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TERTIARY ALCOHOLS AS SOLVENTS FOR THE EXTRACTION OF URANIUM

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TERTIARY ALCOHOLS AS SOLVENTS FOR THE EXTRACTION OF URANIUM

M. R. Poston, B. I. V. Bailey and W. H. Baldwin

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1. Summary and Conclusions

Hexone had long been recommended as a solvent for the selective extraction of heavy metals nitrates (especially uranyl and plutonyl) from aqueous solutions salted with nitrates of lighter metals. Previous work[1] on the comparison of solvents having different chemical structures was limited to one tertiary alcohol (i.e. tertiary butanol). Since tertiary butanol and water have a relatively high mutual miscibility, it was considered desirable to test an homologous series of tertiary alcohols in which miscibility with water would be decreased with increasing molecular weight. Tertiary amyl alcohol (2-methyl 2-butanol) was obtained from commercial sources but the others (2-methyl 2-pentanol, 2-methyl 2-hexanol and 2-methyl 2-heptanol) were synthesized in the laboratory.

The distribution of uranium (10 g U/liter as UNH) and ruthenium tracer was determined between the organic solvents mentioned and an equal volume of an aqueous phase containing 0.2 M HNO_3 and $Al(NO_3)_3$ (0.5 to 2.0 M/l). At 1M $Al(NO_3)_3$, the following distribution coefficients were observed:

Solvent	Uranium D.C. $\frac{\text{mg/ml org.}}{\text{mg/ml aq.}}$	Ruthenium D.C. $\frac{\text{mv/ml org.}}{\text{mv/ml aq.}}$
Tertiary Amyl alcohol	1.19	1.39
2-Methyl 2-Pentanol	0.553	0.55
2-Methyl 2-Hexanol	0.318	0.345
2-Methyl 2-Heptanol	0.292	0.219
Hexone	1.0	0.087
Dibutyl Cellosolve	0.129	--

Hexone extracted more uranium than any of the other solvents tested

except tertiary amyl alcohol and less ruthenium tracer than any of the other solvents tested. Hexone was better in these tests than any of the other solvents used.

The material covered by this report has been summarized from notebooks CL-1618 and CL-1613.

2. Introduction

Earlier work[1] comparing solvent structure with uranium extraction had established that, structurally: (1) ketones are better solvents for U than the corresponding alcohol (2 to 20 times); and (2) little difference exists between normal, secondary, and tertiary butanols in U extraction, but the organic phase volume increases in the order named, due to increasing solubility of water.

The work reported herein was undertaken to study further the relation between solvent structure and uranium extraction, particularly among the tertiary alcohols that are less soluble in water.

3. Physical Properties - Tertiary Alcohols

In Table I are presented physical properties of the series of the tertiary alcohols tested. Tertiary butyl alcohol, which is water soluble, is included. The tertiary amyl alcohol used in these experiments was obtained from Eastman Kodak Company.

Table I

Physical Properties of Tertiary Alcohols

Alcohol	Formula	Mol. Wt.	B.P.*	F.P.*	Sol. H_2O	Density*
Tert. Butyl Alcohol	$(CH_3)_3COH$	74	83°C	25°C	Sol.	$0.779^{26°}$
Tert. Amyl Alcohol	$C_2H_5(CH_3)_2COH$	88	102	-11.9°	SL.Sol	$0.809^{20°/4}$
2- Me 2- Pentanol	$C_3H_7(CH_3)_2COH$	102	122	-107°	V.SL.Sol	$0.835\frac{15.4}{4.4}$
2- Me 2- Hexanol	$C_4H_9(CH_3)_2COH$	116	141		Insol.	$0.815\ \frac{20}{20}$
2- Me 2- Heptanol	$C_5H_{11}(CH_3)_2COH$	130	162/735 m.m. 66.5/15m.m.		Insol.	$0.814\ \frac{25}{4}$

* From the literature.

4. Preparation - Tertiary Alcohols

Three of the four alcohols in the homologous series tested were synthesized in the laboratory. The general method of preparation was a Grignard reaction involving the appropriate reagent and a ketone. In all cases the addition compound was hydrolyzed with dilute acid, washed with a dilute carbonate solution and water and finally purified by fractionation through a packed laboratory column.

2-Methyl 2-Hexanol. Butyl Grignard reagent was prepared[2] by reacting 48 g. (2 mols) of magnesium turnings with 274 g. (2 mols) of butyl bromide in 770 ml. of ethyl ether. One hundred and fifty ml. (2 mols) of acetone in an equal volume of ether was then added with stirring. After standing over-night, the mixture was refluxed gently for 1/2 hour and then

poured into a beaker containing ice and 1.5 liters of water. The product was hydrolyzed by adding 800 ml. of 10% HCl. The layers were next separated and the organic layer washed with 5% Na_2CO_3 and water. The product was dried by allowing it to stand over anhydrous Na_2SO_4 and purified by fractionation through a laboratory column packed with glass helices. A yield of 115 g. (50% theory) boiling at 140° C (uncor.), was obtained.

2-Methyl 2-Pentanol. This was prepared by reacting 48 g. (2 mols) of magnesium turnings with 246 g. (2 mols) of propyl bromide, and adding 150 ml. (2 mols) of acetone. The addition product was hydrolyzed, washed, and purified as above, yielding 156 g. (75% theory) of 2-methyl, 2-pentanol, b.p. 121°C (uncor.).

2-Methyl 2-Heptanol. Magnesium turnings (48 g., 2 mols) were reacted with 284 g. (2 mols) of methyl iodide, to which was added 230 g. (2 mols) of methyl n-amyl ketone. The addition product was hydrolyzed and washed as described above, and purified by fractionating at reduced pressure. There was obtained 87 g. (33% theoretical) of 2-methyl 2-heptanol, b.p. 61°C at 10 mm. (uncor.).

5. Uranium Distribution

A series of experiments was conducted to determine the distribution of macro quantities of uranium between salted solutions of various concentrations and the tertiary alcohols. In order to compare the solvent characteristics of the tertiary alcohols with more widely used solvents, control runs were made using the solvents hexone and dibutyl cellosolve.

It is seen from the results, in Table 2 and Figure 1, that uranium extraction decreases as the normal chain length on the dimethyl carbinol increases. The uranium distribution coefficients for three of the tertiary

alcohols ranged in between those found for hexone and dibutyl cellosolve.

Experimental. Aqueous solutions were prepared containing 0.2 M HNO_3, 10 g. U per liter, and varying amounts of $Al(NO_3)_3$. Equal volume extractions were made on 25 ml. samples of each solution, using hexone, dibutyl cellosolve, and the tertiary alcohols. Equilibration was accomplished with a glass interface stirrer, electrically driven. Aliquots of each phase were submitted for colorimetric uranium analyses. Results are presented in Table 2, and Figure 1.

6. Ruthenium Distribution

The study of the solvent characteristics of the homologous series of alcohols was extended to radioactive ruthenium and its distribution between salted aqueous feeds and the alcohols. Here, as in the case of the uranium reported above, the ruthenium extraction was found to decrease as the length of the normal chain increased. It is noted that hexone extracted less ruthenium than did any of the alcohols. The superiority of hexone over these tertiary alcohols as a solvent for uranium recovery is thus demonstrated: at any given salt concentration, hexone extracted less ruthenium and more uranium than the tertiary alcohols. A single exception to the above statement was noted in the lower salting concentrations with tertiary amyl alcohol, which extracted slightly more uranium than hexone. This slight advantage is more than off-set, however, by the fact that tertiary amyl alcohol extracted more ruthenium by a factor of 10 or greater than did hexone.

Experimental. Solutions were prepared containing 0.2 M HNO_3, ruthenium tracer, and varying concentrations of aluminum nitrate. The Ru

tracer used in these experiments had been previously purified by distillation from a permanganate-sulfuric acid solution, and a sufficient quantity was added to the aqueous feed to give it 2×10^5 B cts/min/ml. (about 10% geometry). Equal volumes of organic and aqueous were equilibrated in a glass test tube with an interface stirrer, electrically driven. After separation of phases, the activity in each layer was determined on the high pressure argon ionization chamber for gammas. Results are presented in Table 3 and Figure 2.

[redacted]

Table 2

Uranium Distribution in Tertiary Alcohols

Aqueous: $Al(NO_3)_3 \cdot 9H_2O$ (varying conc.)
0.2 M HNO_3
10 g. U/liter, as UNH

Solvents: Tertiary alcohols, hexone and dibutyl cellosolve.

Equal volume extractions at room temperature.

Solvent	$Al(NO_3)_3$ Conc.	U Dist. Coef. $\frac{Org.}{Aq}$
Tertiary Amyl Alcohol	0.5 M	0.194
" " "	1.0 M	1.19
" " "	1.5 M	8.5
" " "	2.0 M	26.8
2- Methyl 2- Pentanol	0.5 M	0.049
" "	1.0 M	0.553
" "	1.5 M	5.4
" "	2.0 M	21.6
2- Methyl 2- Hexanol	0.5 M	0.028
" "	1.0 M	0.318
" "	1.5 M	2.9
" "	2.0 M	15.3
2- Methyl 2- Heptanol	0.5 M	0.026
" "	1.0 M	0.292
" "	1.5 M	2.58
" "	2.0 M	14.2
Hexone	0.5 M	0.106
"	1.0 M	1.0
"	1.5 M	8.5
"	2.0 M	35
Dibutyl Cellosolve	0.5 M	0.014
" "	1.0 M	0.129
" "	1.5 M	1.1
" "	2.0 M	4.9

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Table 3

Ruthenium Distribution In Tertiary Alcohols

Aqueous: Al $(NO_3)_3 \cdot 9H_2O$ (varying conc.)

0.2 M HNO_3

Ru tracer

Solvents: Tertiary Alcohols and Hexone

Equal volume extractions at room temperature

Solvent	Al $(NO_3)_3$ Concentration	Ru Dist. Coef. $\frac{Org.}{Aq.}$
Tertiary Amyl Alcohol	0.5 M	0.48
" " "	1.0	1.39
" " "	1.5	2.37
" " "	2.0	3.59
2- Methyl 2- Pentanol	0.5 M	0.14
" "	1.0	0.55
" "	1.5	1.28
" "	2.0	1.60
2- Methyl 2- Hexanol	0.5 M	0.083
" "	1.0	0.345
" "	1.5	0.570
" "	2.0	1.9
2- Methyl 2- Heptanol	0.5 M	0.055
" "	1.0	0.219
" "	1.5	0.555
" "	2.0	2.69
Hexone	0.5 M	0.052
"	1.0	0.087

[redacted]

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7. References

1. MonC-145, Solvent Extraction for Uranium Recovery from Homogeneous Pile Solution, W. H. Baldwin, August 23, 1946.

2. Fieser, Experiments in Organic Chemistry, p. 68, D. C. Heath and Company, New York, 1935.

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FIG. 1

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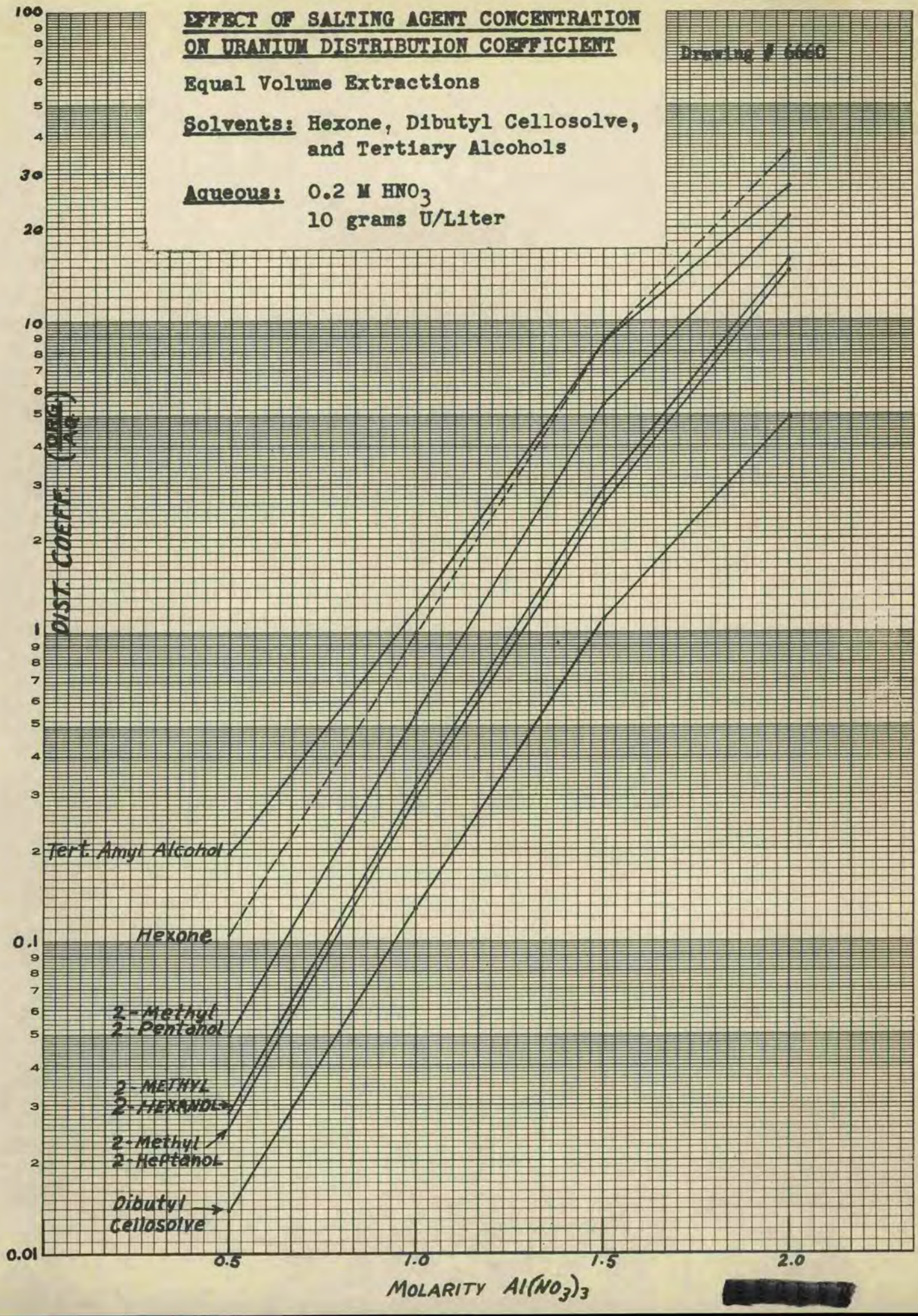

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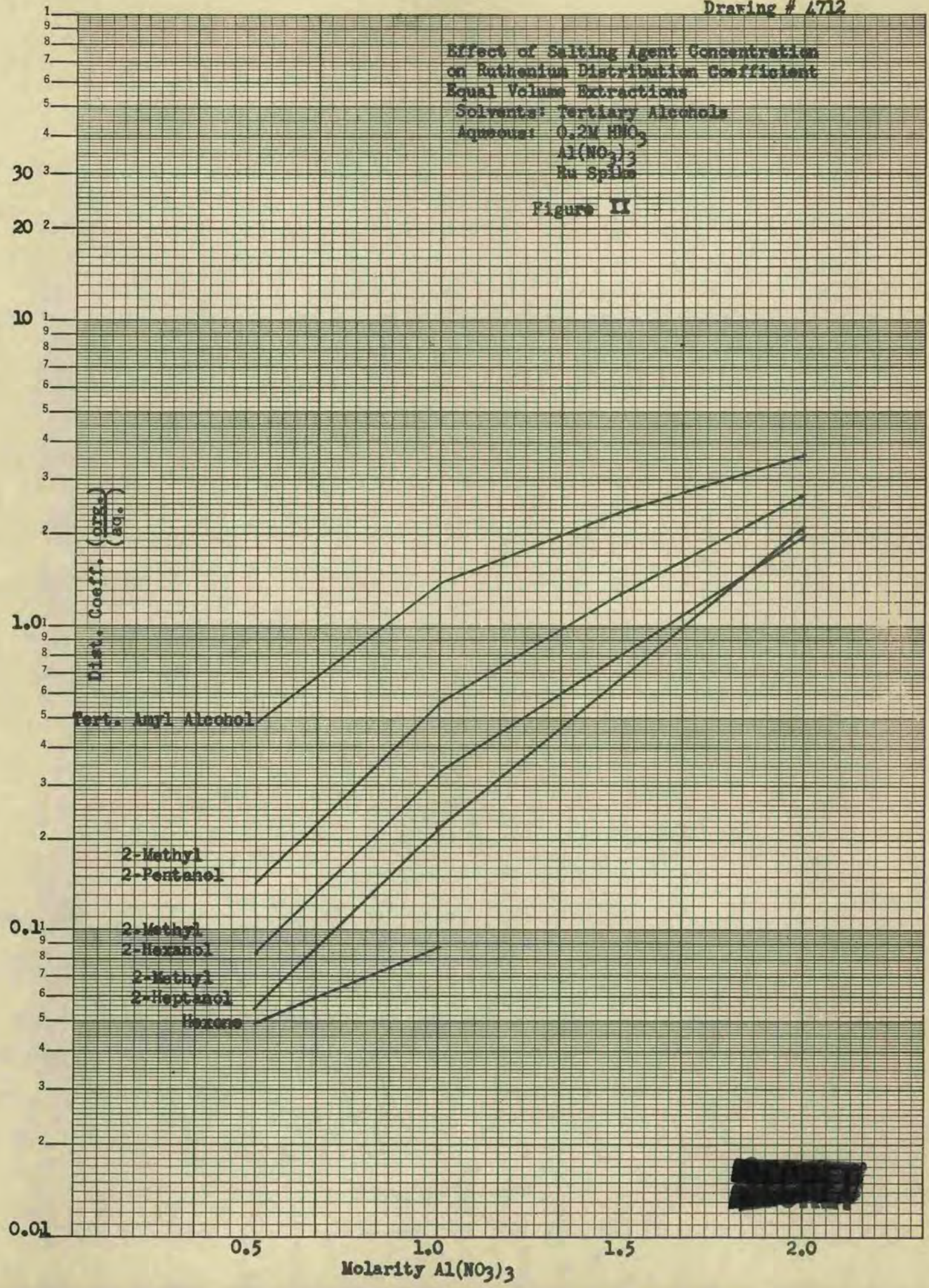

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