Subscripts

c = critical-point property
i = component i
j = component j
1 = CHF_3
2 = $CClF_3$

LITERATURE CITED

(1) Allied Chemical Corp., Brit. Patent, 1,063,416 (March 30, 1967).
(2) Chueh, P. L., Prausnitz, J. M., *Ind. Eng. Chem. Fundam.*, **6**, 492 (1967).
(3) Freon Products Division, E. I. du Pont de Nemours & Co., "Freon-13 Refrigerant Thermodynamic Properties," Technical Bulletin T-13A (1967)
(4) Freon Products Division, E. I. du Pont de Nemours & Co., "Thermodynamic Properties of Freon-23," Technical Bulletin T-23A (no year given); "Properties and Applications of the Freon Fluorocarbons," Technical Bulletin B-2 (1964).
(5) Piacentini, A., PhD Dissertation, Lehigh University, Bethlehem, Pa., 1966.
(6) Pitzer, K. S., Curl, R. F., Jr., *J. Amer. Chem. Soc.*, **79**, 2369 (1957).
(7) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1969, pp 212, 426.
(8) Proust, P. C., MS Thesis, Lehigh University, Bethlehem, Pa., 1970.
(9) Redlich, O., Kwong, J. N. S., *Chem. Rev.*, **44**, 233 (1949).
(10) Sinka, J. V., Rosenthal, E., Dixon, R. P., *J. Chem. Eng. Data*, **15**, 73 (1970).
(11) Stein, F. P., Sterner, C. J., Geist, J. M., *Chem. Eng. Progr.*, **58** (*11*), 70 (1962).
(12) Swietoslawski, W., "Azeotropy and Polyazeotropy," The Macmillan Co., New York, N. Y., 1963, p 47.
(13) Van Ness, H. C., "Classical Thermodynamics of Non-Electrolyte Solutions," The Macmillan Co., New York, N.Y. 1964, p 138.
(14) Wilson, G. M., *J. Amer. Chem. Soc.*, **86**, 127 (1964).

RECEIVED for review November 23, 1970. Accepted March 22, 1971. A fellowship provided by the Organization of American States is sincerely appreciated.

Extraction of Metals from Nitrate and Sulfate Solutions by Amines

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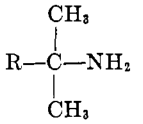
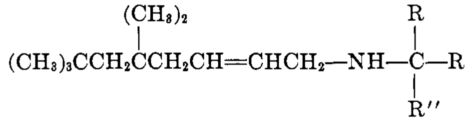
Coefficients for the extraction of 54 metals from acidified lithium nitrate and lithium sulfate solutions were determined by using representative primary, secondary, tertiary, and quaternary alkylammonium nitrates or sulfates in diethylbenzene diluent as extractants. The acid concentration of the aqueous phase was 0.2*N*, and the total nitrate and sulfate concentrations varied from 0.5–10*N* and 0.3–5*N*, respectively.

Since the solvent extraction of mineral acids with high-molecular-weight amines was first reported in 1948 (*30*), extraction characteristics of these reagents have received much study (*1–27, 29, 31, 32*). Most metal extraction surveys have been limited to acid dependence studies; furthermore, the use of a variety of diluents in these studies has made correlation of data from different sources difficult. In this work the extraction of 54 metals from acidified lithium nitrate and lithium sulfate solutions was systematically surveyed using representative primary, secondary, tertiary, and quaternary alkylam-

Table I. Description of Amines

Amine type	Compound[a]	Structure of compound
Primary	Primene JM	 $R-C(CH_3)_2-NH_2$ R = alkyl groups containing 15–21 carbon atoms
Secondary	Amberlite LA-1	 $(CH_3)_3CCH_2C(CH_3)_2CH_2CH{=}CHCH_2-NH-C(R)(R')R''$ where R + R′ + R″ = different alkyl groups totaling 12–14 carbon atoms
Tertiary	Adogen 364	R_3N, where R designates mixed *n*-octyl and *n*-decyl groups
Quaternary	Adogen 464	$[R_3N\text{-}CH_3]^+Cl^-$, where R designates mixed *n*-octyl and *n*-decyl groups

[a] Primene JM and Amberlite LA-1 were supplied by the Rohm and Haas Co. and Adogen 364 and Adogen 464 by the Archer Daniels Midland Co.

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[1] To whom correspondence should be addressed.

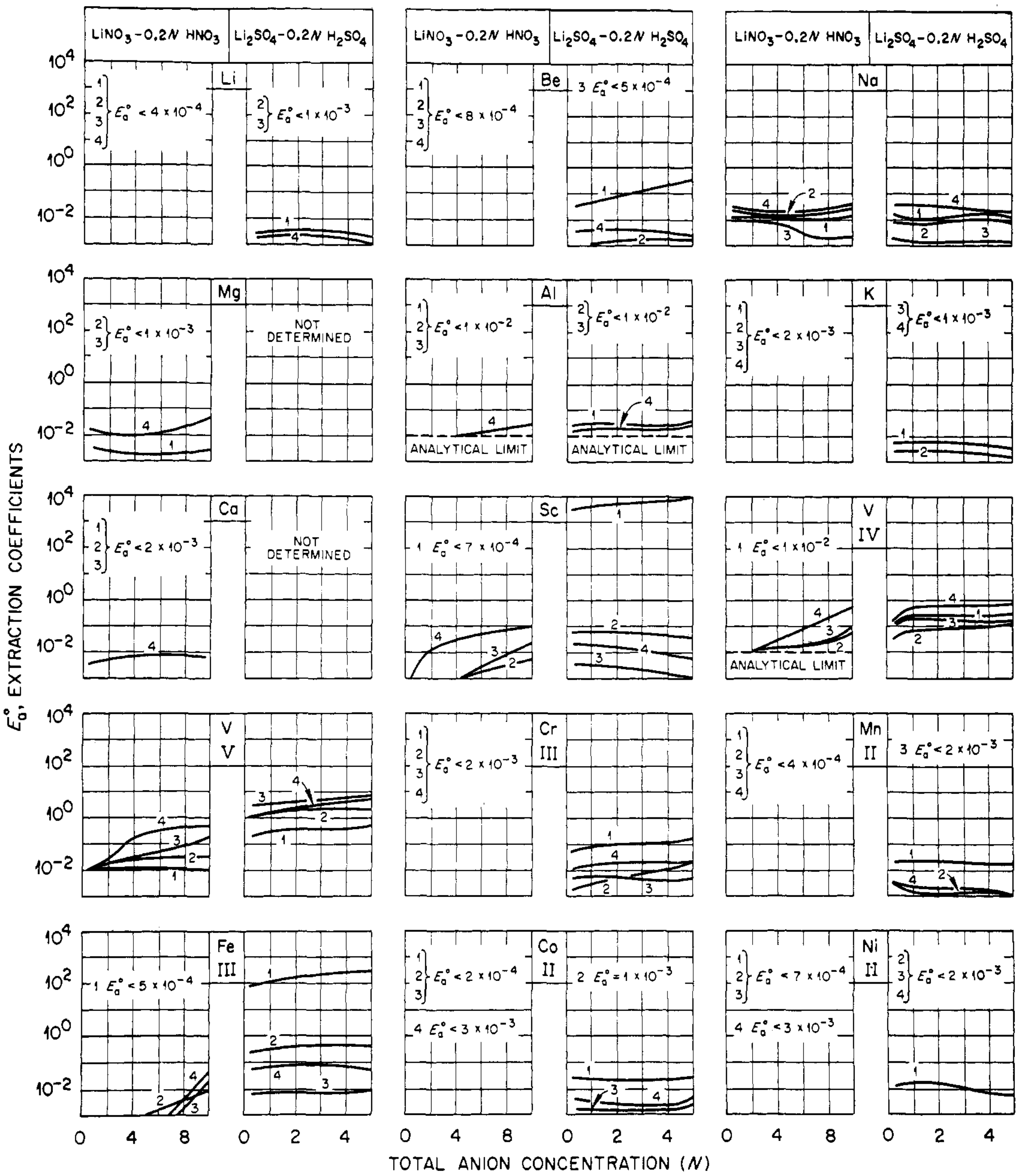

Figure 1. Extraction of metals with 0.1N amine nitrate or amine sulfate solutions

1. Primene JM in diethylbenzene
2. Amberlite LA-1 in diethylbenzene
3. Adogen 364 in diethylbenzene
4. Adogen 464 in 97% diethylbenzene–3% tridecanol

monium nitrates and sulfates in diethylbenzene diluent as extractants. Previously, data were reported for the extraction of 63 metals from hydrochloric acid and from acidified lithium chloride solutions (*28*).

EXPERIMENTAL

Materials. The structures of the compounds chosen to represent the different types of the amines in the metal extraction tests are given in Table I. The amine concentration was 0.1*N* in each case. The diluent was diethylbenzene except in the tests with Adogen 464 in which the diethylbenzene was modified with 3 vol % tridecanol to prevent separation of the amine nitrate or sulfate salts from the diluent as a third liquid phase at high nitrate or sulfate concentrations. The amine solutions, initially at a concentration higher than 0.1*N*, were scrubbed with dilute acid and sodium carbonate solutions to remove lower-molecular-weight amines and other aqueous soluble impurities.

Prior to the extraction tests, the scrubbed amine solutions were titrated to determine the amine concentration, diluted to 0.1*N* with diethylbenzene diluent, and then contacted with a 0.5*N* solution of the appropriate acid to convert the amine to the nitrate or sulfate salt form. The amine nitrate was always prepared just prior to its use in the extraction tests since past experience had shown that extended storage of the amine in the nitrate salt form can result in degradation of the amine as well as the diluent.

The aqueous solutions contained the metal ion in either $LiNO_3$–0.2*N* HNO_3 or Li_2SO_4–0.2*N* H_2SO_4 solutions at total nitrate concentrations of 0.5, 2.0, 5.0, 7.5, and 10*N* or total

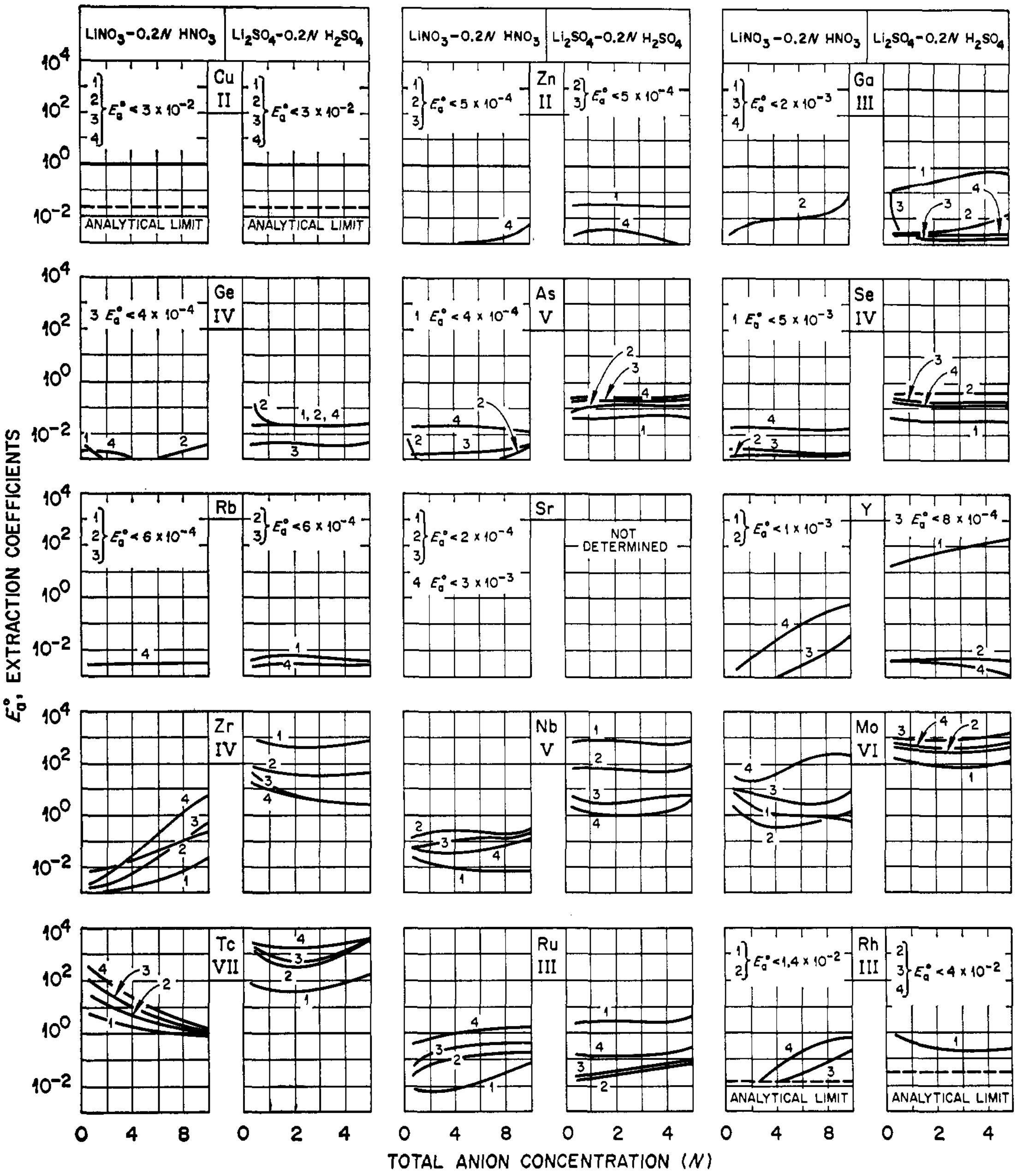

Figure 1 *(Continued)*

1. Primene JM in diethylbenzene
2. Amberlite LA-1 in diethylbenzene
3. Adogen 364 in diethylbenzene
4. Adogen 464 in 97% diethylbenzene–3% tridecanol

sulfate concentrations of 0.3, 1.0, 2.0, 3.5, and 5.0*N*. The nitrate and sulfate dependence curves (Figure 1) were drawn from data obtained for these five concentration points.

In most of the tests, the metal ion was present in macroconcentration (0.01*M*) rather than tracer concentration. This minimized the effect that a small amount of a strong extractant (which could possibly be present as an impurity in the amine or diluent) would have on the extraction coefficient. With an initial metal concentration in the aqueous phase of 0.01*M*, the metal loading of the amine phase was not high enough to depress extraction coefficients appreciably. With germanium, niobium, technetium, antimony, tantalum, tungsten, and osmium, the metal ion either was not soluble to this level or was not available in larger than trace amounts. With these metals, radioactive tracers only were used.

Procedure. Equal volumes of the organic and aqueous phases were contacted vigorously for 10 min in separatory funnels mounted in a wrist-action shaker. Although not all the data points were checked for longer contact times, spot checks of extraction rates indicated that equilibrium conditions were usually established within 10 min. One notable exception was ruthenium. Although the aqueous ruthenium solutions had been aged several weeks to establish equilibrium of the species, equilibrium for the extraction was not achieved even after 24 hr of contact. Figure 1 shows the ruthenium data for the 10-min extraction contact.

In the normal procedure, the appropriate radiotracer was added to the metal–lithium salt solutions, and the distribution of the metal between the phases was determined by gamma- or beta-counting techniques. Where suitable radiotracers were not available, flame spectrophotometric, ionic, or neutron activation analyses were used.

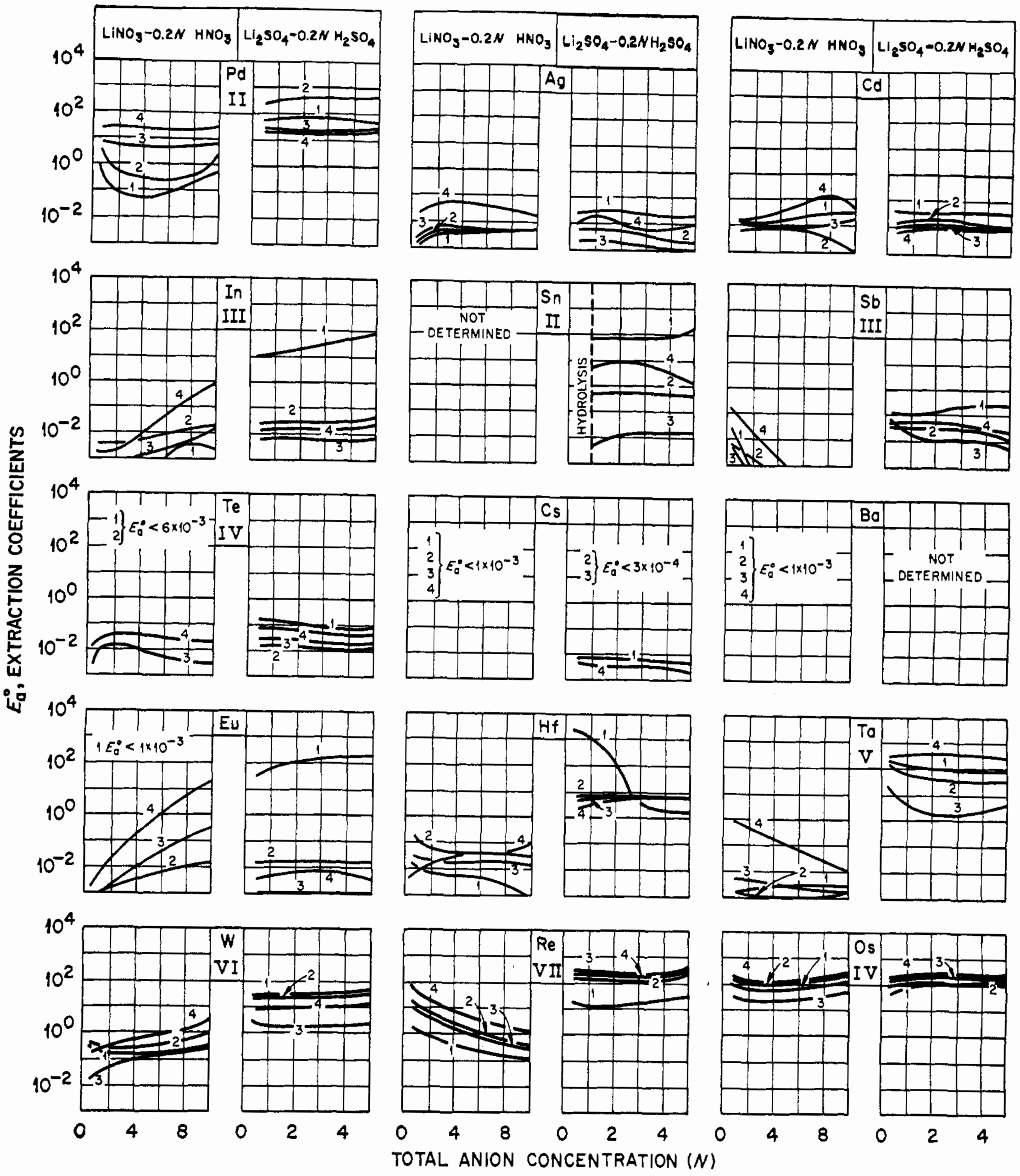

Figure 1 (Continued)

1. Primene JM in diethylbenzene
2. Amberlite LA-1 in diethylbenzene
3. Adogen 364 in diethylbenzene
4. Adogen 464 in 97% diethylbenzene–3% tridecanol

RESULTS

The extraction data obtained are shown graphically in Figure 1 in the order of increasing atomic number of the metal. The extraction coefficient (E_a^o) is the ratio of the molar concentration of the solute in the organic phase to its molar concentration in the aqueous phase at equilibrium:

$$E_a^o = \frac{C_{\text{org}}}{C_{\text{aq}}}$$

This value, a measure of the extraction power of a given amine, is plotted against the total nitrate or sulfate concentration in the aqueous phase. Whereas many of the metals were extracted strongly from chloride solutions (*28*), only a few were extracted strongly from nitrate solutions; fewer than half of those tested were extracted strongly from sulfate solutions. Extraction coefficients tended to increase with increasing nitrate concentration but showed only minor dependence on sulfate concentration. In the nitrate system the amine extraction power for most of the metals varied in the order: Adogen 464 (quaternary) ≥ Adogen 364 (tertiary) > Amberlite LA-1 (secondary) > Primene JM (primary). In the sulfate system the trend is less obvious, but the extraction power varied in the order: Primene JM > Adogen 464 > Amberlite LA-1 > Adogen 364.

ACKNOWLEDGMENT

The authors thank Thomas E. Harmon, Jeannie Tramble, and Delores Porter for assistance in the experimental work.

LITERATURE CITED

(1) Arnold, W. D., Crouse, D. J., *U. S. At. Energy Comm. Rep.*, **ORNL-3030** (1960).
(2) Baybarz, R. D., Kinser, H. B., *ibid.*, **ORNL-3244** (1962).

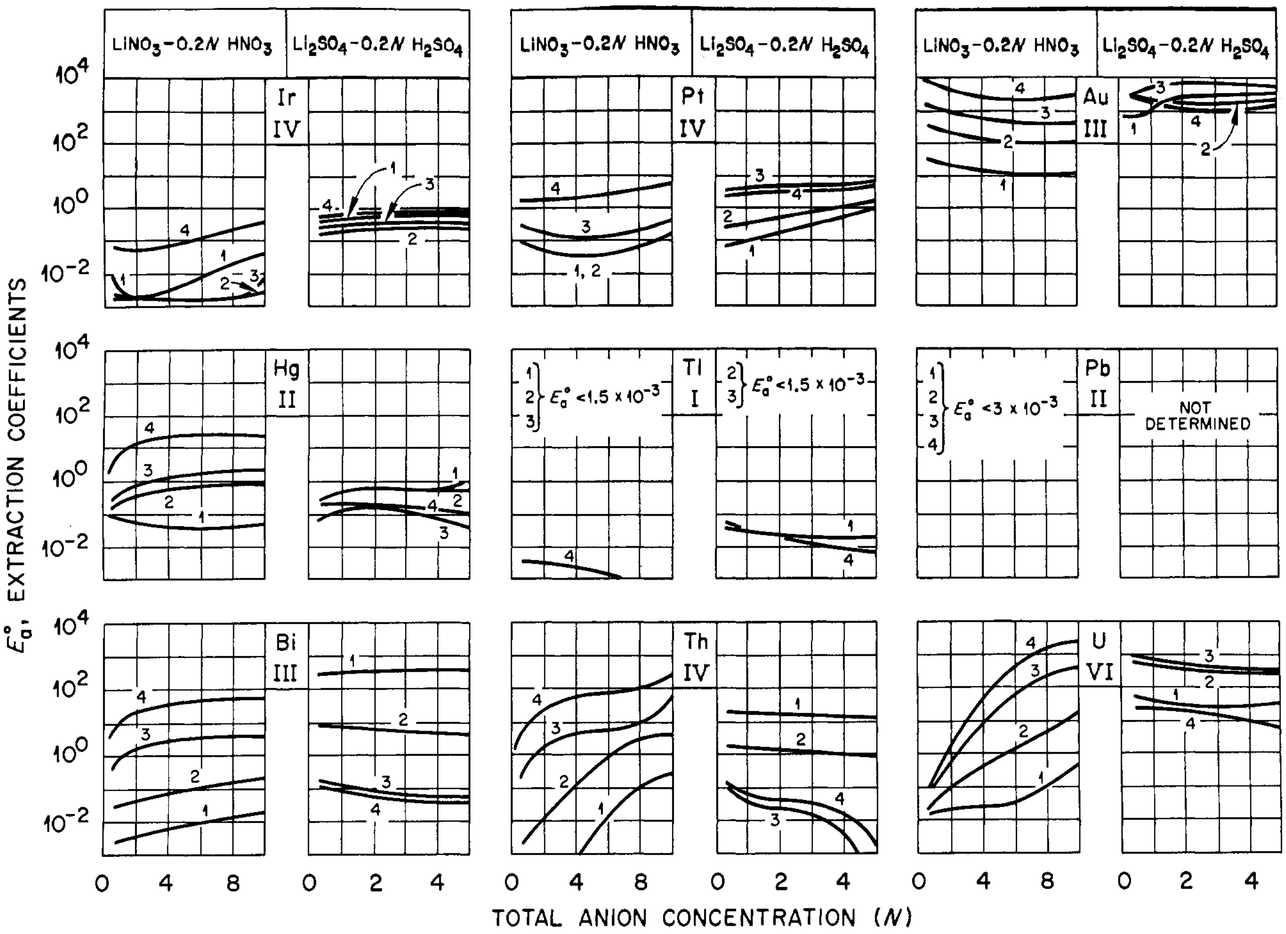

Figure 1 *(Continued)*

1. Primene JM in diethylbenzene
2. Amberlite LA-1 in diethylbenzene
3. Adogen 364 in diethylbenzene
4. Adogen 464 in 97% diethylbenzene–3% tridecanol

(3) Brown, K. B., Coleman, C. F., Crouse, D. J., Blake, C. A., Ryon, A. D., *Proc. U.N. Int. Conf. Peaceful Uses At. Energy, 2nd*, **3**, 472–87, 509 (1958).

(4) Brown, K. B., Coleman, C. F., Crouse, D. J., Denis, J. O., Moore, J. G., *U.S. At. Energy Comm. Rep.* **ORNL-1734** (1954).

(5) Cerrai, E., Testa, C., *Energ. Nucl.*, **6**, 707 (1959).

(6) Coleman, C. F., *At. Energy Rev.*, **2** (2), 3–54 (1964).

(7) Coleman, C. F., *Nucl. Sci. Eng.*, **17**, 274–86 (1963).

(8) Coleman, C. F., Brown, K. B., Moore, J. G., Crouse, D. J., *Ind. Eng. Chem.*, **50**, 1756–62 (1958).

(9) Crouse, D. J., Brown, K. B., *U. S. At. Energy Comm. Rept.*, **ORNL-1959** (1955).

(10) Crouse, D. J., Brown, K. B., Arnold, W. D., Moore, J. G., Lowrie, R. S., *U.S. At. Energy Comm. Rept.* **ORNL-2099** (1956).

(11) Florence, T. M., Farrar, Y. B., *Anal. Chem.* **40**, 1200–06 (1968).

(12) Good, M. L., Bryan, S. E., *J. Amer. Chem. Soc.*, **82**, 8636 (1960).

(13) Good, M. L., Bryan, S. E., *J. Inorg. Nucl. Chem.*, **20**, 140–6 (1961).

(14) Good, M. L., Bryan, S. E., *ibid.*, **25**, 1167–73 (1963).

(15) Ishimori, T., Akatsu, E., Cheng, W., Tsukuechi, K., Osakabe, T., *Jap. At. Energy Res. Inst. Rep.*, **JAERI-1062** (1964).

(16) Ishimori, T., Akatsu, E., Tsukuechi, K., Kobune, T., Usuba, Y., Kimura, K., Onawa, G., Uchyama, H., *ibid.*, **JAERI-1106** (1966).

(17) Ishimori, T., Nakamura, E., *ibid.*, **JAERI-1047** (1963).

(18) Lloyd, P. J., Mason, E. A., *J. Phys. Chem.*, **68**, 3120–9 (1964).

(19) Lloyd, P. J., Mason, E. A., *U. S. At. Energy Comm. Rep.*, **MITNE-43** (1964).

(20) Lloyd, P. J., Mason, E. A., *ibid.*, **MITNE-50** (1964).

(21) Maeck, W. J., Booman, G. I., Kussy, M. E., Rein, J. E., *Anal. Chem.*, **33**, 1775–9 (1961).

(22) Marcus, Y., *Chem. Rev.*, **63**, 139–70 (1963).

(23) Moore, F. L., *Anal. Chem.*, **29**, 1660 (1957).

(24) Moore, F. L., *ibid.*, **30**, 908 (1958)

(25) Moore, F. L., *Nat. Acad. Sci., Nucl. Sci. Ser.*, **NAS-NS-3101** (1960).

(26) Moore, J. G., Brown, K. B., Coleman, C. F., *U. S. At. Energy Comm. Rept.*, **ORNL-1922** (1955).

(27) Roth, J. A., Henry, H. E., *J. Chem. Eng. Data*, **10**, 298–301 (1965).

(28) Seeley, F. G., Crouse, D. J., *ibid.*, **11**, 424–9 (1966).

(29) Skavdahl, R. E., Mason, E. A., *U. S. At. Energy Comm. Rept.*, **MITNE-20** (1962).

(30) Smith, E. L., Page, J. E., *J. Soc. Chem. Ind.* (London), **67**, 48–51 (1948).

(31) Vaughen, V. C. A., Mason, E. A., *Trans. Amer. Nucl. Soc.*, **5**, 462–5 (1962).

(32) Vaughen, V. C. A., Mason, E. A., *U. S. At. Energy Comm. Rept.*, **TID-12665** (1960).

RECEIVED for review December 14, 1970. Accepted June 11, 1971. Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.