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Extraction of Metal Ions with *N,N*-Disubstituted Amides

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In this paper, liquid alkyl amides are studied as solvents for liquid-liquid extraction of metal ions. Feder first showed that *N,N*-dibutylacetamide is roughly comparable to tributylphosphate as an extractant for uranyl nitrate (*1*). Siddall extended the work of Feder and studied the effects of altering the hydrocarbon substituents of the amide molecule on the extraction of U(VI), Pu(IV), Pu(VI), Np(VI), Th(IV), Zr(IV), and HNO_3 from nitric acid solution (*2*). The thermal stability of amides was shown to be comparable to that of tributylphosphate and the hydrolytic stability of amides on solvent extraction about the same as TBP (*3*). Several other brief reports (*4–8*) deal with substituent effects of amides on solvent extraction of several metal ions.

All of the previous work with amides as extractants has been on the extraction of actinide metal nitrates, zirconium nitrate, and on the extraction of nitric acid itself. The purpose of the present work is to extend the study of the extracting power of amides to several other metal ions from nitrate solution, to study the extracting power of amides on several metal ions from perchlorate solution where the mechanism of extraction is entirely different from that in nitrate solution, and to examine the possible use of amides as reagents for analytical separations.

EXPERIMENTAL

Reagents. The standard solution of zirconium was prepared from hafnium-free $ZrOCl_2{\cdot}8H_2O$ prepared with the Ames Laboratory of Energy Research and Development Administration. All other solutions of metal ions were prepared from reagent grade metal nitrates. *N,N*-Diethyldodecanamide (DED), mp 3–4 °C, was purchased from Eastman Organic Chemicals, and *N,N*-dibutylformamide (DBF), bp 120 °C at 15 mm, $n^{20}\mathrm{D}$ 1.4429, was purchased from Aldrich Chemical Company. Both amides were used without further purification. *N,N*-Dihexylacetamide (DHA) was prepared by overnight reaction of acetic anhydride with di-*n*-hexylamine, dissolved in ether. The solution was shaken with several portions of sodium bicarbonate solution to neutralize the acetic acid formed in the reaction. Then the organic layer was shaken with $2.0M$ hydrochloric acid to remove any amine remaining in the solution. The ether was removed from the product by fractional distillation, and the product was dried over magnesium sulfate. The final product was purified by vacuum distillation at 150 °C at a pressure of 4 mm mercury.

The standard $0.05M$ EDTA solution was prepared from reagent grade disodium dihydrogen ethylenediaminetetraacetate dihydrate.

Arsenazo I, 3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalene-disulfonic acid, was purchased from Eastman Organic Chemicals.

Analytical Techniques. Uranium was determined colorimetrically with Arsenazo I. All other metal ions were determined by titration with EDTA. Calcium was determined with Calmagite at pH 10, and magnesium was determined with Eriochrome Black T at pH 10. The other metal ions were determined with Xylenol Orange and Naphthyl Azoxine S (NAS), as specified by Fritz, Abbink, and Payne (*9*).

Procedure. To 60-ml separatory funnels were added exactly 5 ml of $0.1M$ metal ion in $0.02M$ HNO_3, appropriate amounts of $4.0M$ sodium nitrate or sodium perchlorate, and water to make the volume 10 ml, and 10 ml of the appropriate amide in toluene. The mixture was placed on a Burrell Wrist-Action shaker and equilibrated for 1 hr. The lower aqueous phase was run off and analyzed for the amount of metal ion present after extraction.

RESULTS AND DISCUSSION

Extractions from Nitrate Solution. Distribution ratios for metal ions extracted from aqueous nitrate solution with dibutylformamide (DBF), dihexylacetamide (DHA), and diethyldodecanamide (DED) are given in Tables I, II, and III, respectively.

The acetamide (DHA) extracts uranium(VI) and thorium(IV) strongly, and iron(III), mercury(II), and zirconium(IV) to a lesser degree. Dibutylacetamide behaves much like DHA but has the disadvantage of a higher solubility in the aqueous phase. With the formamide (DBF), the distribution ratios for uranium and thorium are a little lower than with DHA under comparable conditions, but zirconium(IV) is more strongly extracted by DBF. The dodecanamide (DED) is a much less effective extractant; only uranium has a distribution ratio greater than 1.0 under the most favorable extraction conditions.

The data show excellent possibilities for separation of uranium from all other metal ions studied, and for separation of thorium and zirconium from each other and from other metal ions using appropriate amide extractants. For example, comparison of extractions with $1.0M$ nitrate and $3.0M$ amide ($3.5M$ for DHA) show the following separation factors:

U/Th: DBF, 23.1; DHA, 9.4; DED, 41.3
Th/Zr: DBF, 11.9; DHA, 297; DED, 8.0

At $1.0M$ nitrate and $5.0M$ DBF, the separation factor for Zr/Fe is 34.3.

The log distribution ratio was plotted vs. the amide concentration (at constant nitrate) and also vs. nitrate concentration (at constant amide) to show the chemical nature of the extracted species. For uranium, straight line plots were obtained for the log D vs. log amide plots with slopes of 2.1 for both DBF and DHA, and 1.6 for DED. At least for the first two amides, this indicates clearly a 2:1 amide–uranium ratio. Data for plots of log D vs. log nitrate were more erratic but suggest two nitrates for uranium. The extracted species is thus indicated to be $UO_2(\text{amide})_2(NO_3)_2$.

For thorium extracted with DBF, a plot of log D vs. log amide has a slope of 4.0; and log D vs. nitrate, a slope of 3.2. The corresponding plots for DHA show slopes of 3.2 and 3.4, respectively. While these results are somewhat inconclusive, a formula of $Th(\text{amide})_4(NO_3)_4$ for extracted species is likely.

Table I. Distribution Coefficients for Metal Ions Extracted from Nitrate Solution with *N,N*-Dibutylformamide[a]

	0.50*M* NO_3^- 2.0*M* DBF	1.0*M* NO_3^- 2.0*M* DBF	2.0*M* NO_3^- 2.0*M* DBF	1.0*M* NO_3^- 1.0*M* DBF	1.0*M* NO_3^- 3.0*M* DBF	1.0*M* NO_3^- 4.0*M* DBF	1.0*M* NO_3^- 5.0*M* DBF
Fe	0.0	0.0	0.0	0.0	0.0	0.33	1.13
Hg	0.11	0.21	0.32	0.6	0.51	1.39	4.85
Pb	0.0	0.0	0.0	0.0	0.0	0.10	0.19
Th	0.14	0.76	6.05	0.07	4.28	15.9	41.2
U	. . .	24.13	63.10	5.41	99.0	103.0	177.0
Zr	0.0	0.17	0.31	0.12	0.36	2.38	38.8

[a] The distribution ratios for Al, Ca, Cd, Co, Cu, Hg, Mg, Ni, and Zn were zero under all conditions studied.

Table II. Distribution Coefficients for Metal Ions Extracted from Nitrate Solution with *N,N*-Dihexylacetamide[a]

	0.50*M* NO_3^- 2.0*M* DHA	,0.75*M* NO_3^- 2.0*M* DHA	1.0*M* NO_3^- 2.0*M* DHA	2.0*M* NO_3^- 2.0*M* DHA	1.0*M* NO_3^- 0.5*M* DHA	1.0*M* NO_3^- 1.0*M* DHA	1.0*M* NO_3^- 3.5*M* DHA
Fe	0.0	0.02	0.03	0.05	0.0	0.0	0.22
Hg	0.10	0.13	0.20	0.31	0.01	0.03	1.12
Pb	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Th	0.36	0.70	2.48	17.8	0.06	0.33	26.5
U	24.5	63.9	105.0	624.0	4.84	25.3	249.0
Zr	0.03	0.01	0.04	0.04	0.04	0.02	0.09

[a] The distribution ratios for Al, Ca, Cd, Co, Cu, Hg, Mg, Ni, and Zn were zero under all conditions studied.

Table III. Distribution Coefficients for Metal Ions Extracted from Nitrate Solutions with *N,N*-Diethyldodecanamide[a]

	0.50*M* NO_3^- 1.0*M* DED	1.0*M* NO_3^- 1.0*M* DED	2.0*M* NO_3^- 1.0*M* DED	1.0*M* NO_3^- 0.25*M* DED	1.0*M* NO_3^- 0.5*M* DED	1.0*M* NO_3^- 2.0*M* DED	1.0*M* NO_3^- 3.0*M* DED
Fe	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hg	0.09	0.09	0.09	0.09	0.09	0.09	0.25
Pb	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Th	0.06	0.08	0.15	0.07	0.08	0.17	0.66
U	1.13	3.62	13.5	0.53	0.80	10.0	27.1
Zr	0.09	0.14	0.18	0.946	0.05	0.08	0.08

[a] The distribution ratios for Al, Ca, Cd, Co, Cu, Hg, Mg, Ni and Zn were zero under all conditions studied.

Extractions from Perchlorate Solution. The results of the extractions from perchlorate solution with DBF and DED were much different than the extraction from nitrate solution. The distribution ratios are shown in Tables IV and V.

All of the metal ions studied were extracted to some extent by the two amides. As with the nitrate system, the separation of uranium, thorium, and zirconium from other metal ions and from each other seems possible. DED is the most selective solvent for uranium, and it appears that uranium can be separated from all other metal ions regardless of the DED and perchlorate concentrations.

Extraction of zirconium with DBF is the most striking difference between the perchlorate and nitrate systems. Zirconium is extracted only at high DBF and nitrate concentrations but, in perchlorate media, it is strongly extracted under all conditions tried.

Table IV. Distribution Coefficients for Metal Ions Extracted from Perchlorate Solution with *N,N*-Dibutylformamide

	0.50*M* ClO_4^- 2.0*M* DBF	1.0*M* ClO_4^- 2.0*M* DBF	2.0*M* ClO_4^- 2.0*M* DBF	1.0*M* ClO_4^- 1.0*M* DBF	1.0*M* ClO_4^- 3.0*M* DBF	1.0*M* ClO_4^- 4.0*M* DBF	1.0*M* ClO_4^- 5.0*M* DBF
Al	0.20	0.93	10.9	0.01	3.37	∞	∞
Ca	0.11	0.29	1.28	0.01	3.02	20.2	49.9
Cd	0.19	0.56	2.47	0.5	3.45	27.4	40.4
Co	0.17	0.47	2.09	0.01	6.39	28.0	32.5
Cu	0.24	0.77	3.69	0.0	11.7	43.4	87.9
Fe	7.78	19.5	23.5	0.93	19.5	19.5	19.5
Hg	0.66	2.21	9.06	0.47	18.8	∞	∞
Mg	0.03	0.25	0.84	0.02	2.18	10.1	23.3
Ni	0.27	0.90	3.66	0.02	8.99	40.9	82.7
Pb	0.66	1.98	7.48	0.03	16.3	416.0	∞
Th	39.4	94.4	∞	1.29	390.0	∞	∞
U	15.9	79.0	504.0	0.53	693.0	805.0	499.0
Zn	0.08	0.37	1.55	0.0	5.21	23.2	47.4
Zr	∞	∞	∞	∞	∞	∞	∞

Table V. Distribution Coefficients for Metal Ions Extracted from Perchlorate Solution with *N,N*-Diethyldodecanamide

	1.0*M* ClO_4^- 0.25*M* DED	1.0*M* ClO_4^- 0.50*M* DED	1.0*M* ClO_4^- 2.0*M* DED	1.0*M* ClO_4^- 3.0*M* DED
Al	0.0	0.0	0.0356	0.20
Ca	0.0	0.0	0.0	0.70
Cd	0.0	0.0	0.0	0.17
Co	0.0	0.0	0.0	0.11
Cu	0.0	0.0	0.0	0.17
Fe	0.0	0.0	0.0	ppt.
Hg	0.03	0.03	0.10	0.99
Mg	0.0	0.0	0.0	0.06
Ni	0.0	0.0	0.0	0.08
Pb	0.0	0.0	0.0	0.43
Th	0.0	0.0	0.08	3.21
U	0.08	. . .	20.8	332.0
Zn	0.0	0.0	0.0	0.09
Zr	0.0	0.0	0.0	0.67

The large differences in the nitrate and perchlorate systems can be attributed to the different roles that the anions play in the extraction mechanism. The nitrate ion is a coordinating ligand and forms coordination complexes with the metal ions that are extracted from nitrate solution. The nitrate ion is competing for the coordination sites with the amide and water, and consequently the species extracted is a coordination complex. The perchlorate ion is a very poor coordinating ligand, and its spherical charge distribution makes it an excellent ion for formation of ion-association complexes. The perchlorate ion reduces the activity of water and the dielectric constant of the solution greatly; therefore, the amides readily coordinate to all of the sites in the coordination sphere and the species extracted is an ion-association complex.

Straight-line graphs were obtained for plots of log *D* vs. log amide concentration (DBF) at fixed perchlorate. The slopes ranged from 5.5 to 6.4, and averaged 5.8 for uranium(VI), thorium(IV), lead(II), zinc(II), cadmium(II), cobalt(II), nickel(II), and aluminum(III). The slopes of graphs plotting log *D* vs. log perchlorate at fixed DBF averaged 2.0 for uranium and four divalent metal ions, and 2.9 for aluminum(III). Thus the extracted species for a divalent metal ion is $M(amide)_6(ClO_4)_2$. This is in agreement with work on amide complexes of nickel(II) and chromium(II) perchorates which indicated six-coordinate octahedral species (*10, 11*).

Very few extractions of metal ion-association complexes from aqueous to nonaqueous solvents have been reported. The extraction of a great many metal ions as amide complexes from perchlorate solution appears to be unique and may be of practical value.

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Thin Layer Chromatographic Separation and Fluorometric Determination of 4-Aminobiphenyl in 2-Aminobiphenyl

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The Occupational Safety and Health Administration (OSHA) has set human exposure limits to 14 carcinogens (*1, 2*). One of these substances is 4-aminobiphenyl (4-ABP), which has been demonstrated to be a potent bladder carcinogen in man (*3–6*). Conversely, 2-ABP exhibits no carcinogenic activity because it is metabolized to innocuous compounds (*7*). Because of its relative safety, 2-ABP is used commonly as an analytical reagent in the determination of carbohydrates (*8, 9*), glycolaldehyde (*10*), and blood glucose (*11*). Since OSHA has imposed a constant exposure limit to 4-ABP of not more than 0.1% by weight (*2*), a rapid, specific sensitive method is needed for the determination of 4-ABP in 2-ABP.

Stagg and Reed (*12*) have described a colorimetric procedure for the determination of 4-ABP in diphenylamine. This method was later modified (*13, 14*) with a subsequent reduction in the detection limit to 2 ppm of 4-ABP (*14*). Masuda and Hoffmann (*15*) have discussed a fairly involved analytical technique which requires derivation, preconcentration, and quantitation using electron capture gas chromatography.

This paper introduces a rapid, specific, inexpensive, and sensitive procedure for the quantitation of traces of 4-ABP in 2-ABP. The technique involves separation of the amines using thin layer chromatography (TLC); extraction of the isolated materials from the plate; and fluorometric determination. The precision of the entire method is 8% with a detection limit of 2 ppm (2 ng of 4-ABP in 1 mg of 2-ABP).

EXPERIMENTAL

Reagents. All chemicals are of analytical grade and are used without further purification.

Procedure. A TLC developing chamber is lined on 3 adjacent, vertical sides with Whatman No. 1 filter paper, and allowed 30 min to saturate with 120 ml of benzene, the developing solvent. Solutions containing 2-ABP spiked with 4-ABP are prepared in absolute ethanol. Using micropipets, 10 μl of each solution, corresponding to 1 mg of 2-ABP containing varying amounts of 4-ABP, are spotted on a 0.25-mm thick, precoated, nonfluorescent, silica gel plate (E. Merck). The plate is developed in the saturated chamber by allowing the solvent front to travel 12 cm above the point of application which is 2.5 cm from the bottom edge of the plate. The developing time is about 40 minutes. The R_f values are 0.42 for 2-ABP and 0.28 for 4-ABP.

The developed plate is viewed using long ultraviolet irradiation (336 nm). The zones corresponding to 4-ABP are scraped and quantitatively transferred into 15-ml centrifuge tubes containing 5 ml of absolute ethanol and extracted into the solvent. The tubes are then centrifuged at 2500 rpm for 15 minutes. The clear supernatants are decanted into 10-ml volumetric flasks and the extraction procedure is repeated with 3 ml of ethanol. The combined extracts are brought up to 10 ml with ethanol. These solutions are then analyzed fluorometrically.

Instrumentation. An Aminco-Bowman Spectrophotofluorometer equipped with a 150-W xenon lamp is used to quantitate 4-ABP. The photomultiplier voltage is set at 0.8 kV with the amplifier sensitivity set at 80%. The slit arrangement employed is 5, 2, 5, 2, 2, 2 (in mm) from the excitation beam to the detector.

RESULTS AND DISCUSSION

The excitation and emission spectra for both 2-ABP and 4-ABP are shown in Figure 1. Bridges and coworkers (*16*)

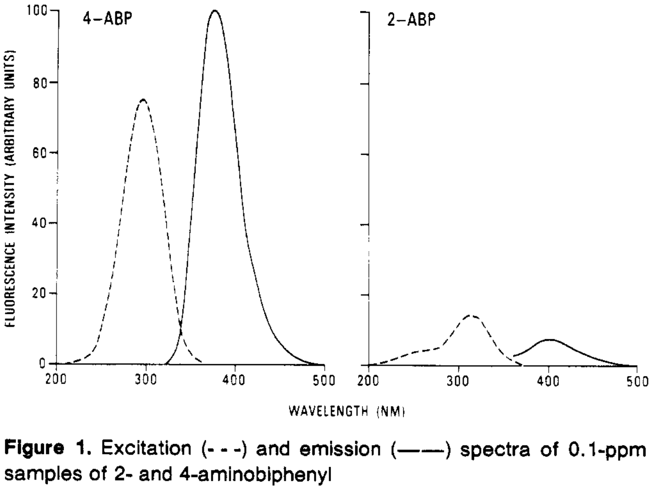

Figure 1. Excitation (- - -) and emission (——) spectra of 0.1-ppm samples of 2- and 4-aminobiphenyl

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