Part IV

Extraction of Americium-Curium-Europium from Lithium Chloride–Hydrochloric Acid by Tertiary Amines

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Phase equilibrium data at 25° C. for the system Adogen 364- or Alamine 336-hydrochloric acid with americium, curium, or europium were determined in the presence of lithium chloride, stannous chloride, and stannic chloride. These data were combined with data in the literature, correlated, and expressed by a mathematical representation for use in analytical investigations of the process.

THERE is current interest in the use of curium isotopes for radioisotopic heat sources (*5*). Cm^{244} is produced by neutron bombardment of a plutonium-aluminum alloy. After neutron bombardment, the alloy is dissolved, and the plutonium isotopes are recovered. Then the americium and curium are purified from the remaining fission products (*1, 2, 4, 6, 7*) by tertiary amine solvent extraction.

Equilibrium distribution data were required to design this final purification process. A mathematical representation of the data was made for use in analytical investigations of the process.

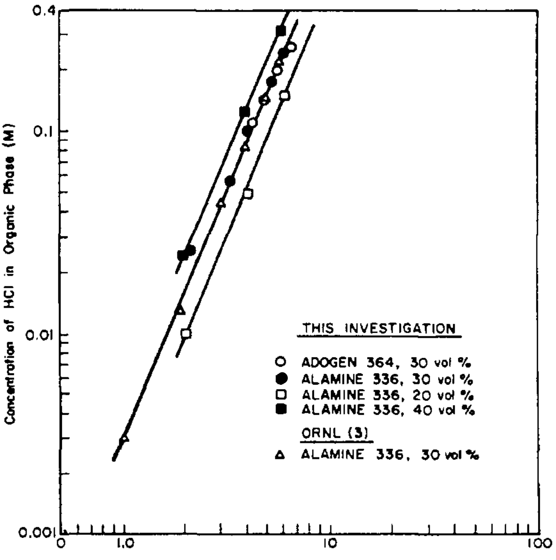

Figure 1. Equilibrium distribution of HCl between organic and aqueous phases at 25° C., other salts absent

MATERIALS

The organic phase was a mixture of *n*-octyl and *n*-decyl tertiary amines, purchased under the trade name Alamine 336 from the Chemical Division of General Mills, Inc., and under the trade name Adogen 364 from Archer-Daniels-Midland Co. This organic phase was diluted, for example, to 30 vol. % (0.60 molar amine) with Eastman Organic Chemicals technical grade diethylbenzene (DEB). The Alamine 336 was purified through a column of dried alumina and activated carbon; and Adogen 364 was used as purchased. Americium and europium tracers were obtained from Oak Ridge National Laboratory. Curium was recovered in the Savannah River Laboratory from plutonium

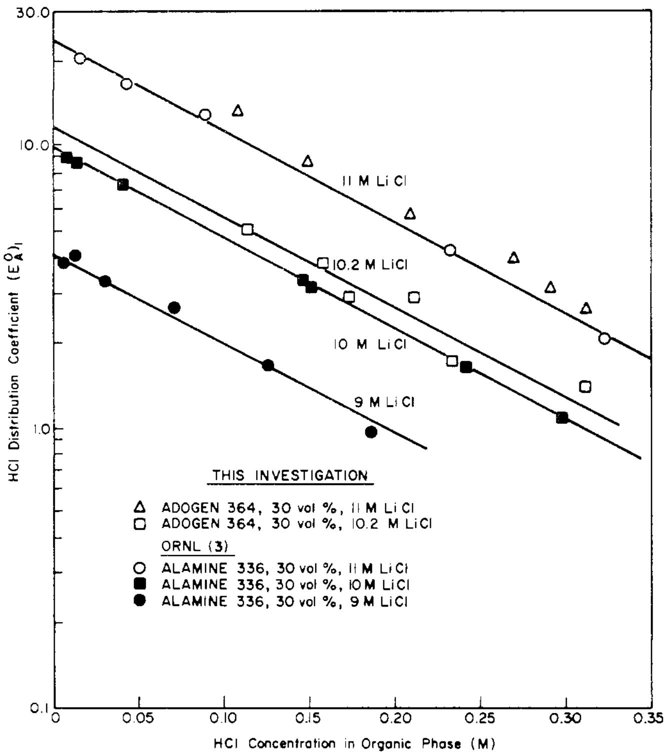

Figure 2. Equilibrium distribution of HCl between organic and aqueous LiCl solutions at 25° C.
Plots of Equation 1 in Table I

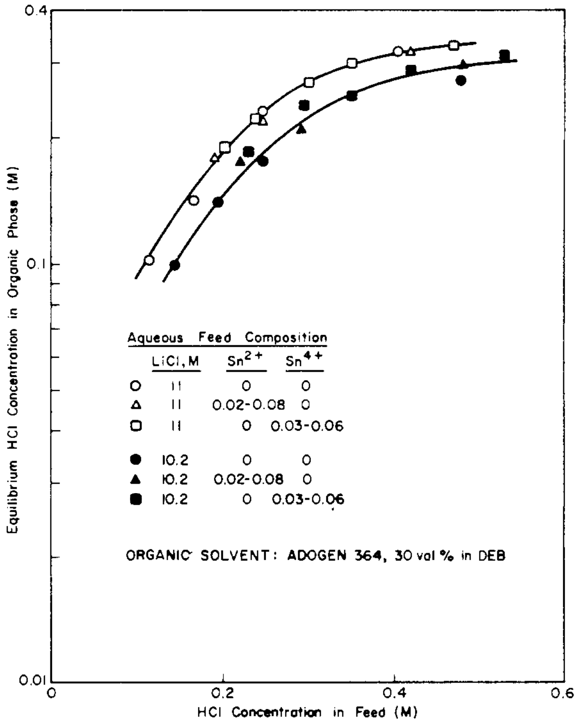

Figure 3. Effect of $SnCl_2$ and $SnCl_4$ on HCl equilibrium at 25° C.

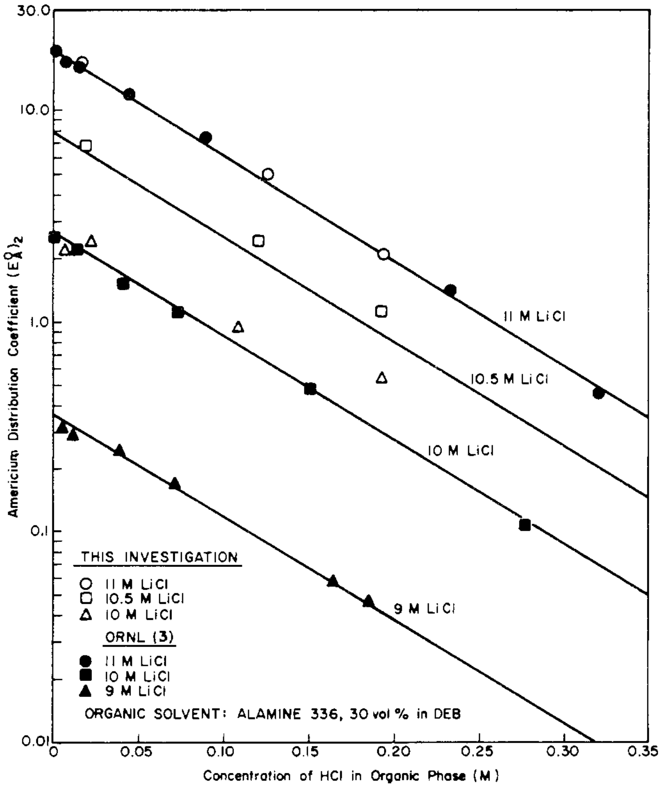

Figure 4. Effect of HCl and LiCl on americium equilibrium distribution at 25° C.
Plots of Equation 2 in Table I

Table I. Equations for Equilibrium Distributions at 25° C. (30 vol. % Adogen 364 or Alamine 336)

Component	Equation[a]
(1) HCL	$(E_a^o)_1 = e^{(-7.4\,y_1 + 0.85L - 6.23)}$
(2) Am	$(E_a^o)_2 = e^{(-11.4\,y_1 + 1.97L - 18.73)}$
(3) Eu	$(E_a^o)_3 = e^{(-11.5\,y_1 + 1.865L - 22.115)}$
(4) Cm	$(E_a^o)_4 = e^{(-10.35\,y_1 + 1.675L - 15.965 - 6SL + 52S)}$

[a] Subscript numbers to E_a^o refer to components.

fuel elements which had been irradiated in Savannah River reactors. Reagent grade lithium chloride, stannous chloride, and stannic chloride were obtained from J. T. Baker Co.

EXPERIMENTAL PROCEDURE

Ten-milliliter portions of organic and aqueous solutions were mixed for 2 to 3 minutes in a Clay-Adams, Inc., Cyclomixer. For the aqueous phase, acid analyses were made using a standard NaOH titration; for the organic phase, potentiometric titration with $0.1M$ NaOH determined the trialkyl amine salt and the excess HCl. The curium and americium concentrations were determined by counting alpha activity in both phases; the europium concentration was determined by gamma counting. The lithium chloride was analyzed with a Technicon Auto-Analyzer equipped with a flame photometer attachment. The stannic ion concentration was determined by chelometric titration. A standard permanganate titration with ferric chloride and Zimmerman-Reinhardt reagent determined the stannous ion concentration.

RESULTS

The hydrochloric acid distribution is shown in Figure 1. There appears to be no significant difference between the use of Adogen 364 and Alamine 336. The effect of lithium chloride on the hydrochloric acid distribution is shown in Figure 2. Stannous chloride, which is added to scavenge radiolytically produced Cl_2 and HOCl, and the resulting stannic chloride had no significant effect on the acid distribution, as shown in Figure 3.

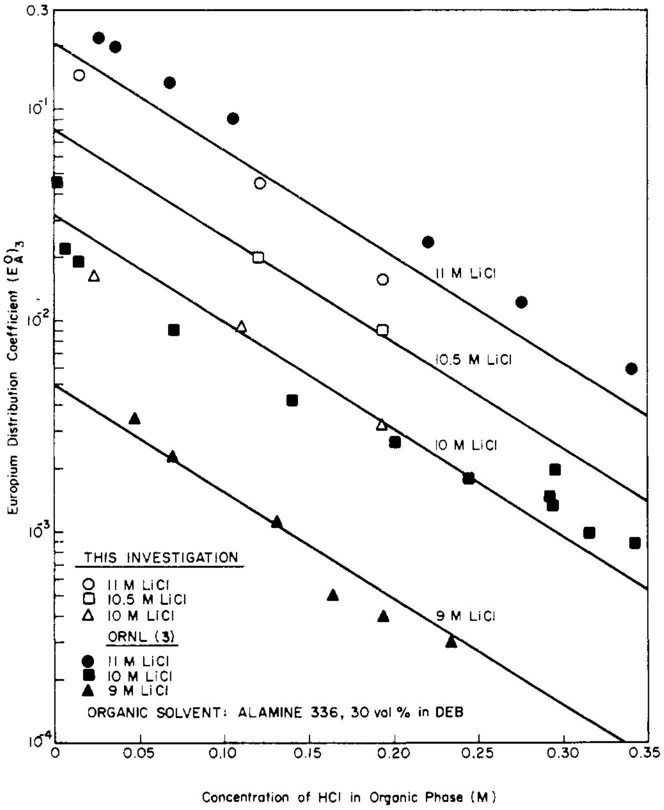

Figure 5. Effect of HCl and LiCl on europium equilibrium distribution at 25° C.

Plots of Equation 3 in Table I

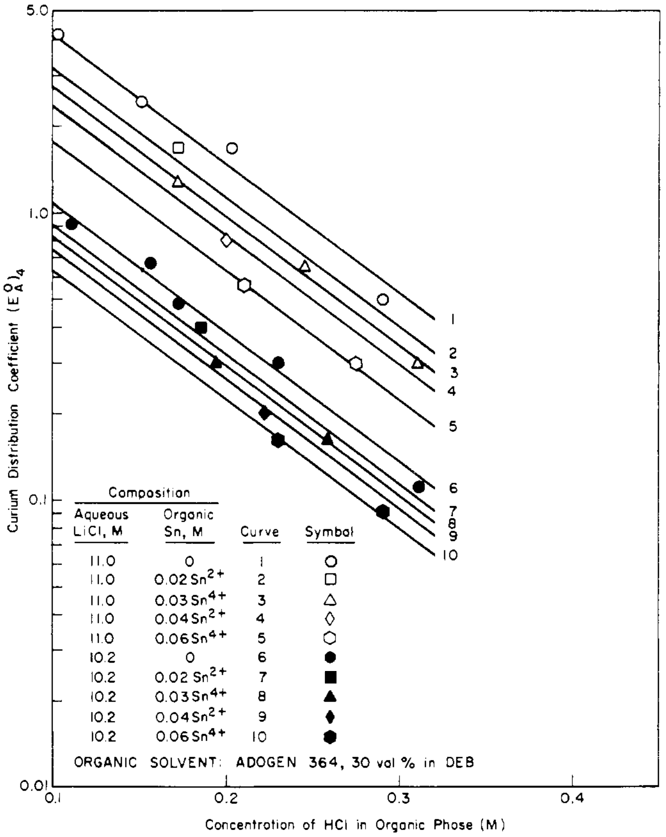

Figure 6. Effect of HCl, LiCl, $SnCl_2$, and $SnCl_4$ on curium equilibrium distribution at 25° C.

Plots of Equation 4 in Table I

The effects of HCl, LiCl, $SnCl_2$, and $SnCl_4$ on the curium distribution are shown in Figure 6. Although data are limited, the effect of the stannous ion concentration appears to be indistinguishable from the effect of stannic ion concentration on the curium distribution. Figures 4 and 5 show the effects of HCl and LiCl on the distribution coefficients for americium and europium.

Distribution data for HCl, americium, and europium were correlated empirically using equations of the form

$$\ln E^c_a = ay_1 + bL + c \qquad (1)$$

No data were obtained for the effect of stannous and stannic chloride on americium or europium. Data for curium distribution were correlated by an equation of the form

$$\ln E^c_a = ay_1 + bL + c + dSL + eS \qquad (2)$$

where S and L are the organic stannous (or stannic) chloride and aqueous lithium chloride concentrations, respectively. These equations, in exponential form, are given in Table I, and they are plotted as solid lines in Figures 2, 4, 5, and 6. These equations are valid, for uses contemplated in future analytical investigations, over lithium chloride concentrations of 9 to 11*M* for hydrochloric acid, americium, and europium. The equation for the curium distribution includes the effect of stannous and stannic chloride from a concentration of 0 to 0.06*M*. The hydrochloric concentration in the organic phase was varied over a range from near zero to approximately 0.3*M*. The lithium chloride remained in the aqueous phase; the stannous and stannic chloride were essentially all in the organic phase at equilibrium. Distributions of americium, curium, and europium were assumed to be independent of each other and to have no significant effect on the hydrochloric acid distributions at the dilutions encountered. These elements were present in tracer levels of about 10^{-8} molar. The distribution data were smoothed by cross plotting as a function of lithium chloride concentrations at fixed acid concentrations. Then, the empirical representation of the data from this investigation and the literature was made. There was good agreement between the experimental data and those reported in the literature (*3*). No satisfactory explanation has been made of the mechanisms involved in this highly salted system.

CONCLUSIONS

The equations in Table I may be used to represent the data presented in Figures 2, 4, 5, and 6; however, caution should be exercised in extrapolating these equations beyond the range of the experimental data. Stannous or stannic chloride affect the distribution of curium, but have no significant effect on hydrochloric acid distribution. (Data for the effect of the stannous and stannic ions on the distribution of americium and europium were not obtained.) Figures 1 and 2 indicate that there is no significant difference between the use of purified Alamine 336 or Adogen 364.

ACKNOWLEDGMENT

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NOMENCLATURE

a, b, c, d, e = empirical constants
E^0_a = equilibrium distribution coefficient, organic concentration divided by aqueous concentration
L = aqueous lithium chloride concentration, molar
S = organic stannous or stannic chloride concentration, molar
y_1 = equilibrium acid concentration in organic phase, molar

LITERATURE CITED

(1) Baybarz, R.D., Weaver, B., Oak Ridge National Laboratory, Oak Ridge, Tenn., **ORNL-3185**, 1961.
(2) Baybarz, R.D., Weaver, B., Kinser, H.B., *Trans. Am. Nucl. Soc.* **5**, No. 1, 17 (1962).
(3) Culler, F.L., Bresse, J.E., *et al.*, Chem. Tech. Div. Ann. Prog. Rept. **ORNL-3452**, May 1963.
(4) Culler, F.L., Ferguson, D.E., *et al.*, *Ibid.*, **ORNL-3314**, June 1962.
(5) "Isotopes and Radiation Technology," **1**, No. 2, 206 (Winter 1963–1964), Oak Ridge National Laboratory, Oak Ridge, Tenn.
(6) Leuze, R.E., Baybarz, R.D., Weaver, B., *Nucl. Sci. Eng.* **17**, 252–8 (1963).
(7) Moore, F.L., *Anal. Chem.* **33**, 748 (1961).

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Phosphines and Phosphine Sulfides Containing Highly Condensed Aromatic Groups

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The preparation and properties of four new phosphines and six new phosphine sulfides are reported. Preparation of the phosphines is accomplished by condensation of a phosphorus trihalide, or substituted halide with the aryllithium compound in an inert atmosphere. The sulfides are prepared by refluxing the phosphine with sulfur in an appropriate solvent. The phosphines and sulfides are colorless solids.

SEVERAL compounds of the type PR_3, PR_2R', PRR_2', and the corresponding sulfides, where *R* is a highly condensed aromatic group and *R′* is a phenyl group, have been prepared as part of an over-all program concerned with studies of the donor properties of group V chalcogenides. These compounds may represent a unique type of coordinating agent, especially in the solid state, since they may be able to act as donors either through the aromatic ring systems, or by way of the free electron pair on the phosphorus atom in the phosphine, or on the sulfur atom in the phosphine sulfide.

Relatively few tertiary phosphines and phosphine sulfides containing highly condensed aromatic groups have been previously reported. Mikhailov and Kucherova (*5*) reported the preparation of tri-1-naphthyl-, tri-9-phenanthryl-, tri-9-anthryl-, tri-1,2-benzanthr-10-yl-, and tri-1,2-benzanthr-7-ylphosphine. Hart and Mann (*3*) reported the preparation of di-1-naphthylphenylphosphine, and Anschutz, Kraft, and Schmidt (*1*) prepared tri-1-naphthylphosphine and several of its derivatives. Worrall (*7*) reported the preparation of tri-4-biphenylphosphine and its sulfide.

PREPARATION

Phosphines. All phosphines were prepared by the reaction of the appropriate phosphorus halide with the aryllithium compound. The aryllithium compounds were prepared by the halogen-lithium interconversion method described by Jones and Gilman (*4*). The aryl bromide, in ethyl ether, was added dropwise with stirring to *n*-butyllithium under a dry nitrogen atmosphere. The phosphine was then prepared by the addition of 80% of the theoretical amount of the appropriate phosphorus halide dissolved ethyl ether. The mixture was refluxed for 1 to 1½ hours, hydrolyzed with 10% aqueous sodium hydroxide, and the organic layer was then separated and dried over anhydrous magnesium sulfate. Evaporation of the organic solvent under reduced pressure led directly to precipitation of the phosphine. The following reactions are involved:

$$\mathrm{ArBr} + n\text{-}\mathrm{BuLi} \rightarrow \mathrm{ArLi} + n\text{-}\mathrm{BuBr}$$

$$3\mathrm{ArLi} + \mathrm{PCl_3} \rightarrow \mathrm{Ar_3P} + 3\mathrm{LiCl}$$

Phosphine Sulfides. All of the phosphine sulfides were prepared by refluxing the phosphine with an equivalent amount of sulfur in *n*-hexanol or *n*-butanol for 2 to 3 hours. The hot solution was filtered to remove the excess unreacted sulfur, and the crystalline product separated upon cooling. Purification was accomplished by several recrystallizations from an appropriate solvent. The list of compounds prepared, along with pertinent physical data, is given in Table I.

DISCUSSION

The triarylphosphines reported here were quite stable in air. Although condensations were carried out in an oxygen-free atmosphere, once the phosphine was isolated, all recrystallizations were carried out in the laboratory atmosphere and no evidence of oxide formation was noted. The melting points of several of the phosphines were redetermined after the compounds had been stored in screw-capped bottles for 1 or 2 months, and no changes were observed.

The reported yields are not necessarily the highest attainable since no organized study was made for this purpose.

Tri-1-naphthylphosphine has been prepared on at least three previous occasions. Mikhailov and Kucherova (*5*) reported its preparation in 1952 by the reaction of 1-naphthyllithium with phosphorus trichloride. They observed a melting point of 278 to 80° for the compound. Anschutz, Kraft, and Schmidt (*1*) reported in 1939 the preparation of tri-1-naphthylphosphine by the reaction of 1-naphthylmagnesium bromide with phosphorus trichloride. After recrystallization from dioxane, they observed a melting point of 282°. Plets (*6*) in 1938 reported a melting point of 189° to 90° for tri-1-naphthylphosphine (recrystallized from benzene–ethyl ether).