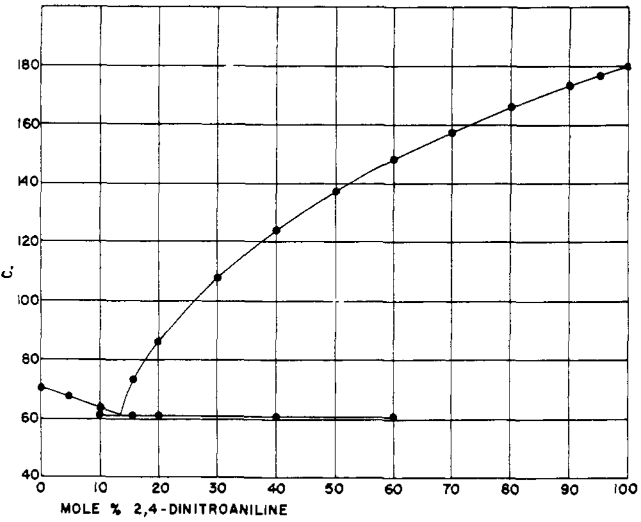

Figure 1. Phase diagram of system o-nitroaniline–2,4-dinitroaniline

system. A eutectic containing 14.5 mole % of 2,4-dinitroaniline and melting at 60.7° C. was found. In one instance, a melt having the composition 90 mole % *o*-nitroaniline, 10 mole % 2,4-dinitroaniline had a liquidus value of 62.3° C., instead of 64.0° C. which was obtained on other runs of the same composition. This point may represent a liquidus value for an unstable phase of *o*-nitroaniline with 2,4-dinitroaniline. Efforts to repeat this point failed.

Table I. Liquidus and Eutectic Temperature Data for Systemo-Nitroaniline–2,4-Dinitroaniline

Mole % 2,4-Dinitroaniline	Liquidus Temp., ° C.	Eutectic Temp., ° C.
0	70.6	...
5	67.0	...
10	64.0	60.7
16	73.1	60.7
20	86.0	60.7
30	108.1	...
40	123.3	60.7
50	136.6	...
60	147.8	60.7
70	157.3	...
80	165.6	...
90	172.9	...
95	176.5	...
100	179.9	...

Data for this system are shown graphically in Figure 1 and given in Table I.

LITERATURE CITED

(1) Burkardt, L.A., McEwan, W.S., Pitman, H.W., *Rev. Sci. Instr.* 27, 693 (1956).

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Extraction of Metals from Chloride Solutions with Amines

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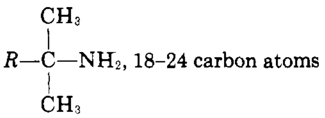
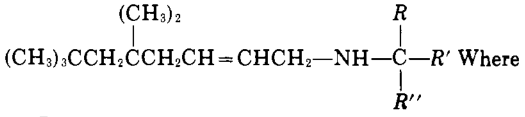
Extraction coefficients for 63 metal ions were determined from both hydrochloric acid and acidified lithium chloride solutions with representative primary, secondary, tertiary, and quaternary alkylammonium chlorides in diethylbenzene diluent. The aqueous chloride concentration was varied from 0.5 to 10*M*.

MUCH INTEREST in the liquid-liquid solvent extraction of metals with high molecular weight amines has developed since their ability to extract acid was reported in 1948 (*13*). Many investigators have examined the extraction characteristics of these reagents in both survey and process-oriented studies (*1–12*). With respect to the chloride system, many of the studies have been only with tertiary amines and, for the most part, have been limited to extractions from hydrochloric acid. In addition, different investigators have used a variety of diluents, making correlation of data from different sources difficult. In the work reported here, the extraction of 63 metal ions from both hydrochloric acid and acidified lithium chloride solutions was systematically surveyed with representative primary, secondary, tertiary, and quaternary alkylammonium chlorides in diethylbenzene diluent.

EXPERIMENTAL

Materials. A description of the amines chosen to represent the different amine types in the metal extraction tests is given in Table I. The amine concentration was 0.1*M*.

Table I. Description of Amines

Amine Type	Compound[a]	
Primary	Primene JM	 $R-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-NH_2$, 18–24 carbon atoms
Secondary	Amberlite LA-1	 $(CH_3)_3CCH_2\overset{\displaystyle (CH_3)_2}{C}CH_2CH{=}CHCH_2-NH-\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}-R'$ Where $R + R' + R'' = 12\text{–}14$ carbons
Tertiary	Alamine 336	R_3N, where the R's are mixed *n*-octyl and *n*-decyl
Quaternary	Aliquat 336	$[R_3N-CH_3]^+Cl^-$, where the R's are mixed *n*-octyl and *n*-decyl

[a] Primene JM and Amberlite LA-1 are supplied by Rohm and Haas Co.; Alamine 336 and Aliquat 336 are supplied by General Mills, Inc.

The diluent was diethylbenzene except for tests with Aliquat 336, wherein the diethylbenzene diluent was modified with 3 vol. % tridecanol to prevent separation of the amine chloride salt from the diluent as a third liquid phase at high chloride concentrations. The amine solutions were scrubbed with dilute hydrochloric 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 with diluent 0.1*M*, and contacted with 0.5*M* HCl to convert the amine to the chloride salt form.

The aqueous solutions contained the metal ion in either hydrochloric acid or LiCl-0.2*M* HCl solutions at total chloride concentrations of 0.5, 2.0, 5.0, 7.5 and 10*M*. The chloride dependence curves (Figure 1) were drawn from data for

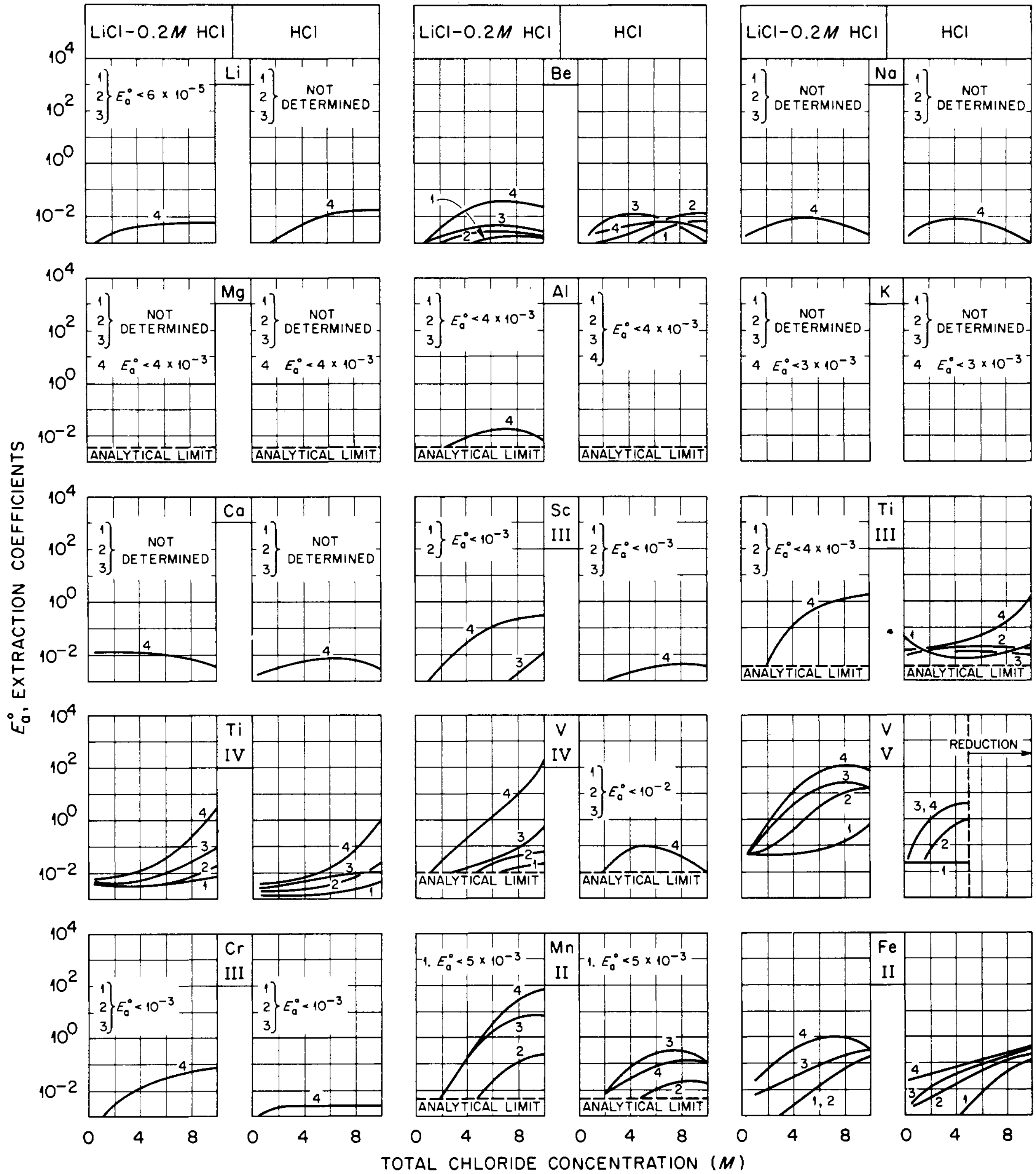


Figure 1. Extraction of metals with 0.1M amine chloride solutions

1. Primene JM in diethylbenzene
2. Amberlite LA-1 in diethylbenzene
3. Alamine 336 in diethylbenzene
4. Aliquat 336 in 95% diethylbenzene–3 % tridecanol

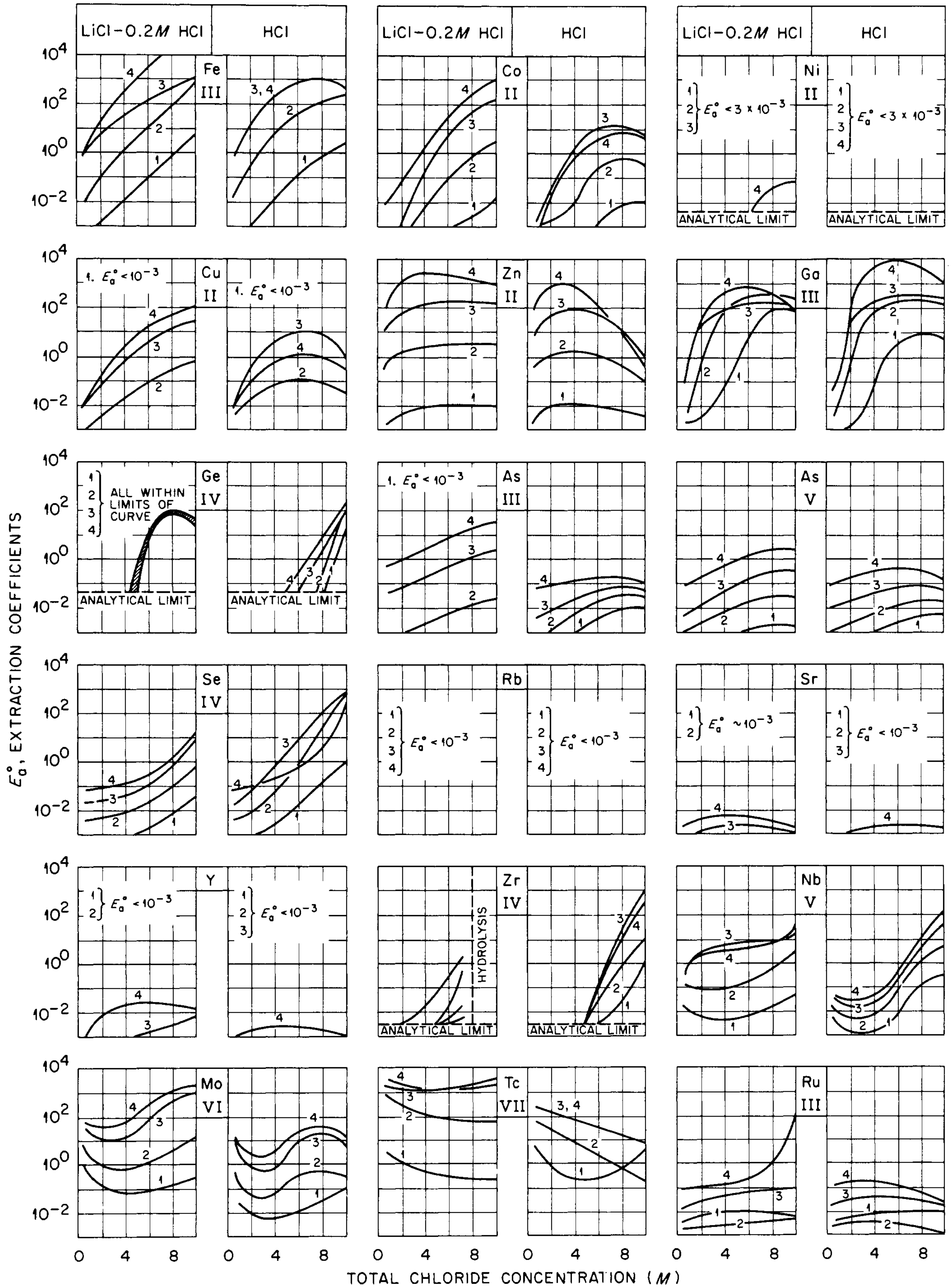


Figure 1. Continued

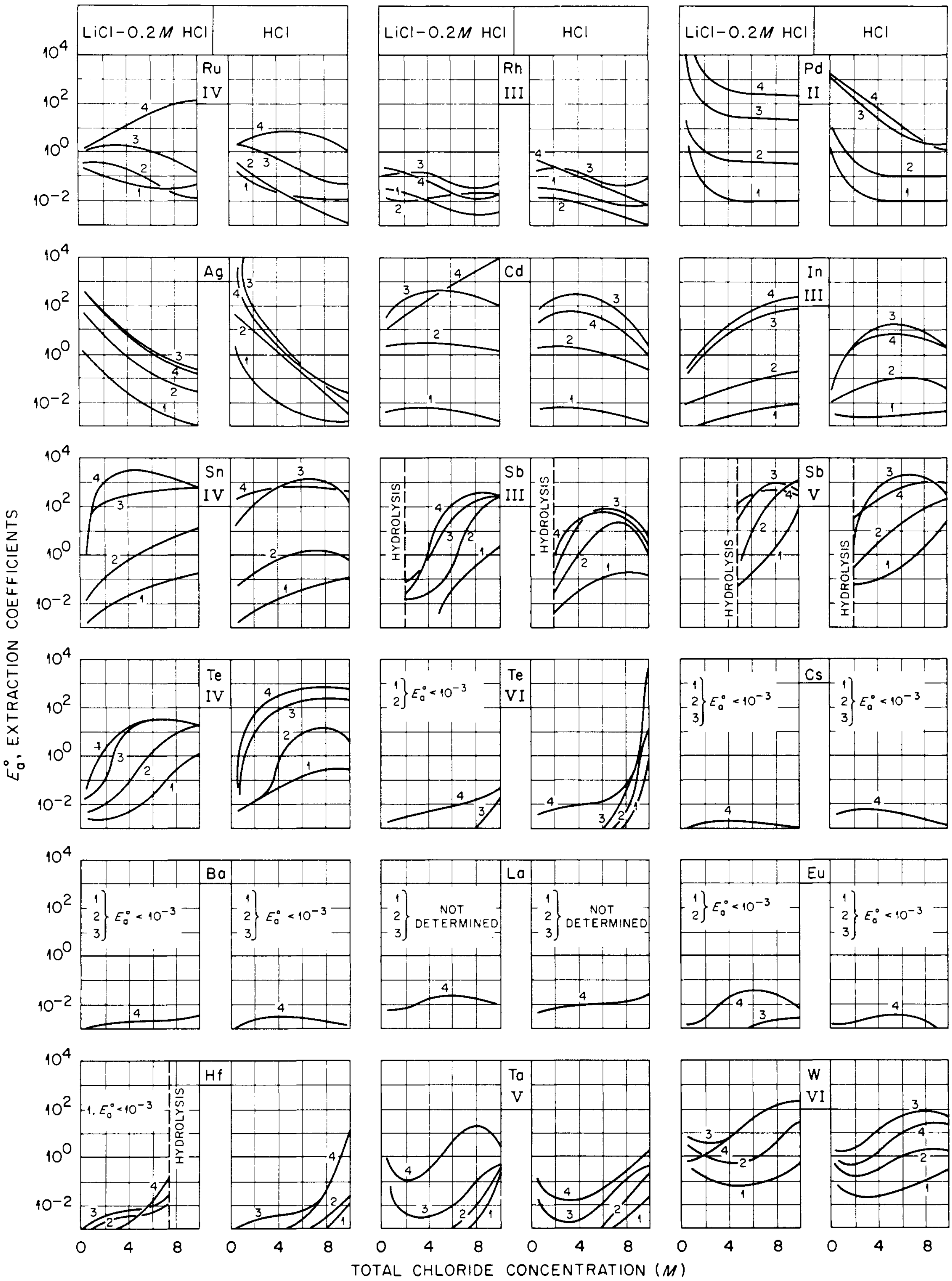


Figure 1. Continued

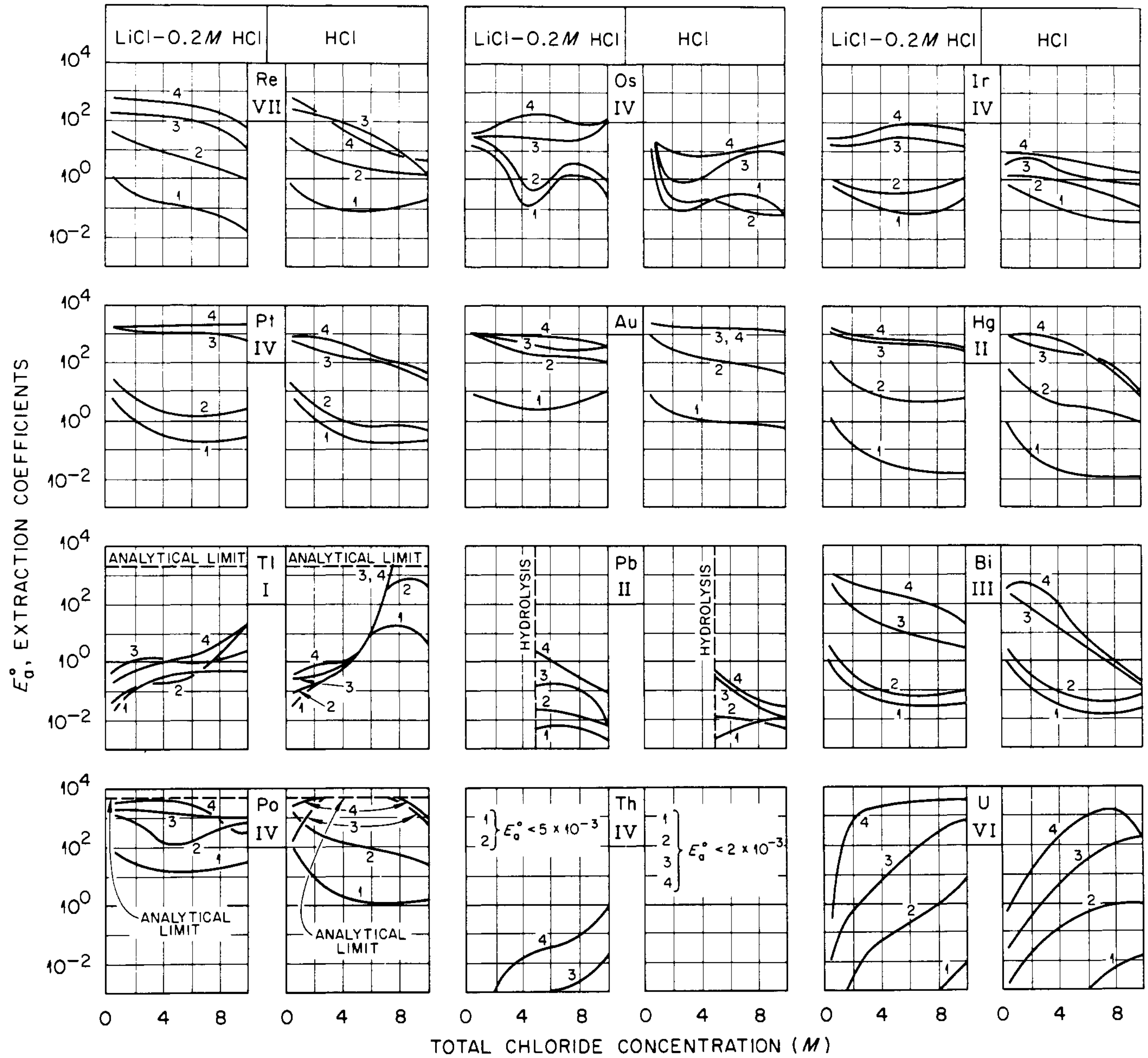


Figure 1. Continued

these five concentration points. In most tests, the metal ion was present at macro concentration (0.01*M*) rather than at radioactive tracer concentration to minimize effects on extraction results of a small amount of a strong extractant which could possibly be present as an impurity in the amine or diluent. With 0.01*M* metal in the initial aqueous phase, metal loading of the amine phase was not high enough to depress extraction coefficients appreciably. With niobium, technetium, silver, tantalum, rhenium, osmium, thallium, and polonium, 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 vigorously contacted for 10 minutes in separatory funnels mounted in a wrist-action shaker. Not all data points were checked for longer contact times, but spot checks indicated that equilibrium conditions were obtained within 10 minutes. Usually, the appropriate radiotracer was added, and the distribution of the metal between the phases was determined by gamma counting. Where suitable radiotracers were not available, flame spectrophotometric, ionic, or neutron activation analyses were made.

RESULTS

The extraction data are shown graphically in Figure 1 in the order of the metal atomic number. The extraction coefficient (E_a^0) is the ratio of the molar concentration of the solute in the organic phase to its molar concentration in the aqueous phase at equilibrium:

$$E_a^0 = \frac{C_{\text{org.}}}{C_{\text{aq.}}}$$

This value, a measure of the extraction power of the amines, is plotted against the chloride concentration in the aqueous phase. Many of the metals were extracted strongly. Extraction coefficients usually were higher in extractions from the salt solutions than from hydrochloric acid. With most metals, the extraction power varied in the order: Aliquat 336 (quaternary) $\geqq$ Alamine 336 (tertiary) > Amberlite LA-1 (secondary) $\gg$ Primene JM (primary).

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LITERATURE CITED

(1) Baybarz, R.D., Kinser, H.B., *U.S. At. Energy Comm. Rept.* **ORNL-3244** (1962).
(2) Brown, K.B., *et al.*, *Proc. U.N. Intern. Conf. Peaceful Uses At. Energy, 2nd Geneva* **3**, 472-487, P/509 (1958).
(3) Brown, K.B., Moore, J.G., Coleman, C.F., Crouse, D.J., Arnold, W.D., *U.S. At. Energy Comm. Repts.* **ORNL-1734** (1954); **ORNL-1922** (1955); **ORNL-1959** (1955); **ORNL-2099** (1956); **ORNL-3030** (1960).
(4) Cerrai, E., Testa, C., *Energia Nucl.* **6**, 707 (1959).
(5) Coleman, C.F., *Nucl. Sci. Eng.* **17**, 274-286 (1963).
(6) Coleman, C.F., Brown, K.B., Moore, J.G., Crouse, D.J., *Ind. Eng. Chem.* **50**, 1756-62 (1958).
(7) Good, M.L., Bryan, S.E., *J. Am. Chem. Soc.* **82**, 8636 (1960); *J. Inorg. Nucl. Chem.* **20**, 140-146 (1961); *Ibid.*, **25**, 1167-1173 (1963).
(8) Ishimori, T., *et al.*, *Japan At. Energy Res. Inst. Rept.* **JAERI-1047** (1963).
(9) Maeck, W.J., Booman, G.L., Kussy, M.E., Rein, J.E., *Anal. Chem.* **33**, 1775-79 (1961).
(10) Moore, F.L., *Ibid.*, **29**, 1660 (1957); *Ibid.*, **30**, 908 (1958).
(11) Moore, F.L., *Nat. Acad. Sci., Nucl. Sci. Ser.* **NAS-NS-3101** (1960).
(12) Roth, John A., Henry, Hugh E., J. CHEM. ENG. DATA **10**, 298-301 (1965).
(13) Smith, E.L., Page, J.E., *J. Soc. Chem. Ind. (London)* **67**, 48-51 (1948).

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Some *p*-Nitrophenyl Esters of *N*-Acylated Amino Acids

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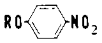
p-Nitrophenyl esters of some N-acylated glycines and N-acylated dl-leucines were prepared. An example of the method of preparation is cited and melting points and yields are listed.

DURING the preparation of analogs of the antibiotic septacidin, *p*-nitrophenyl esters of *N*-acylated amino acids were prepared (*1*, *3*). Dicyclohexyl carbodiimide was used as the condensing agent in the synthesis of these compounds (*2*). As an example, the preparation of the *p*-nitrophenyl ester of *N*-capryl glycine is described.

To a solution of 7 grams *N*-capryl glycine (*4*) (0.031 mole) in 210 ml. of anhydrous ethyl acetate at 5° C., 4.25 grams of *p*-nitrophenol (0.031 mole) and 6.30 grams of dicyclohexyl carbodiimide (0.031 mole) were added. The solution was kept at 5° C. for 30 minutes, then at room temperature for 2 hours, and finally at 35° C. for an additional 2 hours. Several drops of acetic acid were added to destroy any excess dicyclohexyl carbodiimide, and after cooling the solution to 5° C., the urea that formed was filtered off. The ethyl acetate was evaporated, and the ester was crystallized from ether-hexane mixtures. Usually a second recrystallization was necessary to obtain a pure product. The yield was 7.2 grams (66%).

All acyl glycine esters showed absorption in the IR at 5.73, 6.10, 6.20, 6.30 microns and all acyl leucine esters absorbed at 5.72, 6.16, 6.26 and 6.36 microns. IR spectra were determined in nujol with a Perkin Elmer No. 21 Spectrophotometer. Table I lists the new compounds prepared, along with the melting points and elemental analyses.

Table I. Analysis of Acyl Glycine and Leucine Esters

		Yield,		Calculated, %			Found, %		
R	M.P.,[a] ° C.	%	Formula	C	H	N	C	H	N
Acetyl glycyl	125-126 (lit. 125-126) (*6*)	60	$C_{10}H_{10}N_2O_5$	50.42	4.23	11.76	49.81	4.63	11.55
Caproyl glycyl	102-102.5	70	$C_{14}H_{18}N_2O_5$	57.14	6.12	9.49	57.34	5.87	9.79
Capryl glycyl	95-95	66	$C_{18}H_{26}N_2O_5$	61.70	7.48	8.00	61.50	7.55	7.80
Lauroyl glycyl	96-97.5	67	$C_{20}H_{30}N_2O_5$	63.30	8.24	7.38	62.93	8.22	7.48
Myristoyl glycyl	101-103	65	$C_{22}H_{34}N_2O_5$	65.00	8.43	6.89	65.10	8.53	7.00
Palmitoyl glycyl	108-109	58	$C_{24}H_{38}N_2O_5$	66.35	8.75	6.45	66.57	8.96	6.44
Acetyl *dl*-leucyl	118-119 (Lit.125-126) (*5*)	50	$C_{14}H_{18}N_2O_5$	57.13	6.12	9.49	57.56	6.41	9.43
Caproyl *dl*-leucyl	83-85	85	$C_{18}H_{26}N_2O_5$	61.70	7.48	8.00	61.52	7.51	8.13
Lauroyl *dl*-leucyl	78-79	75	$C_{24}H_{38}N_2O_5$	66.35	8.75	6.45	66.55	8.93	6.42
Palmitoyl *dl*-leucyl	83-84	75	$C_{28}H_{46}N_2O_5$	68.59	9.38	5.91	68.69	9.58	6.19

[a] All melting points were taken on a Fisher-Johns apparatus.

LITERATURE CITED

(1) Aszalos, A., Lemanski, P., Berk, B., Dutcher, J.D., Fifth Interscience Conference on Antimicrobial Agents and Chemotherapy, Washington, D. C., October 1965.
(2) Bodanszky, M., du Vigneaud, V., *Biochem. Prep.* **10**, 122 (1963).
(3) Dutcher, J.D., von Saltaz, M.H., Pansy, F.E., "Antimicrobial Agents and Chemotherapy 1963," pp. 83-88, American Society for Microbiology, Ann Arbor, Mich., 1964.
(4) Jungermann, E., Gerecht, J.F., Krems, T.J., *J. Chem. Soc.* **78**, 172 (1956).
(5) Lorand, L., Brannen, W.T., Jr., Rule, N.G., *Arch. Biochem. Biophys.* **96**, 147 (1962).
(6) Zahn, H., Otten, H.G., *Ann.* **643**, 139 (1962).

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