking place.

Part 2 Extraction of Uranium from "ARAD" Phosphate Rock Sample

A. Extraction of Uranyl Chloride

Introduction

In order to study the feasibility of extraction of uranium from HCl solution of "ARAD" Phosphate Rock,[99] experiments were designed to study extraction of uranium from a chloride solution. Extraction of uranium was studied with and without the presence of an additional salting out agent (LiCl).

Experimental

A stock solution was prepared by dissolving 4.455 g of uranyl acetate in water to give 500 ml of solution (5000 ppm in uranium).

Results and Discussion

A foam plug was equilibrated with 150 ml of 500 ppm uranium solution, 6 M in HCl. A very low extraction (about 2%) was observed. Another experiment was performed at low initial concentration of uranium (50 ppm) at 6 M HCl concentration. The foam plug used in this experiment

was previously equilibrated with 6 M HCl for one hour, washed with water till free from HCl and air dried after rinsing with acetone. Due to the instrumental instability, an accurate measurement could not be made but the extraction appeared to be very low (5-10%).

An attempt was made to determine the extraction efficiency in the presence of a salting out agent (LiCl) in solution. A foam plug was equilibrated with 150 ml of 100 ppm uranium solution, 10 M in LiCl and 2 M in HCl concentration. A high extraction (94%) was observed.

B. Feasibility of Extraction of Uranium from "ARAD" Phosphate Rock by OCPUFS

Introduction

An attempt was made to study the feasibility of extraction of uranium from HCl solution of "ARAD" Phosphate Rock[99] containing iron (300-500 ppm) and uranium (10-20 ppm). Extraction of uranium from the chloride solution using OCPUFS could be of industrial importance.

Experimental and Results

About 100 g of the ground rock sample was dissolved by stirring and heating the sample in about 300 ml of concentrated HCl for 3-4 hours and filtered. Final volume of the solution was made up to one litre with 200 ml of water and concentrated hydrochloric acid (giving a solution 9.7 M in HCl). Since iron interferes with the analysis of uranium (i.e. iron (III) thiocyanate also absorbs at 355 nm), it was required to first remove iron from the phosphate solution.

(1) An aliquot of 250 ml of the phosphate solution was passed through a column packed with 7 foam plugs at a rate of 2.5 ml $min.^{-1}$ The solution was then divided into two portions. LiCl was dissolved in one of the portions to give 150 ml of solution 5 M in LiCl. The other portion was diluted to give 150 ml of solution. Both of the solutions were passed through two separate columns, each packed with four foam plugs. Absorbance (due to iron (III) and uranyl) of the solution with LiCl was observed

to be higher than that of the other solution. Obviously LiCl did not help in increasing the extraction of iron (III) chloride.

(2) According to Oren et al.[64] the extraction of iron (III) chloride decreases at concentration of HCl higher than 2.5 M. Thus an attempt was made to compare the extraction of iron (III) chloride from two aliquots of the phosphate solution differing in HCl concentration. The acid concentration in one of the solutions was lowered to 2.5 M by adding NH_4OH. The volume change in the other solution was compensated for by adding an equal volume of 9.7 M HCl. The solutions were then passed through two separate columns each packed with seven foam plugs. The absorbance due to iron (III) and possibly uranium in both solutions decreased but the decrease was greater for the solution with low HCl concentration.

From these eluates, two solutions of uranium (100 ppm) were prepared. In 100 ml of each, a foam plug was squeezed for three hours. The solutions were then analyzed by a difference method. No extraction of uranium was observed from either of the solutions.

(3) Another attempt to study the extraction of uranyl chloride from eluates obtained in step (1) was made. A volume of 100 ml (100 ppm in uranium) was prepared from each eluate, (~9.7 M HCl). The solution without the added lithium chloride, was made 3.6 M in ammonium chloride; (Total $[Cl^-]$ = 13.3 M) whereas the solution already containing lithium chloride was made 0.8 M in aluminum

chloride (Total $[Cl^-]$ = 17.1 M). Only 10% extraction was observed from the ammonium chloride solution, whereas, about 50% extraction was observed from aluminum chloride solution. The high extraction efficiency in the presence of aluminum chloride may be due to the fact that phosphate ion is complexed by the aluminum ion, resulting in the removal of its interference in the extraction of uranyl chloride.(100)

Conclusion

This work demonstrates the feasibility of extraction of uranyl nitrate from aqueous nitrate solution into open cell polyurethane foam sponge in the presence of salting out agent. Under similar conditions the foam is observed to be much more efficient than liquid ether in extracting uranyl nitrate. The distribution coefficient is observed to increase with an increase in the nitrate concentration and is dependent on the type of the cation used. The extraction efficiency is greater, the higher the charge of the cation.

The distribution coefficient decreases with an increase in the equilibrium uranium concentration in the solution. This has been explained by deriving an equation taking into account the extraction of uranyl nitrate as well as salting out agent (ammonium nitrate) and their subsequent ionization in the foam.

The capacity of the foam at 11 M ammonium nitrate concentration and $25 \pm 0.5^{\circ}C$ is observed to be 16% uranium by weight of the foam. The capacity of the foam is lower at lower concentrations of salting out agent.

The extraction is observed to increase with a decrease in temperature. Values of ΔH and ΔS for the extraction process have been calculated to be -4.1 ± 0.5 k cal mole^{-1} and -7.8 ± 1.7 cal $^{\circ}K^{-1}$ mole^{-1} respectively.

The extraction efficiency is independent of pH between 0 and 3 but decreases sharply at higher pH, probably due to formation of unextractable (polyuranyl) species due to hydrolysis of uranyl ion.

The diffusion of uranyl nitrate through polyurethane membrane was observed to be a very slow process. Ammonium nitrate also diffuses through the membrane.

The feasibility of extraction of uranyl chloride using OCPUFS from HCl solution of "ARAD" Phosphate Rock has also been studied. An efficient extraction of uranyl chloride (after removal of interference due to iron (III) chloride by passing through foam) was observed only in the presence of aluminum chloride as salting out agent.

Appendix A.1

Calculation of the distribution ratio

Let initial concentration of uranium in solution = $[U_{in}]$. Therefore amount of uranium initially present in V volume of solution = $[U_{in}]\ V$.

Let $[U_f]$ be the concentration of uranium in foam. Thus amount of uranium extracted by a foam plug of weight $W_f = [U_f]\ W_f$.

The amount of uranium present in solution at equilibrium = $[U_{eq}]\ V$.

Let E be the percent extraction

Then

$$\frac{E}{100} = \frac{[U_f]\ W_f}{[U_{in}]\ V}$$

$$[U_{in}]\ V = \frac{[U_f]\ W_f}{\frac{E}{100}}$$

$$\text{or } [U_{eq}]\ V + [U_f]\ W_f = \frac{[U_f]\ W_f}{\frac{E}{100}}$$

Therefore

$$D = \frac{[U_f]}{[U_{eq}]} = \frac{V}{W_f \left(\frac{100}{E} - 1\right)}$$

Appendix A.2

A correction for the volume change due to the samples taken out for analysis of uranium concentration in the solution after each interval of time in the equilibrium experiments.

let the initial volume of the solution be = V_o
and the initial uranium concentration in the solution be = U_o
Thus the amount of uranium initially present in the solution = $U_o V_o$
After first interval of time, an aliquot of the solution was taken out for analysis of uranium.

Let the uranium concentration in the solution at that time be = U_1 and the volume of solution left be = V_1

The change in the amount of uranium in the solution during first interval of time = the amount of uranium extracted into the foam during that interval = $(U_o - U_1) V_o = \Delta U_1$

Similarly during second interval of time, the amount of uranium extracted into the foam = $(U_1 - U_2) V_1 = \Delta U_2$

and so on.

Therefore

$$\% \text{ Extraction} = \frac{\sum \Delta U_i}{U_o V_o} \times 100$$

Appendix B

Part 1

From the assumption that uranyl nitrate ionizes in the foam

$$DY = K_1K_2K_D \left[NO_3^-\right]^2 \left[1 + \frac{1}{F_2 \left[NO_3^-\right]_f} + \frac{1}{F_1F_2 \left[NO_3^-\right]_f^2} \right]$$

(Equation (10) in Section 1.B) ... (1)

$$\left[UO_2(NO_3)_2\right] \gg \left[UO_2NO_3^+\right] \gg \left[UO_2^{++}\right]$$

$$\left[NO_3^-\right]_f = \left[UO_2NO_3^+\right]_f \qquad .....(2)$$

From equation (5) in section 1.B.

$$\left[NO_3^-\right]_f = \frac{\left[UO_2(NO_3)_2\right]_f}{F_2 \left[NO_3^-\right]_f} \qquad .....(3)$$

$$\text{or } \left[NO_3^-\right]_f^2 = \frac{\left[UO_2(NO_3)_2\right]_f}{F_2} \qquad .....(4)$$

Substituting equation (4) into equation (1)

$$DY = K_1K_2K_D \left[NO_3^-\right]^2 \left[1 + \frac{1}{\left(F_2 \left[UO_2(NO_3)_2\right]_f\right)^{\frac{1}{2}}} + \frac{1}{F_1 \left[UO_2(NO_3)_2\right]_f} \right] \qquad .....(5)$$

From equations (2a) and (3a) in section 1.B.

$$\left[UO_2(NO_3)_2\right]_f = K_1K_2K_D \left[UO_2^{++}\right] \left[NO_3^-\right]^2 \quad \ldots\ldots (6)$$

Therefore

$$DY = K_1K_2K_D \left[NO_3^-\right]^2 \left[1 + \frac{1}{(F_2K_1K_2K_D \left[UO_2^{++}\right] \left[NO_3^-\right]^2)^{\frac{1}{2}}} + \frac{1}{(F_1K_1K_2K_D \left[UO_2^{++}\right] \left[NO_3^-\right]^2)} \right]$$

$$= K_1K_2K_D \left[NO_3^-\right]^2 + \left[NO_3^-\right] \left(\frac{K_1K_2K_D}{F_2 \left[UO_2^{++}\right]} \right)^{\frac{1}{2}} + \frac{1}{F_1 \left[UO_2^{++}\right]} \quad \ldots\ldots(7)$$

At constant $\left[NO_3^-\right]$;

For high $\left[UO_2^{++}\right]$, the second and the third terms in the equation (7) become negligible , therefore

$$\frac{d \log D}{d \log \left[UO_2^{++}\right]} = 0$$

For low $\left[UO_2^{++}\right]$, the third term is negligible compared to the second term, therefore

$$\frac{d \log D}{d \log \left[UO_2^{++}\right]} = -\frac{1}{2}$$

But this is contrary to the experimental results.

Assuming dimerization of uranyl nitrate in the foam

ie. $2\ UO_2(NO_3)_2 \overset{F_d}{\rightleftharpoons} UO_2NO_3^+ \cdot UO_2(NO_3)_3^-$ or $\left(UO_2(NO_3)_2\right)_2$ .....(8)

$$D = \frac{\sum[U]_f}{\sum[U]_{aq}} = \frac{[UO_2(NO_3)_2]_f + [(UO_2(NO_3)_2)_2]_f}{[UO_2(NO_3)_2] + [UO_2NO_3^+] + [UO_2^{++}]} \quad .....(9)$$

From equation (8)

$$D = \frac{[UO_2(NO_3)_2]_f + F_d [UO_2(NO_3)_2]_f^2}{[UO_2(NO_3)_2] + [UO_2NO_3^-] + [UO_2^{++}]}$$

From equations (1) to (5) of section 1.B.

$$D = \frac{[UO_2^{++}]\left[K_DK_1K_2 [NO_3^-]^2 + F_dK_D^2K_1^2K_2^2 [UO_2^{++}][NO_3^-]^4\right]}{[UO_2^{++}]\left[K_1K_2 [NO_3^-]^2 + K_1 [NO_3^-] + 1\right]}$$

substituting $(K_1K_2 [NO_3^-]^2 + K_1 [NO_3^-] + 1) = Y$, we get

$$DY = K_DK_1K_2 [NO_3^-]^2 + F_dK_D^2K_1^2K_2^2 [UO_2^{++}][NO_3^-]^4$$

According to this equation the distribution coefficient increases with an increase in $[UO_2^{++}]$, which is again contrary to the experimental results.

Appendix C

Table C-1.

Abs. vs conc. of uranium in solution (Fig. 2)

U (ppm)	Abs.
5	0.112
10	0.225
15	0.234
20	0.443
25	0.558
30	0.661

Table C-2

Time dependence of the extraction of uranium by open-celled polyurethane foam at various ammonium nitrate concentrations. (Fig. 3)

Time (min)	NH_4NO_3 (M)	5.0	6.0	7.0	11.0
		Concentration of Uranium in Solution (ppm)			
15		491	489	436	228
30		475	446	424	180
45		476	445	392	159
60		459	442	393	147
75		457	440	394	135
90		457	440	392	133
105		457	442	392	128
120		-	-	-	126
135		-	-	-	130
150		-	-	-	126

Table C-3

Time dependence for recovery of uranium loaded on foam into distilled deionized water (Fig. 4)

Time (min)	Conc. of U in soln. (ppm)
15	300
30	350
45	360
60	363
75	363
90	365
105	365
120	365

Table C-4

Time dependence for the extraction of uranium by phosphate type foam from 150 ml of solution, 500 ppm in [U] and 11M in [amm. nitrate] (Fig. 5)

Time (min)	[U] (ppm)
15	278
30	227
45	198
60	178
75	166
90	152
105	142
120	142
135	132
150	125
165	118
180	111
195	111
215	106
225	104
240	100
255	95
300	89

Note: pH of the solution before extraction = 3.0

pH of the solution after extraction = 3.4

Table C-5

Variation of Log D with Log eq. uranium conc. under different conditions of temperature and $[NH_4NO_3]$ (Fig.6)

11 M $[NH_4NO_3]$, 25±0.5°C

$[Ueq]$ (moles l^{-1})	log $[Ueq]$	D	Log D
6.62×10^{-7}	-6.18	3168	3.50
2.94×10^{-5}	-4.53	500	2.70
5.04×10^{-5}	-4.30	555	2.74
8.48×10^{-5}	-4.07	679	2.83
1.91×10^{-4}	-3.72	283	2.45
2.44×10^{-4}	-3.60	383	2.58
3.48×10^{-4}	-3.46	262	2.42
5.29×10^{-4}	-3.28	216	2.33
1.10×10^{-3}	-2.96	212	2.33
1.98×10^{-3}	-2.70	160	2.20
3.11×10^{-3}	-2.51	131	2.12
6.41×10^{-3}	-2.19	78	1.89
1.03×10^{-2}	-1.98	54	1.73
1.33×10^{-2}	-1.88	46	1.66
1.71×10^{-2}	-1.77	36	1.56
2.52×10^{-2}	-1.60	26	1.41
3.42×10^{-2}	-1.46	19	1.27
4.20×10^{-2}	-1.38	16	1.20
5.62×10^{-2}	-1.25	15	1.18
7.52×10^{-2}	-1.12	9	0.97
6.18×10^{-2}	-1.21	11	1.05

Table C-5 continued

7 M $[NH_4NO_3]$, 25± 0.5°C

$[Ueq]$ (moles l^{-1})	log $[Ueq]$	D	Log D
$1.01x.0^{-5}$	-4.99	76	1.88
$1.39x10^{-4}$	-3.86	36	1.56
$4.62x10^{-4}$	-3.34	26	1.41
$9.75x10^{-4}$	-3.01	20.5	1.31
$1.62x10^{-3}$	-2.79	21.3	1.33
$3.46x10^{-3}$	-2.46	16.8	1.23
$6.80x10^{-3}$	-2.17	18.4	1.26
$1.40x10^{-2}$	-1.85	16.4	1.22
$2.09x10^{-2}$	-1.68	14.3	1.15
$3.73x10^{-2}$	-1.43	9.8	0.99

7M $[NH_4NO_3]$, 10±0.5°C

$[Ueq]$ (moles l^{-1})	log$[Ueq]$	D	Log D
$5.17x10^{-4}$	-3.29	45	1.65
$1.39x10^{-3}$	-2.86	36	1.56
$2.94x10^{-3}$	-2.53	30	1.48
$1.36x10^{-2}$	-1.87	19	1.28
$2.91x10^{-2}$	-1.54	11	1.04
$4.43x10^{-2}$	-1.35	9.6	0.98
$3.78x10^{-2}$	-1.42	8.8	0.95

Note: pH of the solutions before extraction = 1.7 to 3.0

pH of the solutions after extraction = 1.8 to 3.3

(pH of the solutions decreases with an increase in the uranyl nitrate concentration.)

Table C-6

Dependence of Log D on Log $[NO_3^-]$ (moles l^{-1}) (Fig. 8)

A. (Nitrate from NH_4NO_3) Log $[NO_3^-]$ (M)	Log D
-2.37*	0.09
0.30	0.20
0.54	0.42
0.70	0.83
0.78	1.04
0.84	1.32
1.04	2.33

*NO_3^- from $UO_2(NO_3)_2 \cdot 6H_2O$ only

B. (Nitrate from $Ca(NO_3)_2 \cdot 4H_2O$)	
0.56	0.62
0.70	1.52
0.84	2.53
1.02	2.93

C. (Nitrate from $Al(NO_3)_3 \cdot 9H_2O$)	
0.32	0.69
0.56	1.16
0.68	1.87
0.78	2.42
0.88	3.07

Table C-7

Variation of amount of uranium loaded on foam as a function of equilibrium uranium Conc. under different conditions. (Fig. 9).

11M $[NH_4NO_3]$, 25±0.5°C

[U]on foam (mg g^{-1})	[Ueq](mg ml^{-1})
0.5	0.00016
3.4	0.007
6.7	0.012
13.7	0.020
12.9	0.046
22.2	0.058
21.8	0.083
26.2	0.146
55.6	0.262
75.5	0.472
96.9	0.740
119	1.52
134	2.46
143	3.16
149	4.08
156	6.00
152	8.15
157	10.00
164	14.70
166	18.00

Table C-7 continued

7M $[NH_4NO_3]$, 25±0.5°C $[U]$ (mg) g^{-1} of foam	$[Ueq]$ (mg ml^{-1})
0.18	0.0024
1.20	0.03
2.80	0.11
4.75	0.23
8.19	0.38
13.87	0.82
29.80	1.62
54.82	3.34
71.27	4.98
88.02	8.89
7M $[NH_4NO_3]$, 10±0.5°C	
5.55	0.12
11.94	0.33
21.00	0.70
61.07	3.23
76.3	6.93
79.6	9.00
102.0	10.60

Table C-8

Effect of change of temperature on distribution ratio from a solution 150 ml in vol., 500 ppm in $[UO_2^{++}]$ and 7 M in [amm. nitrate] (Fig. 10).

T (Kelvin)	$1/T \times 10^3$	log D
273	3.66	1.56
284	3.52	1.56
288	3.42	1.41
299	3.34	1.33
319	3.13	1.11

Table C-9

Log of distribution coefficient as a function of pH (Fig. 11).

pH	log D
0.785	1.415
1.340	1.388
3.178	1.396
4.205	1.076

Table C-10

Variation of specific conductance of Aw and Bw with time (fig. 13).

Time (hours)	Specific Conductance x 10^5 (mhos cm^{-1})	
	in Aw	in Bw
0	0.28	0.315
169	1.21	0.418
287	2.01	0.572
407	2.78	0.751
484	3.25	0.853
575	3.78	0.955
676	4.56	1.07
844	5.92	1.32
1012	7.28	1.51
1180	8.78	1.75
1348	10.1	1.96
1443	11.7	2.06
1799	14.4	2.49
1967	16.0	2.69
2187	18.5	3.00
2407	20.0	3.15
2617	21.8	3.37
2905	24.3	3.59
3199	26.6	3.85
3463	27.9	3.99
3772	29.3	4.26
4040	32.1	4.68
4326	33.5	4.91
4850	36.0	5.33
5498	39.0	5.86
5916	40.4	6.04
6702	44.6	6.87

Table C-11

Diffusion of uranyl nitrate into A_W (fig. 13).

Time (hours)	U (ppm)
628	10
961	15
1249	19
2618	44
3494	72
4312	93
5412	116
6820	146

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