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AMINES AS EXTRACTANTS – SURVEY OF THE DESCRIPTIVE AND FUNDAMENTAL EXTRACTION CHEMISTRY

C. F. Coleman

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AMINES AS EXTRACTANTS — SURVEY OF THE DESCRIPTIVE AND FUNDAMENTAL EXTRACTION CHEMISTRY

C. F. Coleman

Paper presented at the Solvent Extraction Chemistry Symposium,
Gatlinburg, Tennessee, October, 1962

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CONTENTS

AMINES AS EXTRACTANTS — SURVEY OF THE DESCRIPTIVE AND FUNDAMENTAL EXTRACTION CHEMISTRY*

C. F. Coleman

ABSTRACT

Both the study and the use of extractions with high-molecular-weight amines (including quaternary ammoniums) in organic solution are increasing extensively. While equilibria have been measured in the extraction of an increasing range of acids and metal ions, a difficulty remains unresolved in that the amine concentration power-dependence of extraction often indicates a different stoichiometry of the complex existing in the organic phase than do limiting loading and other considerations. Nevertheless, amine extraction serves as a useful tool in studying complexes formed in aqueous systems.

Process applications have progressed especially in nitrate and chloride systems, in addition to the sulfate systems first emphasized. Systematic surveys, together with information accruing from process development, have extended the ranges of extractions that can be correlated in usefully generalized patterns, which in turn should accelerate the development of new applications. However, many more areas remain to be surveyed before the many pertinent variables will have been covered.

New amines of all classes have become available at commercial, development, or research-sample levels, while a few previously promising amines have become less available. Descriptions and current sources are reviewed.

63 references

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*Paper presented at the Solvent Extraction Chemistry Symposium, Gatlinburg, Tennessee, October, 1962.

1. INTRODUCTION

Extraction with high-molecular-weight amines has been known for nearly fifteen years, since reported in 1948 by Smith and Page.[1] Analytical applications were soon begun and have grown steadily.[2,3] Intensive development on hydrometallurgical uses[4] reached commercial application in 1957,[5,6] with rapid expansion since then in the production of uranium and related metals. The availability of heavy amines has grown, during that time and largely in direct response to the hydrometallurgical developments, from the earlier preponderant emphasis on little beyond the primary amines and their methyl derivatives to a wide range of structures in all classes. Currently, amine extraction is receiving increasingly widespread attention for process applications, while many laboratories throughout the world are studying its descriptive and physical chemistry and using it as a physicochemical tool. Several aspects of those studies and developments were presented in other papers of the Solvent Extraction Chemistry Symposium. The present paper attempts a broader review of the current status of amine extraction, with particular attention to amine extraction mechanism, separations and recovery applications, and systematic correlations of extraction systems, together with a summary of the current availability of amines.

2. THE NATURE OF AMINE EXTRACTION

Amine extraction can be expressed either as anion exchange, implying transport of ions, or as adduct formation, implying transport of neutral species, as illustrated by equations in Table 1. Although these alternative implications may sound drastically different, they represent only an arbitrary choice of description for equilibrium extractions, as the alternative equations are thermodynamically equivalent. (Note that the existence of this choice does not detract from analogies and comparisons with resinous anion exchange, which actually presents the same alternatives and equivalence although they are seldom emphasized.) Equilibration is relatively rapid in most amine extraction systems, except when slow redistribution among aqueous species intervenes. The response to the major extraction variables is usually relatively simple, reproducible, and readily established by empirical methods sufficient for process development.

Table 1. Types of Reactions in Amine Extractions

Reactions of the protonated amine can be written to represent the interchange of ions (×) or to represent the addition of neutral species (+). In some cases one form is considerably simpler than the other, e.g., (+) simpler than (×) for acid extraction and (×) simpler than (+) for anion replacement. In other cases there is little difference, as in metal extraction. In all cases the two forms are thermodynamically equivalent, and cannot be distinguished by any measurements made at equilibrium. In the reactions below, the dotted underlines indicate the organic phase.

	Acid Extraction
(×)	$\underset{\bullet\bullet\bullet}{R_3N} + H^+X^- + H_2O \rightleftharpoons \underset{\bullet\bullet\bullet\bullet\bullet\bullet}{R_3NHOH} + H^+X^- \rightleftharpoons \underset{\bullet\bullet\bullet\bullet\bullet\bullet}{R_3NH^+X^-} + H_2O$
(+)	$\underset{\bullet\bullet\bullet}{R_3N} + H^+X^- \rightleftharpoons \underset{\bullet\bullet\bullet\bullet\bullet\bullet}{R_3NH^+X^-}$
	Anion Replacement
(×)	$\underset{\bullet\bullet\bullet\bullet\bullet\bullet}{R_3NH^+X^-} + H^+Y^- \rightleftharpoons \underset{\bullet\bullet\bullet\bullet\bullet\bullet}{R_3NH^+Y^-} + H^+X^-$
(+)	$\underset{\bullet\bullet\bullet\bullet\bullet\bullet}{R_3NH^+X^-} + H^+Y^- \rightleftharpoons \underset{\bullet\bullet\bullet}{R_3N} + H^+X^- + H^+Y^- \rightleftharpoons \underset{\bullet\bullet\bullet\bullet\bullet\bullet}{R_3NH^+Y^-} + H^+X^-$
	Metal Extraction
(×)	$\underset{\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet}{mR_3NH^+X^-} + MX^{-m}_{(m+n)} \rightleftharpoons \underset{\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet}{(R_3NH)_m MX_{(m+n)}} + mX^-$
(+)	$\underset{\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet}{mR_3NH^+X^-} + MX_n \rightleftharpoons \underset{\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet\bullet}{(R_3NH)_m MX_{(m+n)}}$

However, comparison of those empirical relations with the mass-action relations expected of extraction systems early showed an apparent anomaly, which has not yet been resolved: an apparent constant activity of amine salt over a considerable concentration range in the organic solution. This was tentatively ascribed to colloidal dispersion of the amine salt, but subsequent studies in the sulfate system showed that such dispersions do not always occur.*

"Constant activity" of the amine salt was first observed in the intensive studies of uranium extraction from slightly acid sulfate solutions by amine sulfates in hydrocarbon diluents.[7] It showed up in three ways:

1. It correlated sulfuric acid extraction by didecyl-[8,9] and trioctylamine,[10] which otherwise appeared considerably different at different amine concentrations between 0.05 and 0.5 M.

2. Loss of amine sulfate through its aqueous solubility, measured with considerable care because of its economic importance in ore treatment, showed an almost constant concentration of amine sulfate in a given aqueous solution, from a given amine-diluent combination even though varied over a considerable amine concentration range.**,[11] This effect was not due to simple aqueous saturation with the amine salt, since the concentration level of the amine salt in the aqueous phase differed considerably with different diluents for the same amine.

3. Uranyl sulfate extraction coefficients varied with close to the first power of the amine concentration when at low loading, although both the loading limits and the hydrogen exchange from displaced bisulfate

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*The anomalous behavior might best be described as an unexplained large variation of the practical activity coefficient of the amine salt, as some inverse function of its concentration in the organic phase. "Constant activity over a range of concentrations" is, of course, identical with "activity coefficient inversely proportional to concentration." The hypothesis of colloidal dispersion (a third phase of essentially constant composition) offered a simple explanation for such behavior of the practical activity coefficient. When colloidal dispersion was refuted as a general trait of the amine salts concerned (see below), the varying practical activity coefficients remained unexplained and hence "anomalous."

**A few amines showed this effect clearly, while most were either too soluble or too insoluble for definite interpretation, but none contradicted it.

showed four to six amines bound per uranium extracted.[12,13] Moreover, the same linear dependence held into the region of significant loading and even up close to saturation, provided that the concentration of unbound amine were calculated on the basis of four to six amines bound per uranium. That is, the uranium extraction isotherms were well fitted by expressions of the form

$$E_a^o(U) \approx E_1\{[\text{amine}] - n[U]\}^m ,$$

where $E_a^o(U)$ is the extraction coefficient for uranium, m is close to 1, and n equals 6 with didecylamine and between 4 and 5 with trioctylamine. Quantities in brackets represent molarities, and E_1 is the intrinsic extraction coefficient extrapolated to 1 M uncomplexed amine. The expected relation would be $n = 2m$ ($2m$ instead of m because there are two amines per monomeric amine sulfate unit).

Similar behavior has since been found in extraction of uranium(IV) sulfate,[14] thorium sulfate,[15,16] uranyl nitrate,[17] and plutonium nitrate.[18] Again (Table 2), empirical extraction isotherms are fitted by equations of the form

$$E_a^o(M) \approx E_1\{[\text{amine}] - n[M]\}^m ,$$

where m does not equal n (as expected with nitrate) or $n/2$ (as expected with sulfate), although m is not always 1.* While many extraction systems have been reported as involving, for example, one amine or two amines per extracted metal ion on the basis of the observed first- or second-power dependence on amine concentration, there is usually no indication that any other means of measuring n was considered, and hence there is room for suspicion that in these cases also n may differ from m.

As noted above, the situation of m being about 1 while n is greater than 1 (with monovalent anions; etc.) would be accounted for if the amine salt existed in large aggregates, provided that they retained the extracted metal without depolymerization. Alternatively, the situation of n being greater than m would be accounted for by small polymers of aggregation

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*While n appeared constant from low to high loading in each amine-uranyl sulfate system, it decreased somewhat with increasing loading of uranyl and plutonium(IV) nitrates in trilaurylamine.

Table 2. Empirical Extraction Isotherms

$E_a^o(M) \approx E_1\left\{[\text{amine}] - n[M]\right\}^m$	Reference Number
Uranyl sulfate:	
$E_a^o(U) \approx E_1\left\{[\text{DDA}] - 6[U]\right\}$	11,12
$E_a^o(U) \approx E_1\left\{[\text{TOA}] - 4.7[U]\right\}$	11,13
Uranium(IV) sulfate:	
$E_a^o(U) \approx E_1\left\{[\text{PrJM}] - 8[U]\right\}^3$	14
Thorium sulfate:	
$E_a^o(\text{Th}) \approx E_1\left\{[\text{DDA}] - 6[\text{Th}]\right\}^{<1}$	15,16
Uranyl nitrate:	
$E_a^o(U) \approx E_1\left\{[\text{TLA}] - (4 \rightarrow 2)[U]\right\}$	17
Plutonium(IV) nitrate:	
$E_a^o(\text{Pu}) \approx E_1\left\{[\text{TLA}] - (4 \rightarrow 3)[\text{Pu}]\right\}^2$	18

DDA = di-_n_-decylamine; TOA = tri-_n_-octylamine; PrJM = Primene JM-T; TLA = trilaurylamine (see Table 4).

number n/2m for sulfate (or n/m for nitrate, etc.), that is, aggregation number of 2 to 2.5 for trioctylamine sulfate. In contradiction to both of these possibilities, direct evaluation of the weight-average molecular weights by light scattering showed that large aggregates are exceptional rather than usual and that trioctylamine sulfate in particular is monomeric* (Table 3).[19,20] Moreover, the uranyl-didecylamine-sulfate complex proved to be monomeric instead of being retained in the aggregates. This, and the monomeric trioctylamine sulfate, were both confirmed by viscosimetry and by isopiestic vapor balancing.[19]

An entirely different explanation for $m \neq n$ was proposed on the basis that the increased interfacial area during normal agitation might shift the point of equilibrium. Tests comparing uranium extractions in complete-dispersion contacting and in quiescent stirred-interface contacting did indeed show marked and reproducible differences in uranium extraction from 0.005 M sulfuric acid with trioctyl- and didecyl-[21] and 1-(3-ethylpentyl)-4-ethyloctylamine.[22] Quiescent extraction with didecylamine sulfate actually gave the nearly-zero slope theoretically expected in extraction by large aggregates to give monomeric product (Fig. 1). However, such differences were not obtained over all the pertinent extraction conditions, nor with several other amines tested. Thus the observed effect of dispersion is important in itself, and points up a precaution that should be considered in all liquid-liquid equilibrations, but it did not clarify the "anomalous" amine extraction.

Current work in this laboratory includes the direct evaluation of activities of organic-phase components by isopiestic and other vapor-pressure measurements.

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*One possible difference between uranium extraction and light-scattering tests with trioctylamine sulfate at the higher concentrations in benzene is that for the latter tests some water was removed from the organic phase, by gentle warming and centrifugation, to avoid misting in preparing concentration series by dilution. However, this was not required with the series in nonane, which also showed no aggregation.

Table 3. Degree of Aggregation of Some Amine Sulfate Species

		Mole Ratio			
Species	Concentration Range ($\underline{M}$)	H_2SO_4 / Amine	H_2O / Amine	U / Amine	Aggregation No.
	Solutions in benzene[19]				
Tri-n-octylamine sulfate	0.02 -0.17	0.508	2.03		1[a]
--bisulfate	0.04 -0.18	0.917	0.92		2
--sulfate-uranyl sulfate	0.02 -0.05	0.464	0.93	0.244	1
Bis(1-isobutyl-3,5-dimethylhexyl)amine sulfate	0.005-0.04	0.505	1.36		4
--sulfate-uranyl sulfate	0.003-0.04	0.449	1.12	0.224	~1
Methyl di-n-octylamine sulfate	0.02 -0.3	0.495	5.15		9
--sulfate-uranyl sulfate	0.002-0.05	0.474	1.45	0.242	1
1-(3-Ethylpentyl)-4-ethyloctylamine sulfate	0.02 -0.3	0.510	4.23		11
--sulfate-uranyl sulfate	0.004-0.03	0.442	1.17	0.167	2
Di-n-decylamine sulfate	0.006-0.04	0.505	1.01		38
--sulfate-uranyl sulfate	0.002-0.01	0.417	0.42	0.208	~1[a]
	Solutions in 97% n-nonane—3% tridecanol[20]				
Tri-n-octylamine sulfate	0.006-0.1	0.5			1
Trilaurylamine sulfate	0.006-0.1	0.52			1
Bis(1-isobutyl-3,5-dimethylhexyl)amine sulfate	0.006-0.1	0.505	0.5		2
1-(3-Ethylpentyl)-4-ethyloctylamine sulfate	0.004-0.07	0.515	0.6		6
Di-n-decylamine sulfate	0.007-0.05	0.52	0.7		5-12[b]

[a] Aggregation number of 1 confirmed by isopiestic vapor balancing.

[b] Aggregation number varying with concentration.

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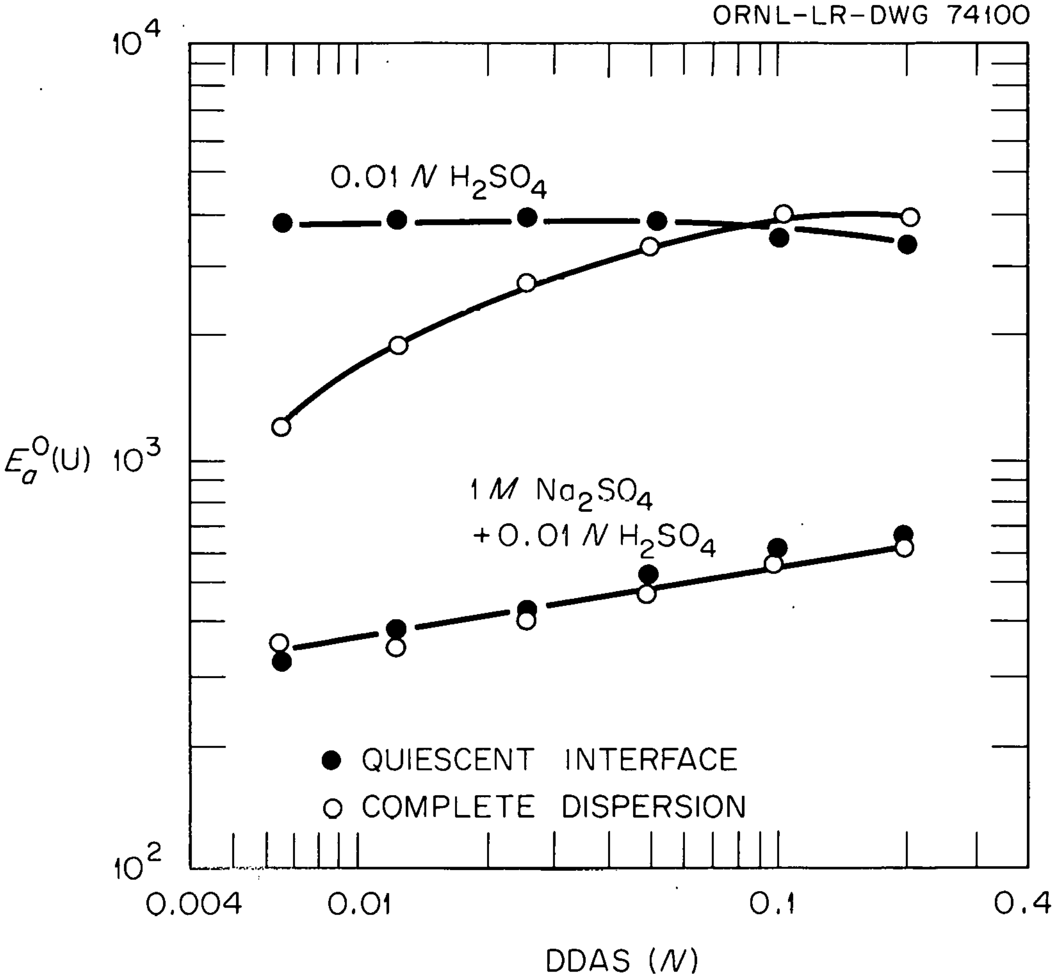

Fig. 1. Effect of Degree of Agitation on Extraction.[21] Di-*n*-decylamine (as normal sulfate, DDAS) in benzene; constant loading at mole ratio U:amine = 0.05.

3. PHYSICOCHEMICAL USES

Uncertainty of mechanism and lack of evaluated activity coefficients within the organic phase do not prevent effective use of amine extraction as a probe in the study of aqueous-phase systems. This is rigorously true when tests are arranged so that an unchanging organic phase is used to determine the conditions for constant activity of an extractable species in a series of changing aqueous phases. In addition, its use can often be extended to tests with varying composition of the organic phase provided that it is reasonable to assume that any variations of the organic-phase activity coefficients of the pertinent species will be in constant ratio, and especially if some kind of cross-check is available to support the results.

Such use of amine extraction closely parallels long-established uses of resinous ion-exchange sorption. Extraction has the advantage of using a truly distinct phase that can be separated cleanly from the aqueous phase for chemical analysis or other examination. It does not have the problem that anion-exchange resins do of invasion by nondistributing aqueous-phase species. Often the difference in distribution between extractable and "nonextractable" species is so great that the latter can be ignored; when they cannot be ignored, complete separation of the phases allows direct analysis. These general advantages are of course characteristic of all liquid-liquid systems where there is negligible miscibility between the phases. Of these, amine extraction is advantageous when simple or complex anions are the pertinent species, and it should also be a useful complement to cation-exchange extraction, which reflects (especially) the uncomplexed cation.

The first such use of amine extraction reported was a study of plutonium(IV)-nitrate complexing in aqueous nitrate-nitric acid solution.[23] Amine phases of varying composition were used, against aqueous nitrate solutions adjusted to constant ionic strength with perchlorate, so that adjustments for perchlorate extraction and assumptions about organic-phase activities were required. The conclusion that $Pu(NO_3)_4$ is the only significant complex at 1-4 $\underline{M}$ HNO_3 or >1 $\underline{M}$ $NaNO_3$ was supported by spectrophotometric data and by other extraction data. The evaluation of formation constants was not attempted.

In a recent study, rapid equilibration in amine extraction was used to infer transient concentrations in the time-dependent nitrosylruthenium nitrate complex system.[24] Extractions with and without loading effects were combined with spectrophotometric measurements to identify the nitrato species of different extractabilities, and to determine their proportions in aqueous solutions.

The utility of this type of approach should increase as empirical and theoretical information on activities in the organic phase increases. Some applications will depend only on a few (often two) activity coefficients remaining in constant ratio. In the plutonium nitrate study cited, the activity coefficient ratio for nitrate and perchlorate was shown to be fairly constant over the aqueous composition range used.[*] A recent study of trace bromide distribution between amine chloride and aqueous chloride solutions showed that the activity coefficient ratio of organic-phase chloride and bromide was constant over a greater than 100-fold aqueous chloride concentration range, except when excess acid was extracted from concentrated hydrochloric acid.[25]

The other approach, that based on a constant composition of the amine phase, was used in investigating the aqueous sulfate complexing of uranyl[13] and thorium,[15,16] using the established information that the amine-sulfate-bisulfate equilibrium depends only on aqueous-phase sulfuric acid activity,[9,10] and that the activity of the sulfuric acid can be maintained constant over a considerable range of sulfate ion concentrations.[26] The achievement of constant organic-phase composition was confirmed by direct analyses. Since the aqueous ionic strength necessarily varied, the results were

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[*] The test was stated in terms of the aqueous-phase activity coefficient ratio only, all organic-phase activity coefficients having been assumed to be constant.[23] The test actually showed that the aqueous-phase and organic-phase activity coefficient ratios were close to proportional, but the activity coefficient of the organic-phase plutonium species was not included in the proportionality test.

all adjusted to zero ionic strength on the basis of the Debye-Hückel limiting law.*

Another attractive field for the use of amine extraction with constant organic-phase composition is the evaluation of acid activities in acid-salt mixtures, provided that the experimental proof of constant composition can be made sufficiently precise and accurate in each case.

4. USE IN SEPARATIONS PROCESSES

Figure 2 summarizes elements for which production or preparative processes with amine extractions have been indicated. Most of the development was concentrated on the actinide metals. Several circumstances obviously contributed to this emphasis: (1) the first major development being on uranium production and being prosecuted within a nuclear energy program brought the possibilities directly to the attention of many workers having prime interest in actinides, (2) the established extensive use of solvent extraction methods in nuclear energy programs provided a receptive field, and (3) the recently preceding advances in resinous anion exchange of actinides gave both a guide to application and a considerable promise of success. Thus, the present emphasis on actinides does not reflect any limitation of other potential, but rather suggests the extent of applications likely to be reached in other fields when explored to a similar extent.

Figure 11 shows the high extraction power of amine nitrate for plutonium(IV) nitrate[27] and also illustrates both the similarities and the differences between amine extraction and resinous anion exchange. The

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*This assumption, that the aqueous activity coefficients conform to Debye-Hückel behavior (or at most deviate from it in constant ratio) over a range of ionic strengths, is of course more questionable as far as the aqueous phase alone is concerned than is the assumption that they are constant (or at most vary in constant ratio) at constant ionic strength. However, this procedure is free of question about organic-phase activities, and the results will be amenable to correction on the basis of future improved aqueous-phase activity information alone. It should also be noted that constants evaluated at constant ionic strength can be used at other ionic strengths only be means of corresponding adjustments.

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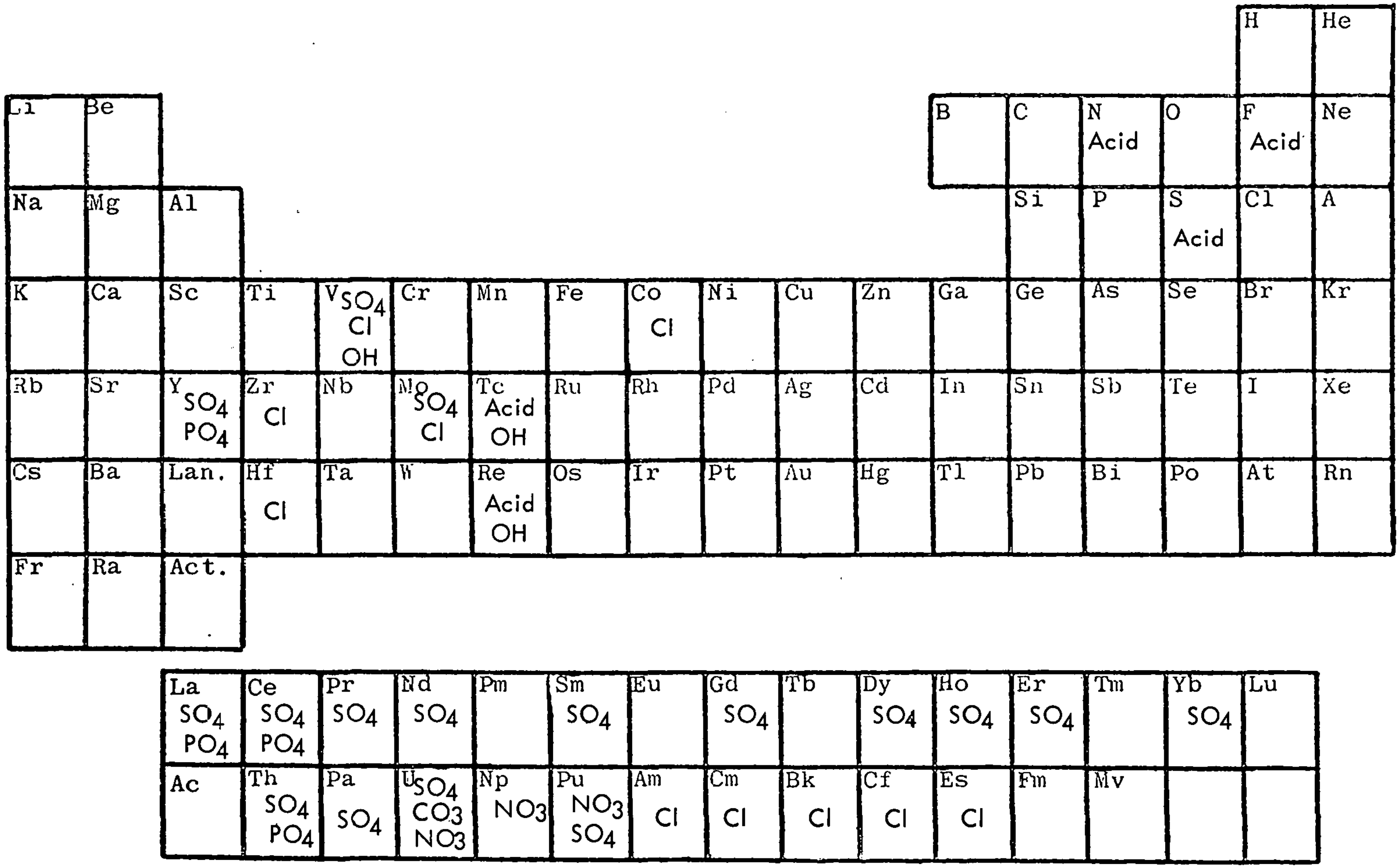

																H	He
Li	Be											B	C	N Acid	O	F Acid	Ne
Na	Mg	Al											Si	P	S Acid	Cl	A
K	Ca	Sc	Ti	V SO_4 Cl OH	Cr	Mn	Fe	Co Cl	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y SO_4 PO_4	Zr Cl	Nb	Mo SO_4 Cl	Tc Acid OH	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lan.	Hf Cl	Ta	W	Re Acid OH	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Act.															
		La SO_4 PO_4	Ce SO_4 PO_4	Pr SO_4	Nd SO_4	Pm	Sm SO_4	Eu	Gd SO_4	Tb	Dy SO_4	Ho SO_4	Er SO_4	Tm	Yb SO_4	Lu	
		Ac	Th SO_4 PO_4	Pa SO_4	U SO_4 CO_3 NO_3	Np NO_3	Pu NO_3 SO_4	Am Cl	Cm Cl	Bk Cl	Cf Cl	Es Cl	Fm	Mv			

Fig. 2. Elements Extracted in Production or Preparative Processes, from the Aqueous Media Indicated.

dashed line shows plutonium sorption by a strong-base resin, as a function of varying nitric acid concentration.[28] Extraction by primary and secondary amines and by some quaternary ammoniums is qualitatively similar to sorption by the resin. Quantitatively, the extraction peaks vary over a thousand-fold range at a given amine concentration (here 0.1 M), and can be varied still more by shifting the concentration. Extraction by tertiary amines fits into the same series at high acidities but displays a broad maximum instead of the sharp peak, maintaining high extraction power down to around 1 M HNO_3. Because of this characteristic, tertiary amines were chosen in several laboratories for development of processes for the final purification of plutonium nitrate[61] and are being considered for the recovery of plutonium nitrate occurring in various liquors at moderate to very low concentrations. On the other hand, a secondary amine was chosen for extraction of plutonium at high concentrations resulting from the dissolution of metallurgical scrap,[29] where neither a high extraction coefficient nor limitation of acidity was needed.

Extraction curves for neptunium(IV) nitrate are similar in shape to those for plutonium(IV), but nearly an order of magnitude lower.[30,31] Tertiary amine extraction is being considered for neptunium scavenging and by-product recovery.[32] Although neptunium and plutonium are highly extractable only in the tetravalent states, while usually neptunium(IV) nitrate coexists with plutonium(III) and neptunium(V,VI) coexists with plutonium(IV), neptunium and plutonium can be coextracted by tertiary amines from nitrate salt solutions of low acidity, perhaps because the strong complexing shifts their redox potentials to overlapping. This results in several obvious possibilities for separation either by selective extraction or by coextraction and selective stripping.

Extraction curves for uranyl nitrate are lower than for neptunium but are raised by the presence of nitrate salt sufficiently for process extraction.[32,33,62]

Extraction of the tetravalent actinide sulfates is very high with primary amines, much lower with secondary, and lowest with tertiary amines.[27,31] Primary amine extraction has been considered for the scavenging of plutonium and uranium from "decladding" solutions — sulfuric acid solutions used to remove stainless-steel cladding from fuel elements.[14]

The hydrometallurgical processes for uranyl sulfate extraction by tertiary and secondary amines are widely used and well known; processes have been developed for thorium sulfate extraction by secondary and primary amines.[4,34]

The transplutonium actinides are almost completely limited to trivalence in aqueous processing. While the actinide(III) nitrates are not extracted by amines from even moderately acid solutions, they are extracted from nitrate salt solutions at very low acidity.[27] They are also extracted from concentrated chloride solutions at very low acidity, less strongly than from nitrate solutions but with the important advantage of high selectivity over lanthanides.[35,36,63]

The extraction of vanadium was necessarily studied extensively in the development of processes for recovering uranium from ores because of their relationship in many ores, and vanadium recovery processes have been developed.[37-39] Molybdenum extraction, studied in similar association with some uranium ores, offers a potential recovery process.[37,40]

Processes have been developed for the separation of zirconium from hafnium in chloride solutions,[41,42] the separation of cobalt from nickel in chloride solution,[43] the recovery of rhenium[44,45] and technetium[32,45] from both acid and basic solutions, and the recovery of nitric acid from waste liquors[34,46] (as salt) and of hydrofluoric[47] and sulfuric acids[48] (as acids). Adjustment of process liquors to lower acidity, with or without recovery of the anion, has been recognized as an obvious use, starting with the original report of amine extraction.[1,34,46]

Other elements have been separated from mixtures or concentrated from solution in analytical and other laboratory applications,[2,3] as indicated in Fig. 3. Although analytical requirements may differ greatly from process requirements, these separations warrant consideration by those concerned with process separations, as a guide to possibilities and as an indication of the pertinent extraction chemistry.

5. SYSTEMATIC CORRELATIONS

Recently reported and current survey programs compare the extraction of many elements by several amines, especially in the chloride[35,36,48-56] and nitrate[24,27,30,31,57-59] systems. Further data contributing to systematic correlations continually become available through other

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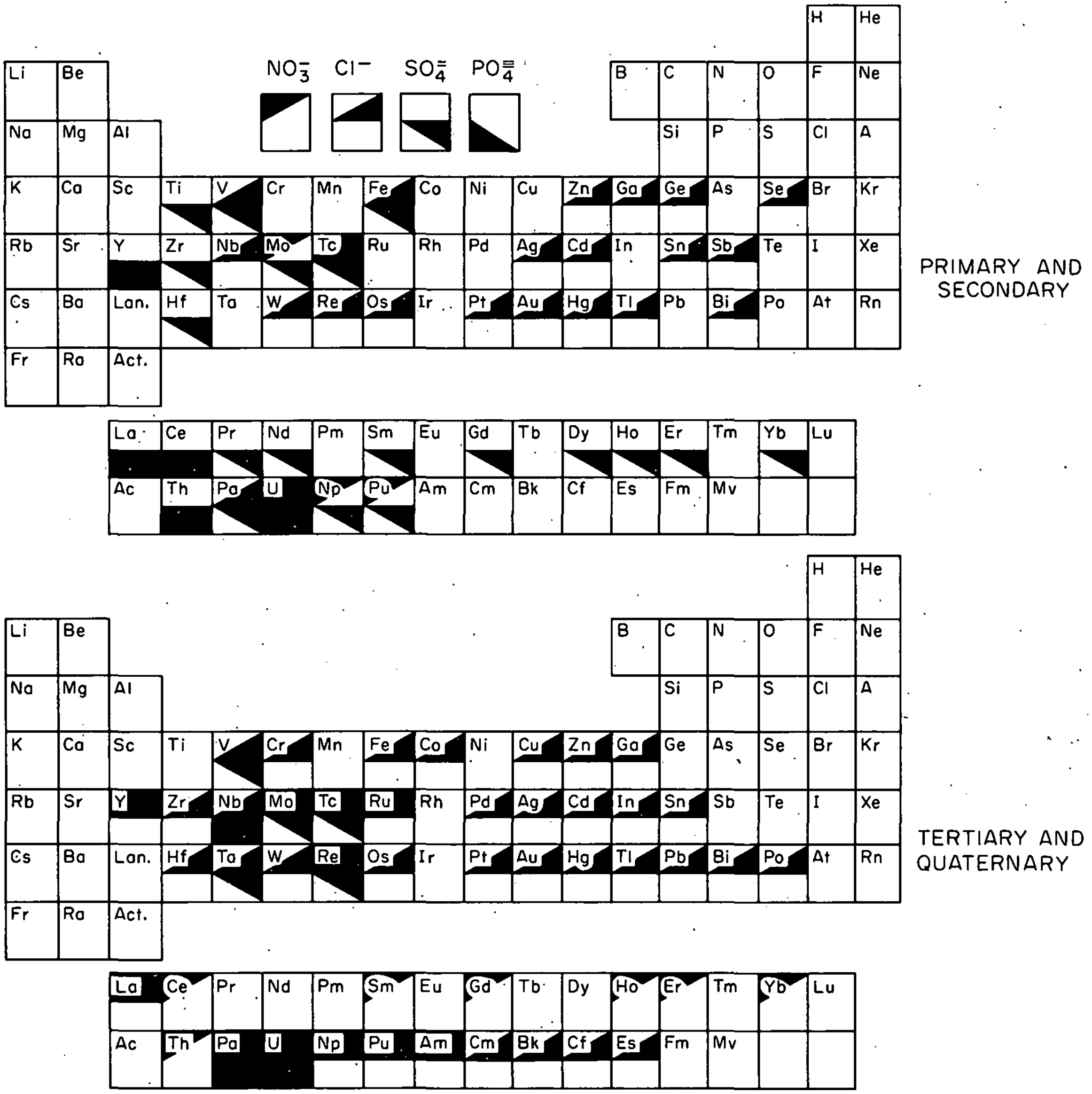

Fig. 3. Elements Extracted in Process, Analytical, and Physicochemical Applications. From ref 3, revised.

extraction studies, even though they are directed primarily toward other objectives. Some examples of such data for the hydrochloric acid system are summarized in Figs. 4-7 for typical quaternary, tertiary, secondary, and primary amines.

However, amine extraction presents so many variables that the direct-survey programs necessarily have a very large scope, and the data from different sources are difficult to fit together within any single or few frames of reference. These variables include the class of amine (primary, secondary, tertiary, or quaternary), structure (size, shape, and nature of each alkyl or aryl group, and their interrelations in symmetry and steric effects), concentration of amine, type of diluent, and option of auxiliary agents or additives (Figs. 8-13), in addition to the variables of the aqueous phase. Each of these has important effects on extraction, and in addition it has been shown that extractions from mixed anion solutions are not always predictable on the basis of extractions measured from solutions of those anions separately. The main purpose for noting this multiplicity of variables is to emphasize that there is and will be room for a great deal more systematic work on the descriptive chemistry of amine extraction.

As illustrated in Figs. 4-7, the accumulating amine extraction patterns continue to show a general resemblance to resin sorption patterns,[*] overlain with wide variations in response to the variables cited above. This is shown better by the larger scale curves in Figs. 8-11 for iron(III), vanadium(V), and zinc chlorides and plutonium nitrate. To a considerable extent, the quaternary ammonium extraction and (strong-base) resin sorption curves are of similar shape and slope, with the tertiary amine extraction curves not much different. The close quantitative agreement between Q and R curves in Figs. 8 and 10 must be considered fortuitous, since the arbitrary choice of 0.1 M concentration of the extractant had no relation to the composition and capacity of the

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[*] While the resin sorption curves cited are placed in Fig. 7 for graphical expedience, they should be compared principally with the quaternary ammonium curves in Fig. 4.

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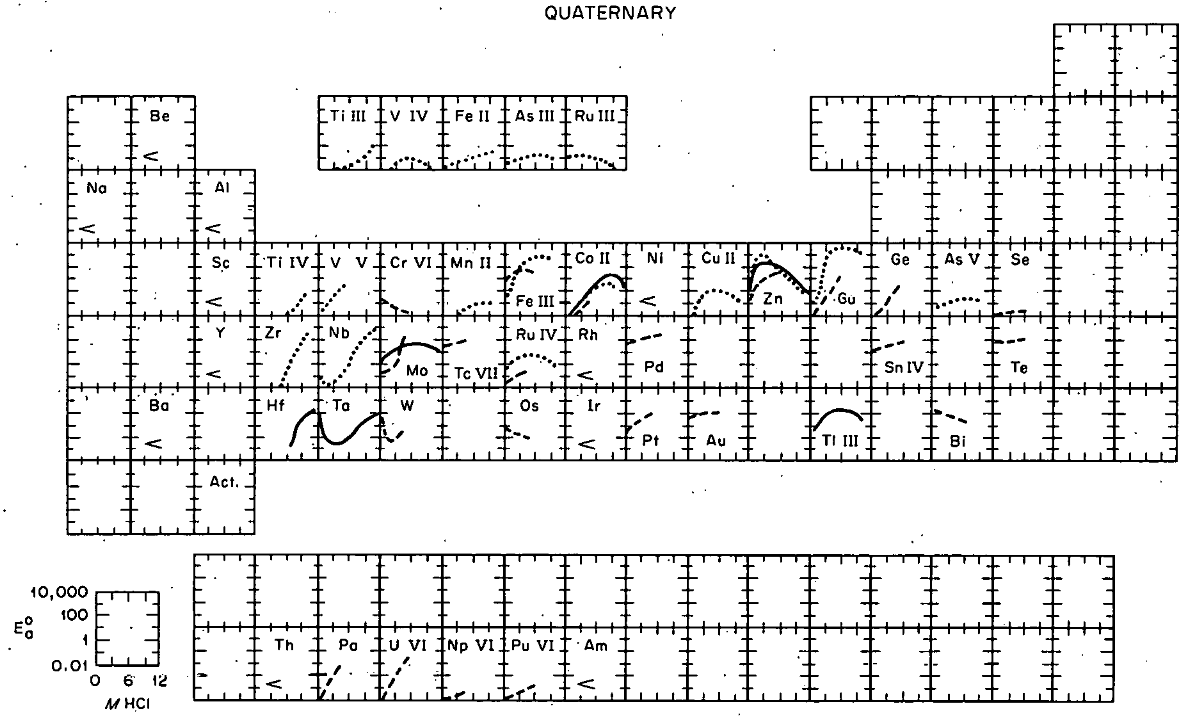

Fig. 4. Extractions from Hydrochloric Acid Solutions by Quaternary Ammoniums.

.... 0.1 M Aliquat 336 in diethylbenzene (+ 3% tridecanol)[48]

—— 0.1 M Hyamine 1622 in 1,2-dichloroethane[49]

- - - 0.2 M Tetra-n-hexylammonium Iodide in Hexone[50]

<: $E_a^o \leqslant 10^{-2}$ at 0.2 to 5 M HCl (<*: 0.5 to 10 M HCl)

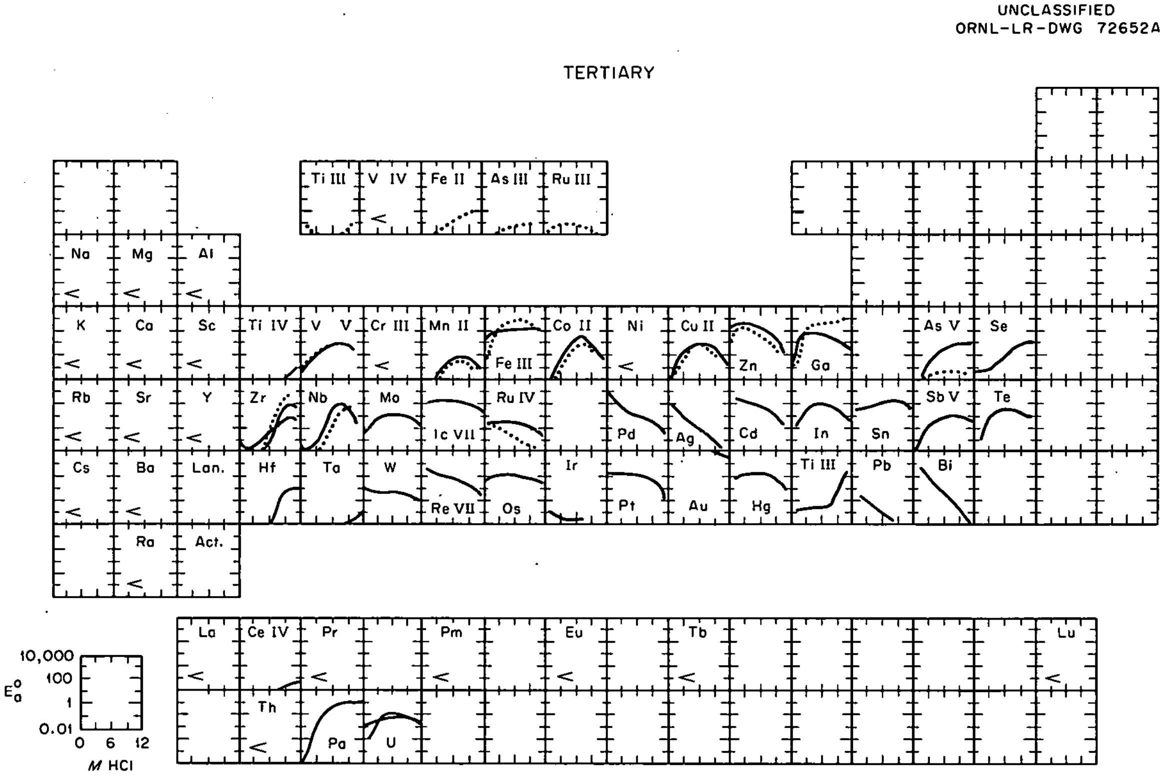

Fig. 5. Extractions from Hydrochloric Acid Solutions by Tertiary Amines.

—— 0.14 M Tri-iso-octylamine in xylene or kerosene[51]

.... 0.1 M Alamine 336 in diethylbenzene[48]

<: $E_a^o \leq 10^{-2}$ at 0.5 to 12 M HCl

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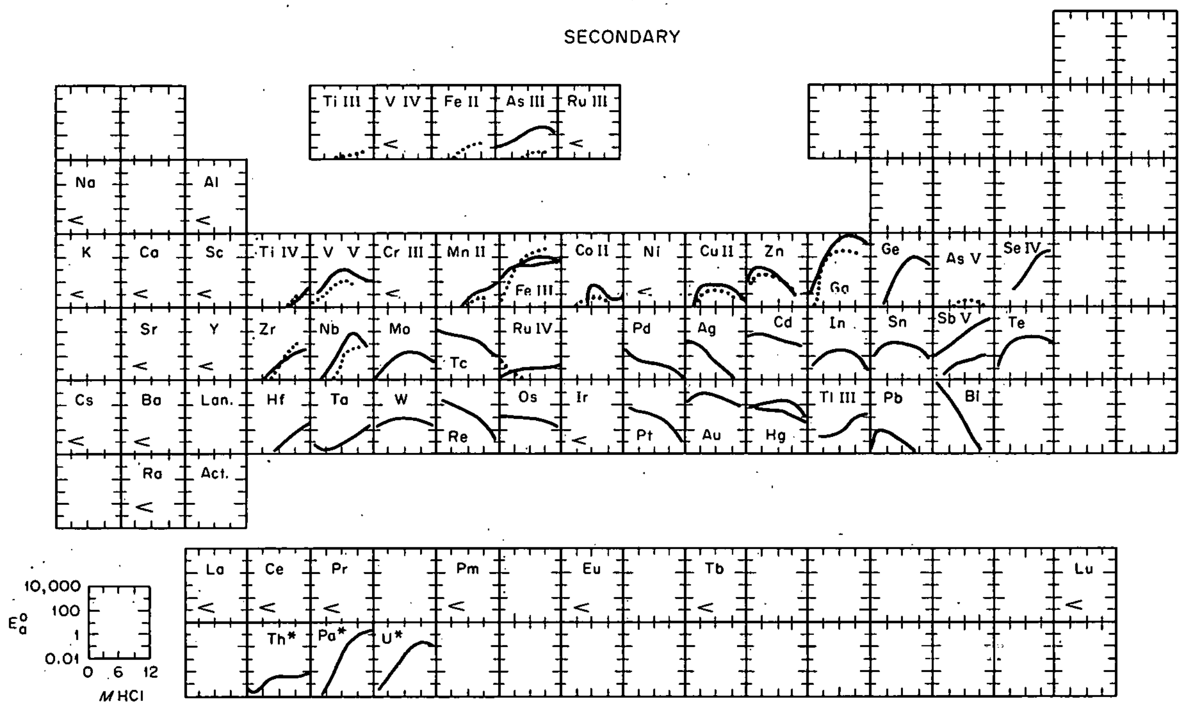

Fig. 6. Extractions from Hydrochloric Acid Solutions by Secondary Amine.

—— 0.3 M Amberlite LA-1 in xylene or kerosene (*: 0.15 M)[51]

. . . . 0.1 M Amberlite LA-1 in diethylbenzene[48]

<: $E_a^o < 10^{-2}$ at 0.5 to 12 M HCl

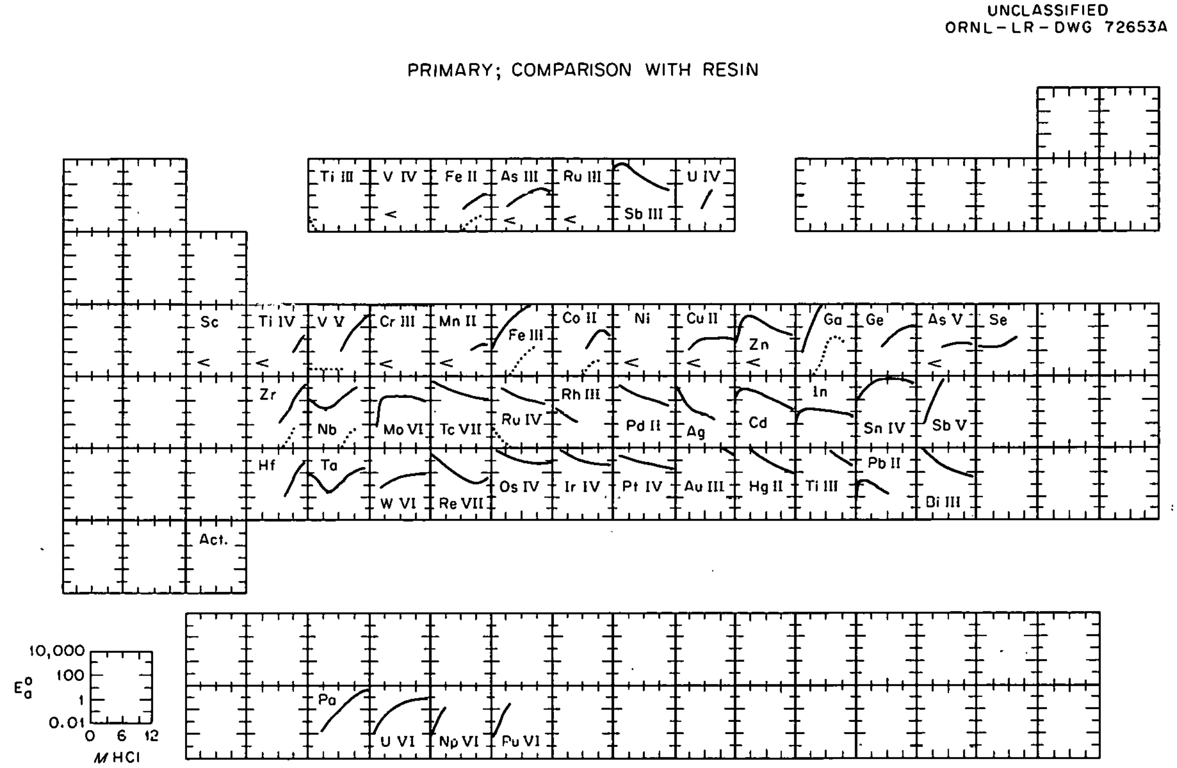

Fig. 7. Extractions from Hydrochloric Acid Solutions by a Primary Amine; Comparison with Anion Exchange Resin Sorption.

.... 0.1 M Primene JM in diethylbenzene[48]

—— Distribution Coefficient, D_v, to resin[60]

<: $E_a^o \leqslant 10^{-2}$ at 0.5 to 10 M HCl

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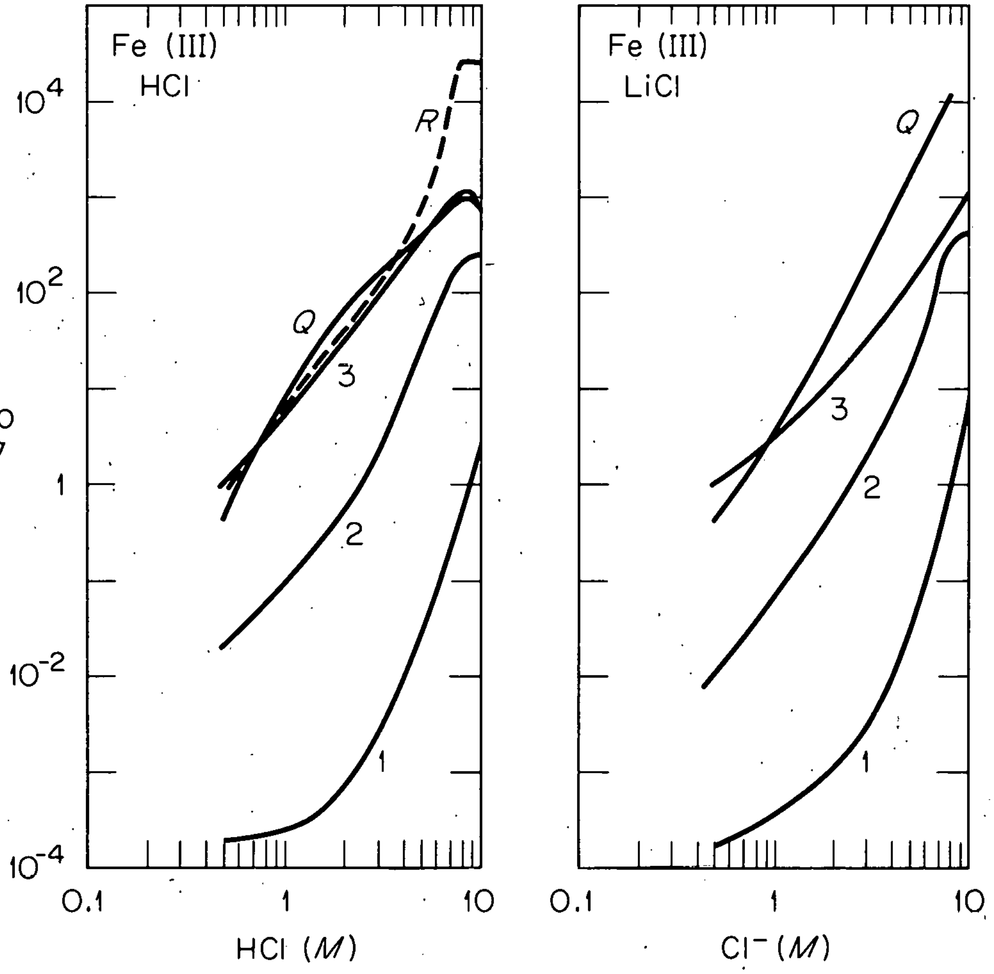

Fig. 8. Iron(III) Extraction from Hydrochloric Acid and Lithium Chloride Solutions by 0.1 M Amines in Diethylbenzene. Curve 1, Primene JM; curve 2, Amberlite LA-1; curve 3, Alamine 336; curve Q, Aliquat 336 (+ 3% tridecanol); curve R, sorption by anion exchange resin.

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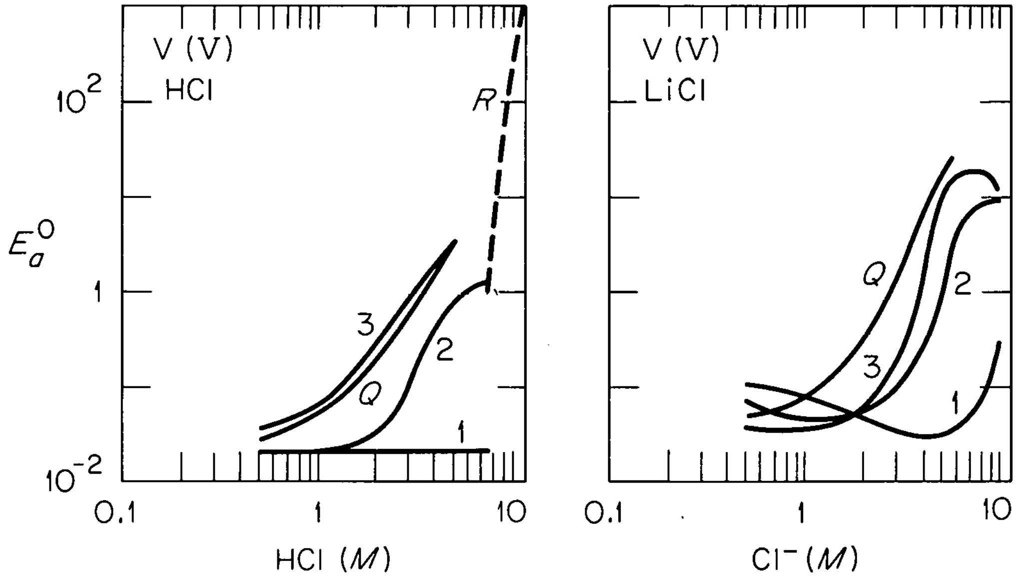

Fig. 9. Vanadium(V) Extraction from Hydrochloric Acid and Lithium Chloride Solutions by 0.1 $\underline{M}$ Amines in Diethylbenzene. Curve 1, Primene JM; curve 2, Amberlite LA-1; curve 3, Alamine 336; curve Q, Aliquat 336 (+ 3% tridecanol); curve R, sorption by anion exchange resin.

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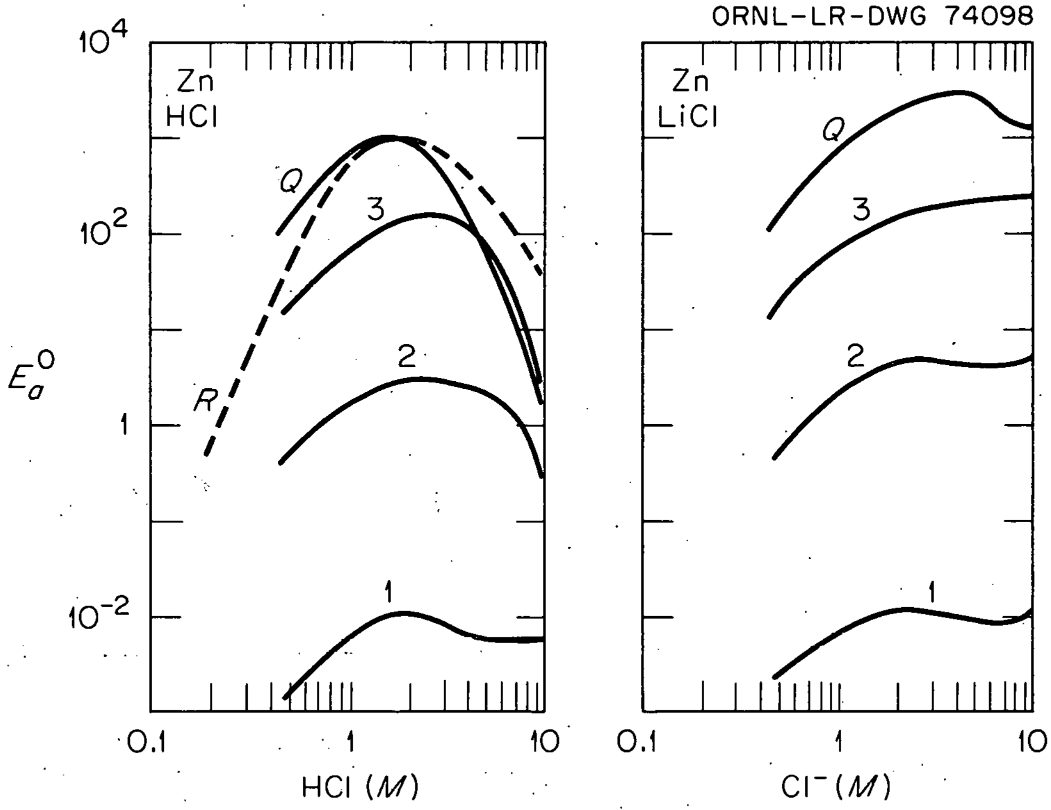

Fig. 10. Zinc Extraction from Hydrochloric and Lithium Chloride Solutions by 0.1 M Amines in Diethylbenzene. Curve 1, Primene JM; curve 2, Amberlite LA-1; curve 3, Alamine 336; curve Q, Aliquat 336 (+ 3% tridecanol); curve R, sorption by anion exchange resin.

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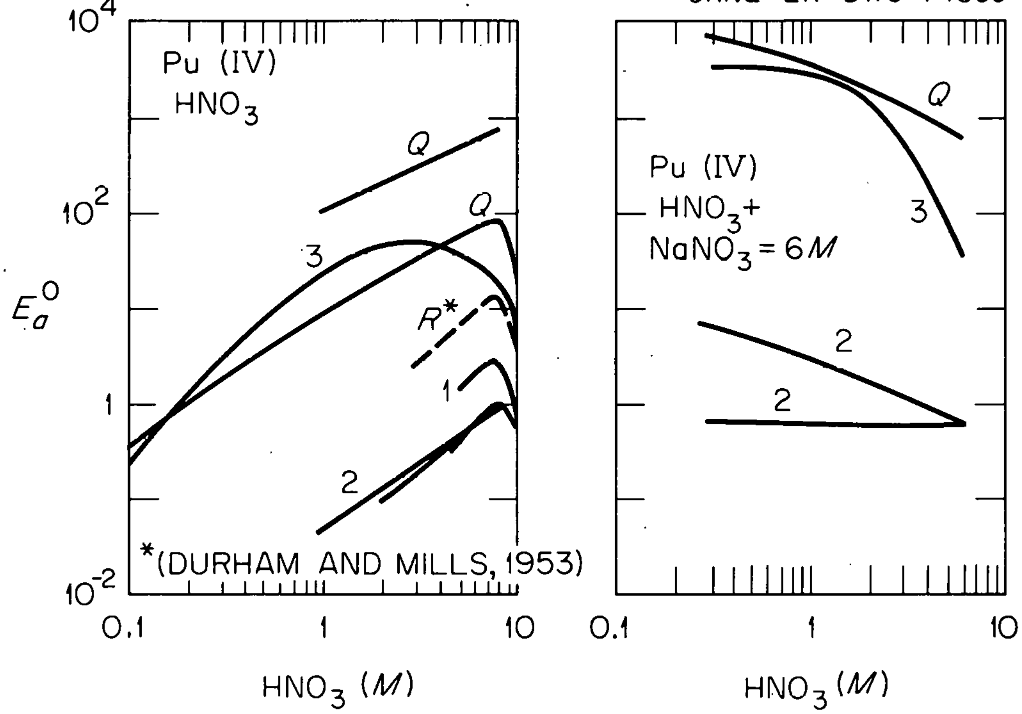

Fig. 11. Plutonium(IV) Extraction from Nitric Acid and Nitric Acid-Sodium Nitrate Solutions by 0.1 M Amines. Curve 1, Primene JM in Amsco 125-82 (+ 5% tridecanol); curves 2, Amberlite LA-1 and N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine in xylene, bis(1-isobutyl-3,5-dimethylhexyl)amine in Amsco 125-82; curve 3, tri-iso-octylamine in Amsco 125-82 (+ 8% tridceanol); curves Q, Aliquat 336 in xylene, Quaternary B-104 in Amsco 125-82 (+ 8% tridecanol);[27] curve R, sorption by anion exchange resin.[28]

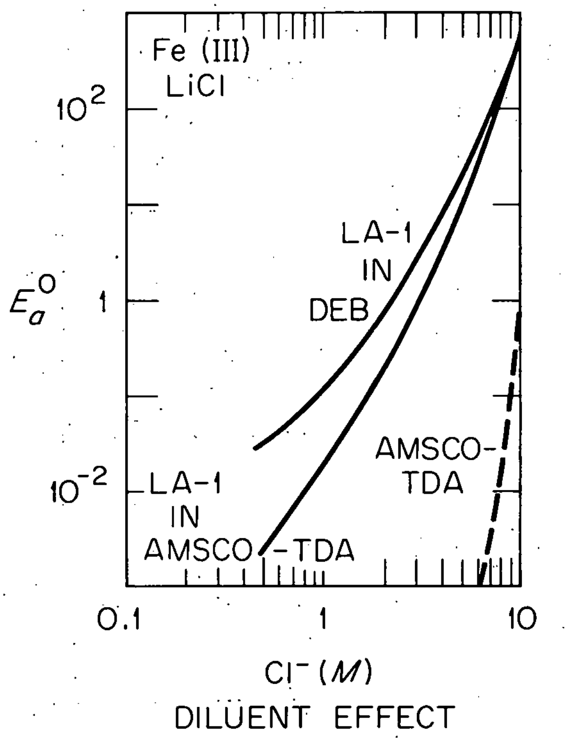

Fig. 12. Diluent Effect on Iron(III) Extraction from Lithium Chloride Solutions by 0.1 M Amberlite LA-1 in (I) diethylbenzene, (II) Amsco 125-82 (+ 3% tridecanol), (III) extraction by Amsco 125-82 (+ 3% tridecanol) alone.

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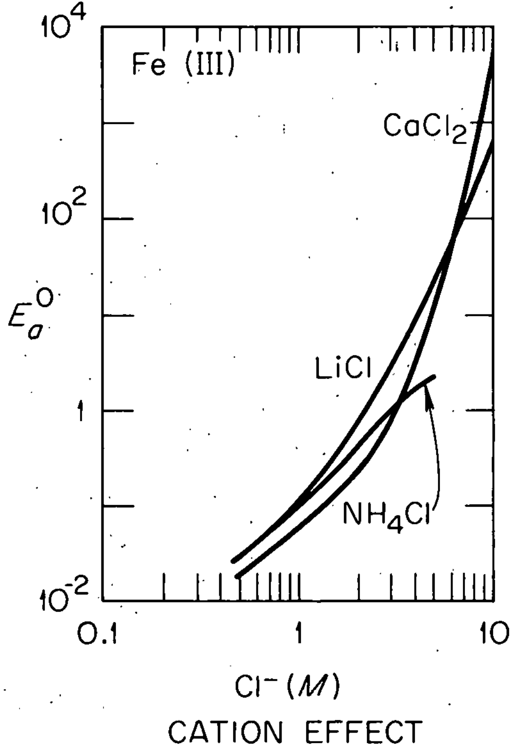

Fig. 13. Cation Effect on Iron(III) Extraction from Chloride Solutions by 0.1 M Amberlite LA-1 in Diethylbenzene.

resins. The extraction coefficients usually decrease in the order, quaternary > tertiary > secondary > primary, in the chloride (and nitrate) systems. However, the spread can vary greatly (compare vanadium and zinc, Figs. 9 and 10), and at least thorium appears to be an exception with the opposite order, secondary > tertiary.[51] It should be re-emphasized that the amine-diluent combination should be considered in intercomparisons (Fig. 12) rather than the amine alone, even with diluents ordinarily looked upon as "inert."

6. AVAILABILITY OF AMINES

Over a number of years, new amines of all classes have become available at commercial, development, or research-sample levels, while a few previously promising amines have become less available. Table 4 lists most of the amines that have been used extensively, with a statement of present availability as indicated on recent inquiry. This list is intended to cover nearly all the important amines and to give typical domestic sources, but it may well have some omissions and obsolete entries. A few amines from foreign sources are included where special information has been encountered, but without any attempt to cover the foreign sources. A few amines marked "not available" were retained in the list for identification because of important uses or comparisons already reported; similarly a few amines are listed that were synthesized in the laboratories where used and may never have been generally available. Structures are not shown in Table 4 that are obvious or are readily available in refs 3 and 7.

Table 4. Availability of Amines

No. of Carbons	Amine, Source	Availability[a]
	Primary Amines	
15	1-n-Heptyl-n-octylamine (Armour Chemical Div., Chicago)	Research
17	Amine 21F81, 1-(3-Ethylpentyl)-4-ethyloctylamine (Union Carbide Chem. Co., N.Y.)	Not avail.
18-24	Primene JM-T, trialkylmethylamine (Rohm and Haas Co., Philadelphia)	Commercial
23	1-n-Undecylaurylamine (Armour Chemical Div.)	Research
	Secondary Amines	
18	Di(2-propyl-4-methylpentyl)amine (Eastman Chemical Products, Kingsport, Tenn.)	Not avail.
20	Di-n-decylamine (Eastman Organic Chemicals, Rochester, N.Y., No. P7724)	Specialty
	(Chemical Procurement Laboratories, Inc., College Point, N.Y.)	(Specialty)
24	Dilaurylamine (Eastman Organic Chemicals, No. P4519)	Specialty
	(Chemical Procurement Laboratories, Inc.)	(Specialty)
24	Amine S-24, bis(1-isobutyl-3,5-dimethylhexyl)-amine (Union Carbide Chem. Co.)	Not avail.
24	NBHA, N-benzylheptadecylamine, N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine (Union Carbide Chem. Co.)	Not avail.
24-27	Amberlite LA-1, N-dodecenyltrialkylmethylamine (Rohm and Haas Co.)	Commercial
24-27	Amberlite LA-2, N-lauryltrialkylmethylamine (Rohm and Haas Co.)	Commercial
26	Ditridecylamine, "Tridecyl" = mixture of 13-carbon alkyls from tetrapropylene. (Union Carbide Chem. Co.)	Research
26	N-Benzyl-(1-n-nonyl-n-decyl)amine (Armour Chemical Div.)	Research
	(Chemical Procurement Laboratories, Inc.)	(Specialty)

Table 4 (continued)

No. of Carbons	Amine, Source	Availability[a]
30	N-Benzyl-(1-n-undecyllauryl)amine (Armour Chemical Div.)	Research
	(Chemical Procurement Laboratories, Inc.)	(Specialty)
30	Di(1-n-heptyl-n-octyl)amine (Armour Chemical Div.)	Not avail.
31	N-(1-n-Nonyl-n-decyl)laurylamine (Armour Chemical Div.)	Research
35	N-(1-n-Undecyllauryl)laurylamine (Armour Chemical Div.)	Research
38	Di(1-n-nonyl-n-decyl)amine (Armour Chemical Div.)	Not avail.
	Tertiary Amines	
17	MDOA, methyldioctylamine (Chemical Procurement Laboratories, Inc.)	(Specialty)
21	Tribenzylamine (Eastman Organic Chemicals No. 1015)	Development
	(Chemical Procurement Laboratories, Inc.)	(Specialty)
24	TOA, tri-n-octylamine (Eastman Organic Chemicals No. P7723)	Development
	(Chemical Procurement Laboratories, Inc.)	(Specialty)
	(The British Hydrological Corp., London)	
24	TIOA, tri-iso-octylamine "iso-octyl" = mixture of dimethylhexyls and methylheptyls, etc. (Union Carbide Chemical Co.)	Not avail.
	(Gulf Oil Corporation, Pittsburgh)	
	(Archer-Daniels-Midland Co., Minneapolis, Minn.)	Ltd. comm.
26-32	Alamine 336, "Tricaprylyl Amine," three straight-chain alkyls, principally octyl and decyl (General Mills, Inc., Kankakee, Ill.)	Commercial
	"Tricaprylylamine" (Chemical Procurement Laboratories, Inc.)	(Specialty)

Table 4 (continued)

No. of Carbons	Amine, Source	Availability[a]
27	Triisononylamine, tris(3,5,5-trimethylhexyl)-amine (I.C.I. (Heavy Organic Chemicals) Ltd., Billingham, England)	
27	Adogen 364, tri-n-alkylamine, average C_9 (Archer-Daniels-Midland Co.)	Ltd. comm.
28	n-Butyldilaurylamine (Laboratory Prep.)	
28	Amberlite XE-204, didodecenyl-n-butylamine (Rohm and Haas Co.)	Not avail.
30	Tri-isodecylamine (Archer-Daniels-Midland Co.)	Ltd. comm.
30	Adogen 368, tri-n-alkylamine, average C_{10} (Archer-Daniels-Midland Co.)	Ltd. comm.
36	TLA, trilaurylamine (Archer-Daniels-Midland Co., "Adogen-363")	Commercial
	(General Mills, Inc., "Alamine 304")	Commercial
	(Eastman Organic Chemicals, No. 7727)	Development
	(Rhone-Poulenc, Seine, France)	Commercial
	Quaternary Ammoniums	
16	Tetra-n-butylammonium (Eastman Organic Chemicals, No. 7377, as bromide)	Development
17-21	Roccal, dimethylbenzyl-n-alkylammonium, (Sterwin Chemicals, Inc., as chloride)	(Specialty)
24	Tetra-n-hexylammonium (Eastman Organic Chemicals, No. 7627, as Iodide)	Development
	(Chemical Procurement Laboratories, Inc.)	(Specialty)
25-31	Adogen 464, methyltri-n-alkylammonium, C_8-C_{10} (Archer-Daniels-Midland Co., as chloride)	Commercial
26	Experimental Quaternary B-104, dimethyldidodecenylammonium (Rohm and Haas Co., as chloride)	Not avail.
27	Hyamine 1622, benzyldimethyl(aryl-alkyl-alkoxy)alkylammonium (Rohm and Haas Co., as chloride)	Commercial

Table 4 (continued)

No. of Carbons	Amine, Source	Availability[a]
27-33	Aliquat 336, methyltri-n-alkylammonium, principally octyl and decyl (General Mills, Inc., as chloride)	Commercial
28	Tetra-n-heptylammonium (Eastman Organic Chemicals, No. 7630, as iodide)	Development
	(Chemical Procurement Laboratories, Inc.)	(Specialty)
28	Hyamine 10X, benzyldimethyl(aryl-alkyl-alkoxy)alkylammonium (Rohm and Haas Co., as chloride)	Commercial
31	Adogen 468, methyltri-n-alkylammonium, average C_{10} (Archer-Daniels-Midland Co., as chloride)	Ltd. comm.

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[a] Availabilities confirmed (except where marked with parentheses)by current advertisements or recent inquiry.

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