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Modeling the Effect of Temperature on Thorium and Nitric Acid Extraction and the Formation of Third Phase for Modification of the SEPHIS—Thorex Computer Program

S. B. Watson
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MODELING THE EFFECT OF TEMPERATURE ON THORIUM AND NITRIC ACID EXTRACTION AND THE FORMATION OF THIRD PHASE FOR MODIFICATION OF THE SEPHIS - THOREX COMPUTER PROGRAM

S. B. Watson and R. H. Rainey*

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*Oak Ridge Associated Universities

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TABLE OF CONTENTS

TABLE OF FIGURES

TABLE OF TABLES

MODELING THE EFFECT OF TEMPERATURE ON THORIUM AND NITRIC ACID EXTRACTION AND THE FORMATION OF THIRD PHASE FOR MODIFICATION OF THE SEPHIS - THOREX COMPUTER PROGRAM

S. B. Watson and R. H. Rainey*

ABSTRACT

Mathematical models have been developed for use with the SEPHIS - Thorex code which correct for the effect of temperature on thorium and nitric acid extraction and which provide a signal to indicate the formation of a second organic phase. Experimental programs have provided data which have been analyzed and indicate that increasing temperature decreases the distribution coefficient of thorium. Also increasing the temperature increases the concentration of thorium in the organic phase at which the third phase is formed.

INTRODUCTION

The tri-n-butyl phosphate (TBP) extraction process (Thorex process) for the reprocessing of HTGR Thorium fuel is being studied at Oak Ridge National Laboratory (ORNL). To facilitate this study, a computer package has been designed which models Solvent Extraction Processes Having Interacting Solutes (SEPHIS).[1,2] The code simulates countercurrent multi-stage extraction of three interacting solutes — uranium, thorium, and nitric acid. The code has been useful for several types of design, optimization, and problem evolutions of flow sheets for plant operations.

The objective of our present work is improvement of the SEPHIS code by incorporation of a mathematical model which corrects for the effect of temperature on the contactor system and by inclusion of a test for the formation of third phase. The effect of temperature is an

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*Chemical Technology Division

important consideration in a Thorex flow sheet. Temperature effect on the extraction of uranium and thorium has an important bearing on the overall extraction and stripping efficiencies, while temperature effect on the extraction of fission products is important from the standpoint of decontamination efficiency. A number of papers have reported the equilibrium distribution of the effect of uranyl and thorium nitrate and their thermodynamic quantities,[3-10] but these data were not satisfactory for determining a mathematical model. New experimental data determined by A. J. Weinberger[11] provided for this need.

In addition to the study of temperature effects on the distribution coefficients of thorium and nitric acid, data have also been obtained for the effects of temperature on the formation of a second organic phase. The second organic phase occurs when the concentration of thorium-TBP complex exceeds its solubility in the TBP-NDD mixture. High concentrations of thorium in the organic phase increase the decontamination from fission products. Fuel reprocessing plants, therefore, operate near, or above, the concentration of thorium at which the second organic phase may occur. If the second organic phase should occur, adjustments are required in operations to maintain process control and to prevent a potential criticality hazard. For these reasons knowledge of the conditions under which the second organic phase occurs is necessary prior to specifying flow sheet conditions.

This report presents the results of the laboratory tests done at Oak Ridge National Laboratory (ORNL) and the modeling of these results for implementation in the SEPHIS code in order to increase our understanding of both temperature effects and third-phase formation.

EXPERIMENTAL PROCEDURE AND LABORATORY RESULTS

Laboratory analyses have been prepared by members of the Analytical Chemistry Division at ORNL.[11] Stock solutions of concentrated nitric acid, thorium nitrate, and solvent were prepared as follows:

1. Concentrated nitric acid - prepared and analyzed a solution containing 13 $\underline{M}$ HNO_3.
2. Thorium nitrate - prepared a solution containing 2 $\underline{M}$ $Th(NO_3)_4$ and analyzed for thorium, nitrate, and H+.
3. Solvent - prepared a 30 vol% solution of TBP in n-dodecane (NDD) by adding 312 ml TBP to 700 ml NDD. This solution was mixed vigorously with 1/10 volume of 0.5 $\underline{M}$ Na_2CO_3 for 10 minutes. The organic phase was filtered through fine filter paper which had been wetted with a minimum of NDD. This was stored in a dark bottle and then analyzed for TBP and total phosphates. Duplicate analyses were required to agree with 1% and the two methods within 2%.

Working solutions (a total of 31) were prepared in the combinations shown in Fig. 1 from the stock solutions. The experimental ranges required to bracket the Acid Thorex flow sheet conditions are 20°–60°, 0.05 to 1.4 $\underline{M}$ $Th(NO_3)_4$, and 0.0 to 3.0 $\underline{M}$ $HNO_3(0.0\ UO_2(NO_3)_2)$. These are the limits for use of the correlation. The circled solutions were analyzed. These analyses were required to agree with the values calculated from the dilution within 1%.

The working solutions (aqueous and 30% TBP) were brought to the desired temperature. Equal volumes of the two solutions were mixed in a constant temperature bath for two minutes. The phases were allowed to separate for about 10 minutes. The solution was examined to determine

$H^+\underline{M}/Th\underline{M}$	0.05	0.10	0.20	0.30	0.50	0.75	1.00	1.25	1.50
0.00	x		x		x		x		ⓧ
0.05		x						x	
0.10	x		x		x		ⓧ		x
0.25				x					
0.50	x		x		ⓧ		x		x
0.75						x			
1.00	x		ⓧ		x		x		x
1.50		x						x	
3.00	ⓧ		x		x		x		x

Fig. 1. Combinations of Thorium and Acid Used to Obtain the Working Solutions.

whether there were two or three phases, and the results were recorded. Then the experimental procedure progressed as follows.

1. If there were only two phases, a portion of each phase was transferred to centrifuge tubes and centrifuged at high speeds for 15 minutes. The organic phase was examined to confirm that there was only one phase. If there were two organic phases, the organic sample was returned to the equilibration tube and processed as described in 2 below. If there was only one organic phase, the density was measured at the operating temperature along with the thorium and acid content of each phase.
2. If the equilibration tube contained three phases, as much as possible of the aqueous phase was carefully removed. Then an equal volume of 30% TBP was added and mixed to convert to one organic phase. The density of the aqueous phase was measured, and each phase was analyzed for thorium and acid.

3. The work continued until all concentrations had been equilibrated at each temperature.

For analyzing the conditions for third-phase formation, the following procedure was used:

> The combination of thorium concentration and minimum acid concentration at which third phase was observed was determined by adding small aliquots of fresh 30% TBP-NDD and equilibrating carefully to the point at which third phase just disappeared. The volume of solvent required to do this was recorded. A sample of organic and aqueous was removed for possible analysis. An additional volume of 0.1 ml fresh aqueous solution was added, and the mixture was equilibrated. If third phase was observed, the samples which were previously removed were analyzed. If third phase was not observed, the procedure was repeated since too much solvent must have been added.

It should be noted that this is a difficult procedure with $Th(NO_3)_4$–HNO_3 solutions because they have no color. Thus it may take several tests to be able to see the end point of the third-phase iteration. It is possible to add a little $UO_2(NO_3)_2$ to add color to see the end point better, but this should be avoided because the result would be modified somewhat.

The laboratory results for 30°, 40°, and 60° are presented in Table 1, Table 2 and Table 3, respectively.

EFFECT OF TEMPERATURE ON THE DISTRIBUTION OF THORIUM

This report studies the temperature effect on the extraction of thorium nitrate in nitric acid with 30% TBP in NDD. Of the data measured by Weinberger, plots of the logarithm or organic thorium versus the reciprocals of absolute temperature for each acidity are given in Figs. 2, 3, and 4 for initial aqueous thorium concentrations of 0.05 M, 0.2 M and 0.5 M, respectively. From these plots it appears that a

Table 1. Equilibration of Thorium Nitrate + Nitric Acid Solutions With 30% Tributylphosphate in n-Dodecane at 30°C.

ORNL-DWG 79-8398

Before equilibration aqueous thorium sol'n.		After equilibration						Distribution coefficient (O/A)	
		Thorium		Free acid		Density at temp.			
Thorium (m/l)	Free acid (m/l)	Aqueous (m/l)	Organic (m/l)	Aqueous (m/l)	Organic (m/l)	Aqueous (g/ml)	Organic (g/ml)	Thorium	HNO_3
0.0500	0.000	0.0496	0.0003	0.0000	0.0004	1.0162	0.8076	0.0061	-
0.0500	0.100	0.0490	0.0014	0.0931	0.0081	1.0187	0.8081	0.0286	0.087
0.0500	0.500	0.0420	0.0080	0.429	0.066	-	0.8125	0.190	0.154
0.0500	1.000	0.0336	0.0167	0.841	0.167	1.0366	0.8185	0.497	0.198
0.0500	3.000	0.0160	0.0320	2.538	0.497	1.0840	0.8342	2.00	0.196
0.1000	0.050	0.0944	0.0052	0.0449	0.0054	1.0360	0.8094	0.0551	0.120
0.1000	1.500	0.0544	0.0449	1.268	0.236	1.0590	0.8316	0.825	0.186
0.2000	0.000	0.1734	0.0239	-0.0003	0.0016	1.0677	0.8164	0.138	-
0.2000	0.100	0.1661	0.0308	0.0863	0.0142	1.0677	0.8192	0.185	0.165
0.2000	0.500	0.1478	0.0517	0.424	0.0771	1.0701	0.8389	0.350	0.182
0.2000	0.996	0.1275	0.0700	0.846	0.148	1.0754	0.8385	0.550	0.175
0.200	2.991	0.0872	0.1074	2.604	0.395	1.1145	0.8609	1.23	0.152
0.300	0.250	0.2224	0.0706	0.214	0.0378	1.0951	0.8360	0.317	0.177
0.500	0.000	0.3323	0.1228	-0.0060	0.0016	1.1472	0.8550	0.370	-
0.500	0.100	0.3690	0.1327	0.0869	0.0149	1.1475	0.8580	0.360	0.171
0.500	0.500	0.3510	0.1503	0.431	0.068	1.1512	0.8661	0.428	0.158
0.500	1.000	0.3224	0.1610	0.864	0.127	1.1579	0.8743	0.499	0.147
0.500	3.000	0.2112	0.1940*	2.443	0.314*	1.1623	0.882*	0.918	0.128
0.750	0.750	0.475	0.208*	0.623	0.0891*	1.2083	0.889*	0.438	0.143
0.999	0.000	0.624	0.226*	-0.0131	0.0035*	1.2461	0.891*	0.362	-
1.000	0.100	0.596	0.223*	0.0797	0.0118*	1.2391	0.892*	0.374	0.148
1.000	0.500	0.532	0.216*	0.380	0.539 *	1.2215	0.889*	0.406	0.142
1.000	1.000	0.453	0.208*	0.743	0.1018*	1.2030	0.890*	0.459	0.137
1.250	0.050	0.613	0.224*	0.0272	0.0061*	1.2421	0.884*	0.365	0.224
1.250	1.500	0.409	0.201*	1.007	0.1343*	1.190	0.888*	0.490	0.133
		Third phase (organic concentrations are average of two phases)							
0.500	3.000	0.2971	0.2165	2.728	0.312	1.1974	-	0.754	0.114
0.750	0.750	0.5336	0.2340	0.671	0.104	1.2278	-	0.439	0.155
0.999	0.000	0.750	0.276	-0.0092	0.0057	1.2919	-	0.368	-
1.000	0.100	0.6582	0.2631	0.0850	0.0067	1.2940	-	0.400	0.079
1.000	0.500	0.6802	0.2848	0.451	0.0618	1.3016	-	0.419	0.137
1.000	1.000	0.737	0.299	0.910	0.113	1.3126	-	0.406	0.124
1.000	3.000	0.7289	0.3138	2.844	0.238	1.3643	-	0.431	0.084
1.250	0.500	0.958	0.320	0.0320	0.0079	1.3751	-	0.334	0.100
1.250	1.500	0.9509	0.3171	1.416	0.147	1.4126	-	0.333	0.104
1.499	0.000	1.1991	0.3359	-0.0137	0.0049	1.4623	-	0.280	-
1.500	0.500	1.2082	0.3402	0.504	0.045	1.4753	-	0.282	0.089
1.500	3.000	1.1966	0.3578	2.920	0.191	1.5420	-	0.299	0.065

*Boundary of third phase.

Table 2. Equilibration of Thorium Nitrate + Nitric Acid Solutions With 30% Tributylphosphate in n-Dodecane at 40°C.

ORNL-DWG 79-8399

Before equilibration aqueous thorium sol'n.		After equilibration						Distribution coefficient (O/A)	
		Thorium		Free acid		Density at temp.			
Thorium (m/l)	Free acid (m/l)	Aqueous (m/l)	Organic (m/l)	Aqueous (m/l)	Organic (m/l)	Aqueous (g/ml)	Organic (g/ml)	Thorium	HNO_3
0.0500	0.000	0.0496	0.00066	0.0006	0.0006	1.0123	0.7996	0.0133	-
0.0500	0.100	0.0491	0.00133	0.0955	0.00682	1.0149	0.8002	0.0270	0.0714
0.0500	0.500	0.0431	0.00710	0.438	0.0597	1.0235	0.8040	0.165	0.136
0.0500	1.000	0.0347	0.0155	0.844	0.1452	1.0332	0.8098	0.447	0.172
0.0500	3.000	0.0177	0.0322	2.483	0.489	1.0789	0.8257	1.82	0.197
0.1000	0.050	0.0950	0.00440	0.0458	0.00439	1.0326	0.8012	0.0463	0.0959
0.1000	1.500	0.0575	0.0431	1.256	0.229	1.0554	0.8226	0.750	0.182
0.2000	0.000	0.181	0.0200	-0.00135	0.00159	1.0653	0.8069	0.110	-
0.2000	0.100	0.174	0.0263	0.0885	0.01264	1.0656	0.8097	0.151	0.143
0.2000	0.500	0.155	0.0473	0.427	0.0808	1.0679	0.8192	0.305	0.166
0.2000	0.996	0.134	0.0670	0.845	0.1434	1.0726	0.8289	0.500	0.170
0.2000	2.991	0.0921	0.1065	2.580	0.414	1.1106	0.8512	1.16	0.160
0.3000	0.250	0.238	0.0670	0.2146	0.0357	1.0934	0.8257	0.280	0.166
0.5000	0.000	0.388	0.1240	-0.00574	0.00266	1.1461	0.8438	0.319	-
0.5000	0.100	0.384	0.1300	0.0792	0.01314	1.1461	0.8474	0.338	0.166
0.5000	0.500	0.365	0.1470	0.422	0.0670	1.1487	0.8557	0.403	0.159
0.5000	1.000	0.349	0.1655	0.854	0.1290	1.1551	0.8639	0.474	0.151
0.5000	3.000	0.312	0.2031	2.648	0.318	1.1968	0.898	0.651	0.120
0.7502	0.750	0.547	0.2119	0.642	0.0888	1.2268	0.8829	0.387	0.138
0.9992	0.000	0.761	0.2552*	-0.0136	0.00439	1.2862	0.892	0.335	-
1.0000	0.100	0.738	0.2549*	0.0769	0.0126	1.2787	0.892	0.345	0.164
0.9996	0.500	0.660	0.2412*	0.418	0.0575	1.2635	0.890	0.365	0.137
0.9998	1.000	0.598	0.2373*	0.815	0.1075	1.2471	0.890	0.397	0.132
1.0000	3.001	0.383	0.2153*	2.275	0.282	1.2104	0.886	0.562	0.124
1.2498	0.050	0.751	0.2546*	0.0280	0.00697	1.2827	0.894	0.339	0.249
1.2501	1.500	0.553	0.2318*	1.085	0.1395	1.2369	0.889	0.419	0.129
			Third phase (organic concentrations are average of two phases)						
0.9992	0.000	0.763	0.2509	-0.0127	0.00580	1.2908	-	0.229	-
1.0000	0.100	0.759	0.2582	0.0827	0.01389	1.2923	-	0.340	0.168
0.9996	0.500	0.746	0.2668	0.437	0.0586	1.2988	-	0.358	0.134
0.9998	1.000	0.741	0.2767	0.895	0.1078	1.3091	-	0.373	0.120
1.0000	3.001	0.728	0.2888	2.752	0.246	1.3590	-	0.397	0.089
1.2498	0.050	0.979	0.308	0.0349	0.00822	1.3706	-	0.315	0.236
1.2501	1.500	0.979	0.315	1.393	0.1304	1.4064	-	0.322	0.094

*Boundary of third phase.

Table 3. Equilibration of Thorium Nitrate + Nitric Acid Solutions With 30% Tributylphosphate in n-Dodecane at 60°C.

ORNL-DWG 79-8400

Before equilibration aqueous thorium sol'n.		After equilibration						Distribution coefficient (O/A)	
		Thorium		Free acid		Density at temp.			
Thorium (m/l)	Free acid (m/l)	Aqueous (m/l)	Organic (m/l)	Aqueous (m/l)	Organic (m/l)	Aqueous (g/ml)	Organic (g/ml)	Thorium	HNO_3
0.0500	0.000	0.0499	0.000608	0.00093	0.000572	1.0030	0.7838	0.0122	-
0.0500	0.100	0.0494	0.00113	0.0981	0.00558	1.0055	0.7842	0.0229	0.0569
0.0500	0.500	0.0443	0.00603	0.451	0.0523	1.0145	0.7873	0.136	0.116
0.0500	1.000	0.0368	0.0137	0.866	0.138	1.0241	0.7928	0.372	0.159
0.0500	3.000	0.0202	0.0293	2.516	0.525	1.0676	0.8087	1.45	0.209
0.1000	0.050	0.0970	0.00334	0.0475	0.00357	1.0233	0.7852	0.0344	0.075
0.1000	1.500	0.0615	0.0392	1.265	0.230	1.0463	0.8047	0.637	0.182
0.2000	0.000	0.1875	0.0150	-0.00176	0.00238	1.0570	0.7892	0.080	-
0.2000	0.100	0.1832	0.0212	0.0912	0.01127	1.0573	0.7918	0.116	0.124
0.2000	0.500	0.163	0.0410	0.431	0.0654	1.0600	0.8005	0.252	0.152
0.2000	0.996	0.142	0.0605	0.852	0.1390	1.0645	0.8102	0.426	0.163
0.2000	2.991	0.103	0.0980	2.564	0.427	1.1009	0.8319	0.951	0.166
0.3000	0.250	0.248	0.0580	0.127	0.0332	1.0863	0.8060	0.234	0.153
0.5000	0.000	0.405	0.1055	-0.0066	0.00483	1.1399	0.8224	0.260	-
0.5000	0.100	0.395	0.1145	0.0843	0.01561	1.1396	0.8261	0.290	0.185
0.5000	0.500	0.377	0.1340	0.434	0.0710	1.1413	0.8350	0.355	0.164
0.5000	1.000	0.358	0.150	0.868	0.1370	1.1468	0.8438	0.427	0.158
0.5000	3.000	0.325	0.1798	2.656	0.366	1.1874	0.8606	0.553	0.138
0.7502	0.750	0.551	0.2056	0.654	0.0966	1.2170	0.8626	0.373	0.148
0.9992	0.000	0.775	0.2409	-0.0127	0.0068	1.2825	0.8726	0.311	-
1.0000	0.100	0.764	0.2456	0.0750	0.0152	1.2838	0.8757	0.321	0.203
0.9996	0.500	0.755	0.2529	0.429	0.0651	1.2907	0.8809	0.335	0.152
1.0000	1.000	0.748	0.258	0.871	0.125	1.3014	0.8875	0.345	0.144
1.0000	3.001	0.624	0.235*	2.654	0.314*	1.2978	0.880*	0.377	0.118
1.2498	0.050	0.966	0.278*	0.0332	0.0112*	1.3541	0.889*	0.288	0.337
1.2501	1.500	0.776	0.257*	1.255	0.163 *	1.3201	0.884*	0.331	0.130
1.4993	0.000	0.970	0.278*	-0.0089	0.0083*	1.3619	0.886*	0.287	-
1.4995	0.100	0.948	0.281*	0.0681	0.0145*	1.3542	0.889*	0.296	0.213
1.4998	0.500	0.901	0.275*	0.388	0.0565*	1.3430	0.886*	0.305	0.146
1.5002	1.000	0.845	0.270*	0.778	0.108 *	1.3333	0.884*	0.320	0.139
		Third phase (organic concentrations are average of two phases)							
1.0000	3.001	0.751	0.290	2.692	0.299	1.3486	-	0.386	0.111
1.2498	0.050	0.979	0.290	0.0310	0.0123	1.3616	-	0.296	0.397
1.2501	1.500	0.978	0.302	1.362	0.167	1.3944	-	0.309	0.123
1.4993	0.000	1.206	0.331	-0.0156	0.0104	1.4429	-	0.274	-
1.4995	0.100	1.210	0.333	0.0827	0.0158	1.4437	-	0.275	0.191
1.4998	0.500	1.209	0.333	0.448	0.0581	1.4535	-	0.275	0.130
1.5002	1.000	1.213	0.325	0.925	0.108	1.4469	-	0.268	0.117

*Boundary for third phase

ORNL-DWG 79-8622

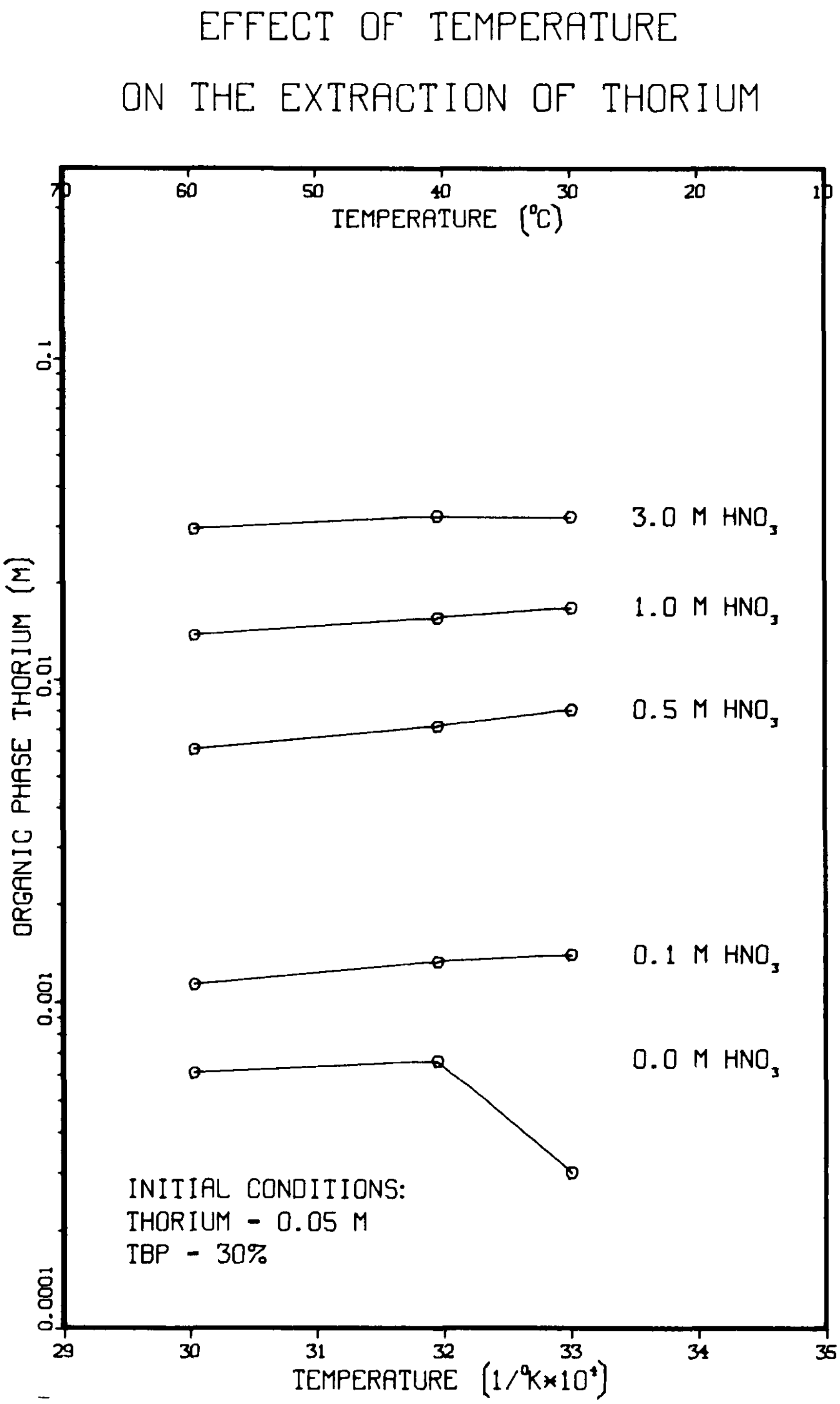

Fig. 2. Logarithm of Organic Thorium Versus the Reciprocal of Absolute Temperature for Five Initial Aqueous Acidities at an Initial Aqueous Thorium Concentration of 0.05 M.

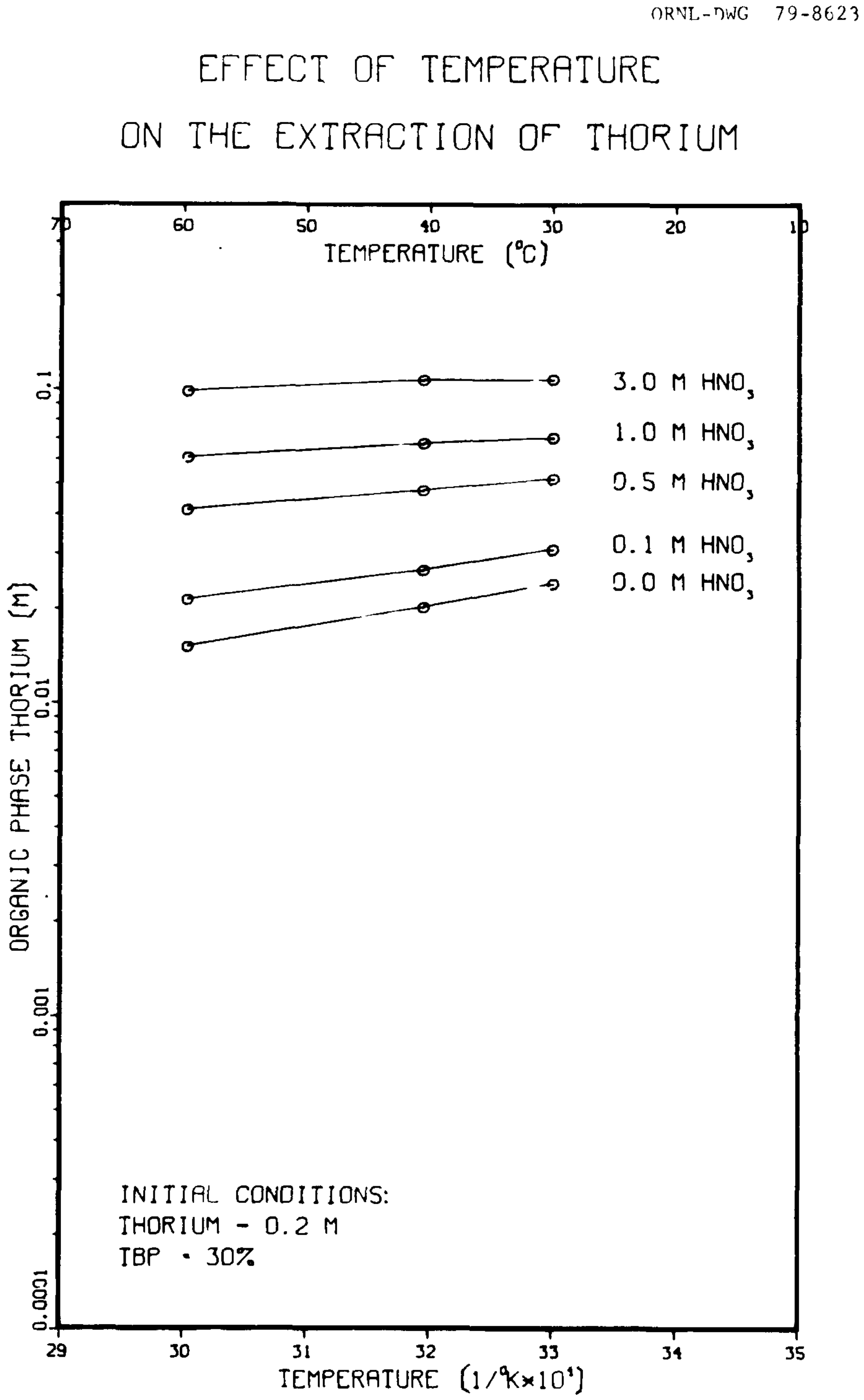

Fig. 3. Logarithm of Organic Thorium Versus the Reciprocal of Absolute Temperature for Five Initial Aqueous Acidities at an Initial Aqueous Thorium Concentration of 0.2 M.

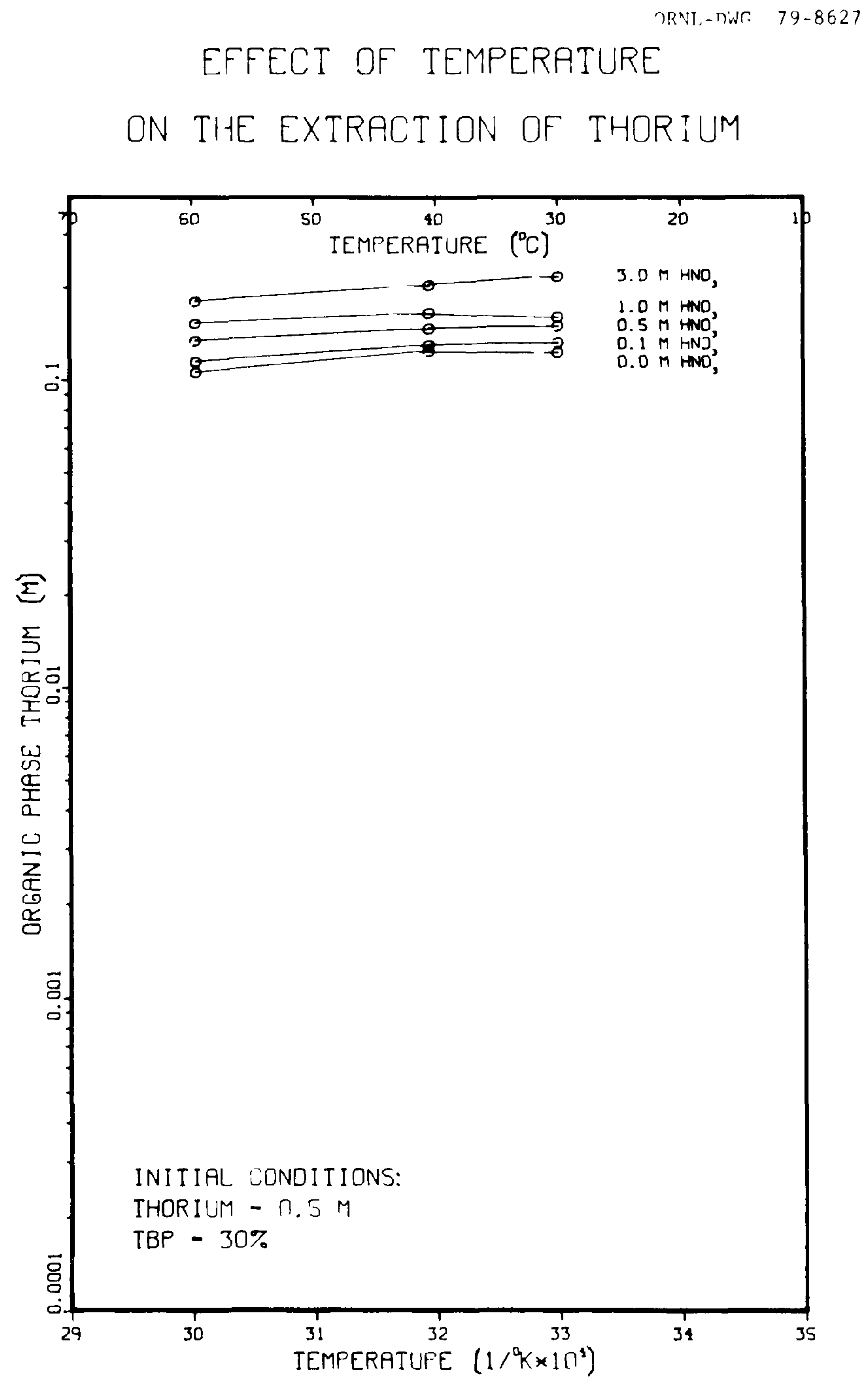

Fig. 4. Logarithm of Organic Thorium Versus the Reciprocal of Absolute Temperature for Five Initial Aqueous Acidities at an Initial Aqueous Thorium Concentration of 0.5 M.

temperature effect is significant, and, after statistical testing, was found to be significant at the 5% level but not at the 1% level. The data in Figs. 2, 3, and 4 group in parallel straight lines with very little scatter in the points. These plots indicate that the formation of organic thorium decreases as the temperature increases and increases as the concentration of nitric acid increases.

Incipient third-phase thorium data has also been plotted in the same manner for initial aqueous thorium concentrations of 1.0 M and 1.25 M in Figs. 5 and 6, respectively. These data show that the concentration of thorium in the organic phase required to result in a second organic phase increases with temperature. Increasing the nitric acid concentration decreases the thorium concentration required to form the third phase.

The average concentration of thorium in the third phase has been plotted in Figs. 7 and 8 for initial aqueous thorium concentrations of 1.0 M and 1.25 M, respectively. These plots resemble those in Figs. 2, 3, and 4 with respect to slope of the lines and positions of lines with respect to aqueous acid, illustrating that the system does not change due to the formation of the third phase. The experimental data measured by Weinberger, with the exclusion of third-phase data, has been used to determine a mathematical model which simulates the effect of temperature. An Arrhenius equation of the form

$$O_T = O_0 \exp K\left(\frac{1}{A_T} - \frac{1}{A_0}\right) \tag{1}$$

where

O_T = organic phase thorium at temperature A_T,

O_0 = organic phase thorium at 298°K (25°C),

A_T = operating temperature, °K,

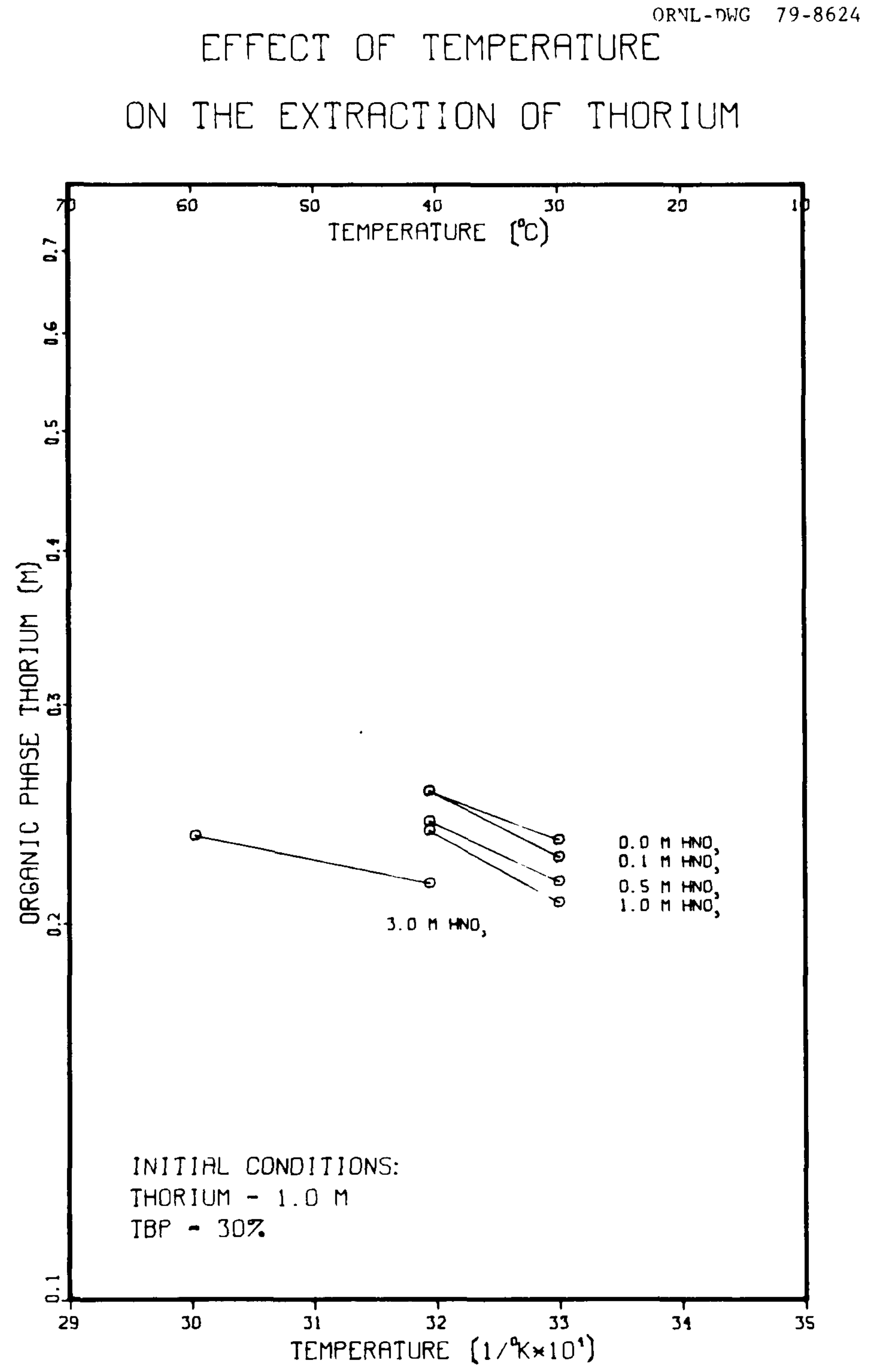

Fig. 5. Logarithm of Incipient Third-Phase Organic Thorium Versus the Reciprocal of Absolute Temperature for Five Initial Aqueous Acidities at an Initial Aqueous Thorium Concentration of 1.0 M.

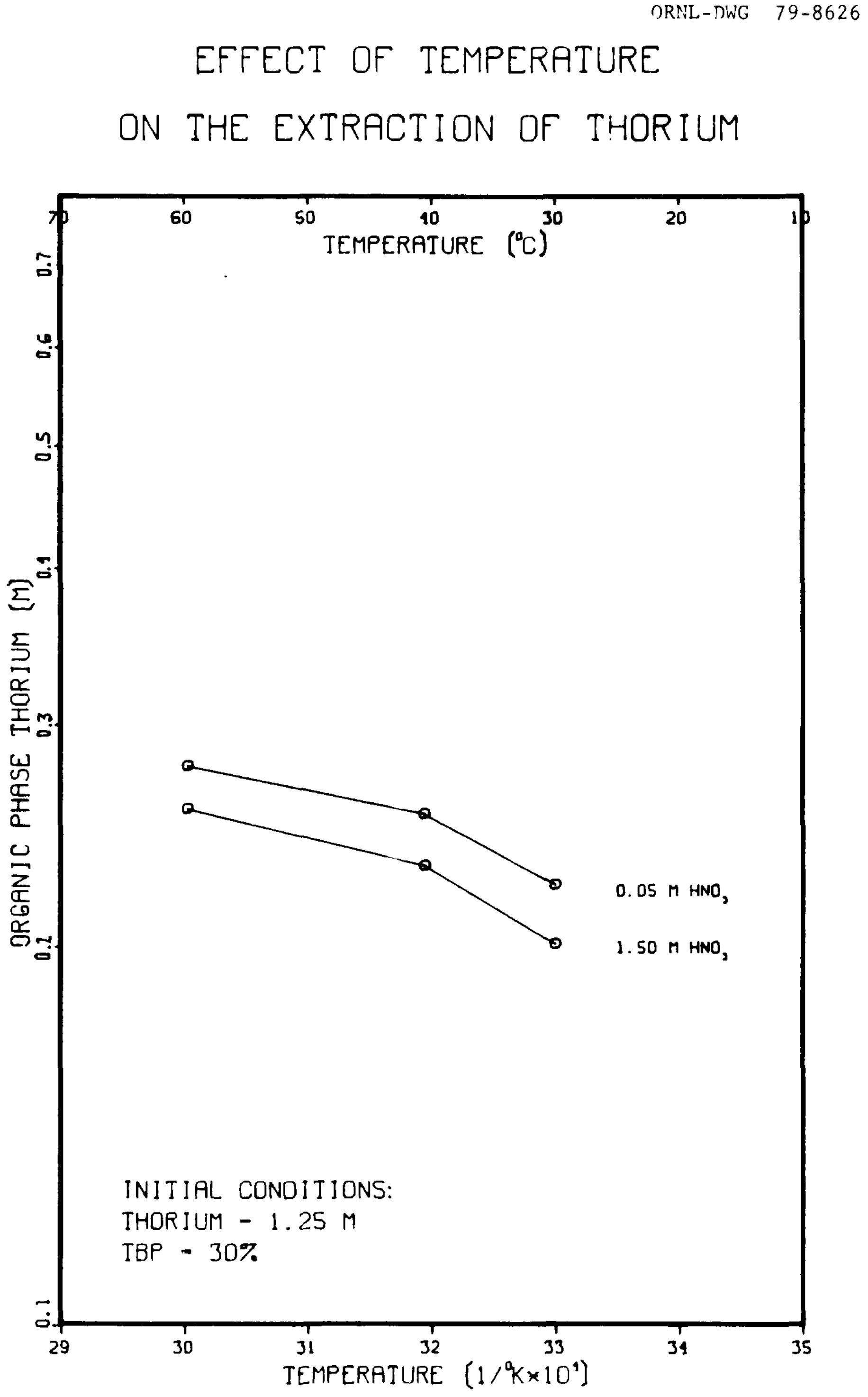

Fig. 6. Logarithm of Incipient Third-Phase Organic Thorium Versus The Reciprocal of Absolute Temperature for Two Initial Aqueous Acidities at an Initial Aqueous Thorium Concentration of 1.25 M.

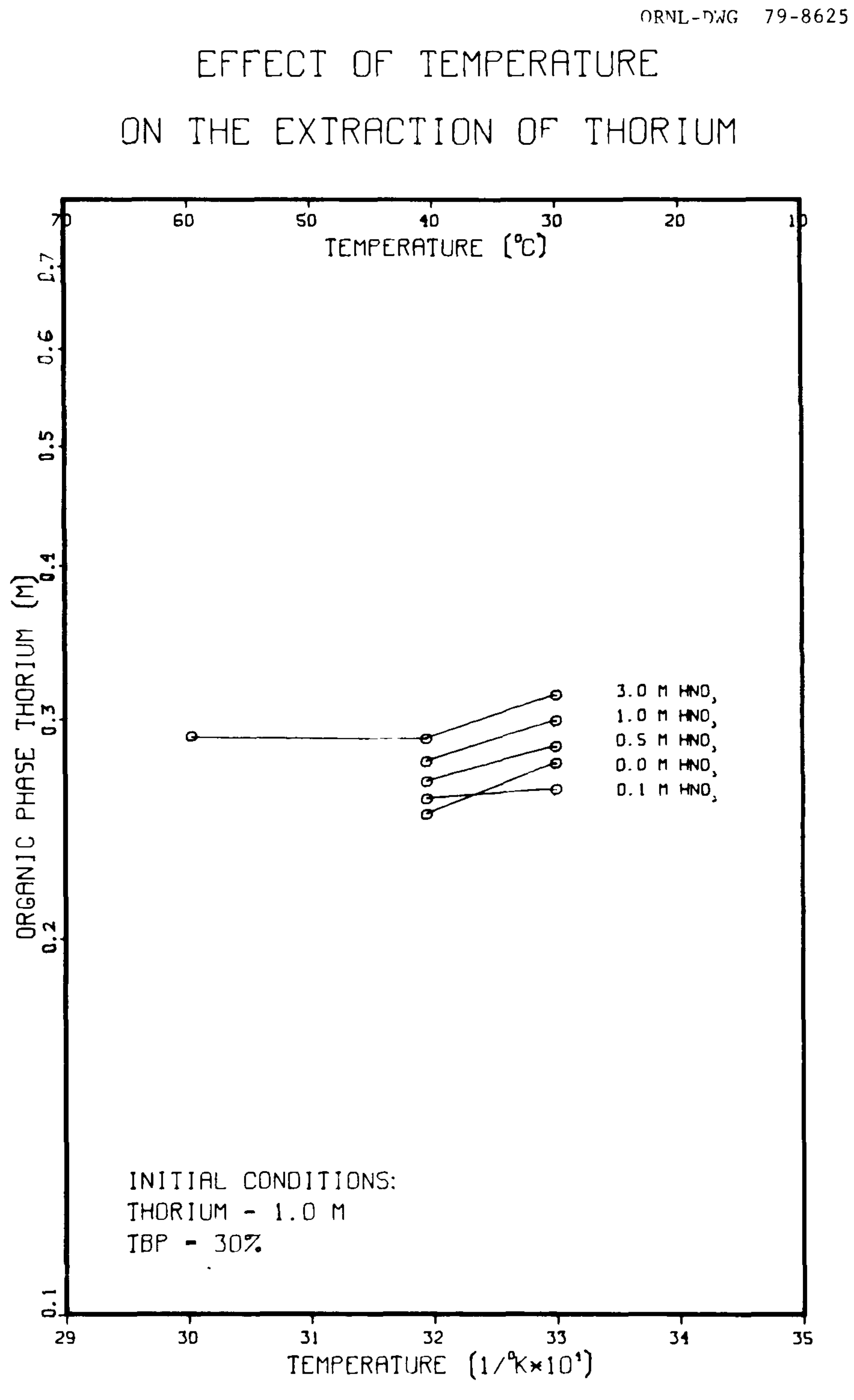

Fig. 7. Logarithm of Third-Phase Organic Thorium Versus the Reciprocal of Absolute Temperature for Five Initial Aqueous Acidities at an Initial Aqueous Thorium Concentration of 1.0 M.

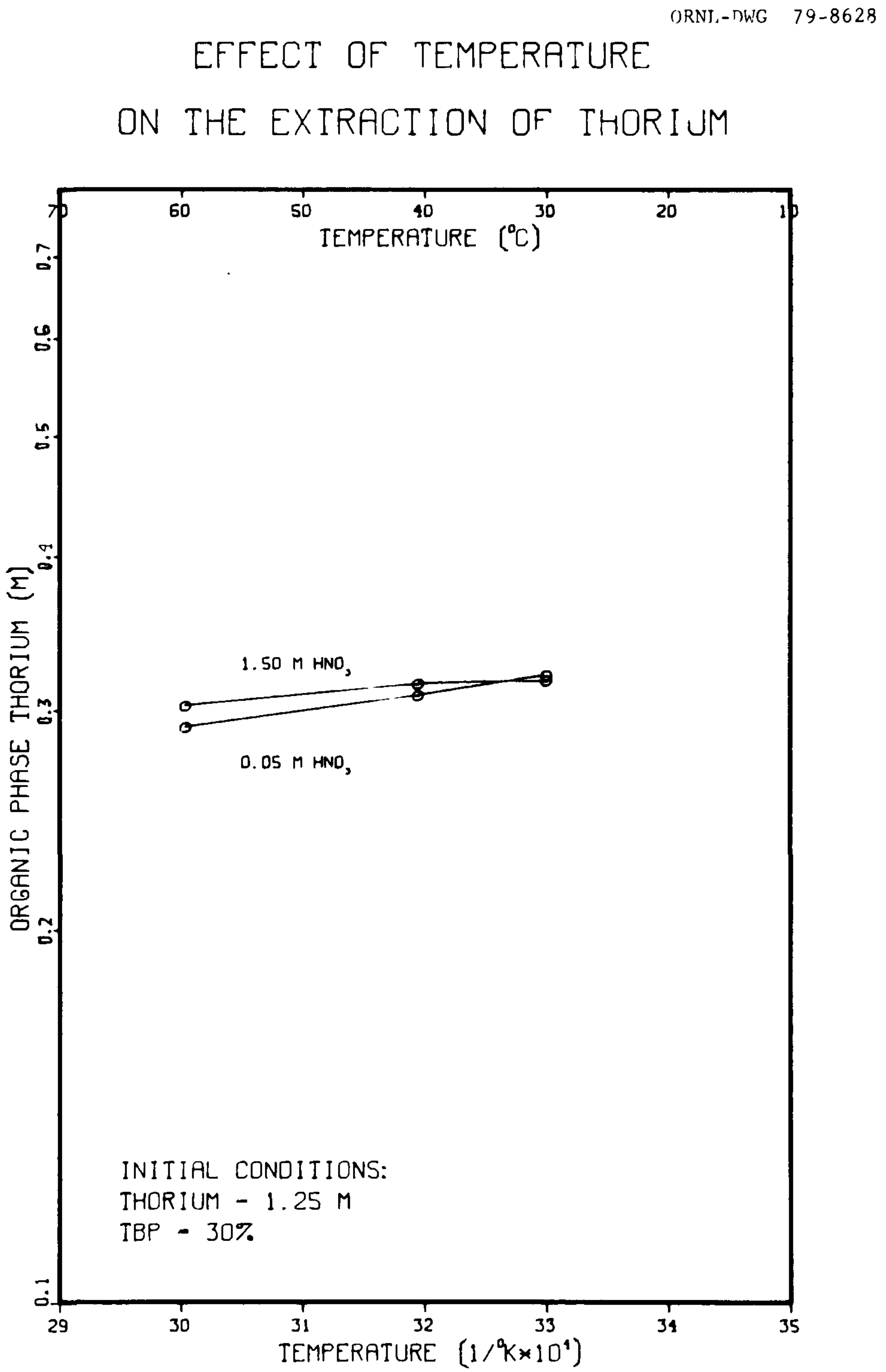

Fig. 8. Logarithm of Third-Phase Organic Thorium Versus the Reciprocal of Absolute Temperature for Two Initial Aqueous Acidities at an Initial Aqueous Thorium Concentration of 1.25 M.

A_0 = 298°K (room temperature),

K = slope of parallel lines in semi-log plot of organic thorium versus 1/temperature (°K),

is frequently used to model the effect of temperature.[5,6,10] This model is probably adequate for low concentrations of thorium (slope positive with inverse temperature) but would not fit the high concentration range of data where the slope is negative with inverse temperature. Thus, we have replaced the constant K with a quadratic function in aqueous thorium. A least squares fit has been performed using Equation (1) to model the Weinberger data. For the fit, O_0 represents thorium in the organic phase at 25°C calculated by the SEPHIS computer code and O_T represents the calculated temperature-corrected organic thorium values. The quadratic function K has been found to be

$$K = 891.664 + 879.688(Th_a) - 1474.38(Th_a)^2 \tag{2}$$

where Th_a = aqueous phase thorium. The thorium concentration in the organic phase at the various temperatures fits the Weinberger data quite well below incipient third phase. However, the calculated incipient third-phase data shows as much as 10% disparity from the laboratory data primarily due to the fact that the data set used to determine the parameters in the SEPHIS code did not include incipient third-phase data. The modified SEPHIS code calculates an O_0, organic phase thorium at 25°C, which is greater than the corresponding 30°C value for all the laboratory data. This is correct for data not in the incipient third-phase range (see Figs. 2–4) but incorrect for incipient third-phase data (see Figs. 5 and 6).

A plot of laboratory organic phase thorium, O_L, versus organic phase thorium calculated using Equations (1) and (2), Fig. 9, shows that there is a close fit of calculated and experimental data over the whole range of concentrations. A plot of $O_L - O_T$ versus temperature, Fig. 10, shows that the scatter in the fit is nearly the same for the three temperatures. Chen and Ting[10] used Equation (1) to fit their data and have calculated a constant K value of 414.

In order to model the start of the third phase, which will be discussed in the next section, it has been necessary to determine the effect of temperature on the extraction of nitric acid in the presence of thorium. These data agree with the findings of Adamskie[12] in that temperature has only a slight effect on the extraction. Temperature effect on the extraction of nitric acid for our data is modeled by the Equation (1) where $K = -818.8$ and O_T and O_0 represent nitric acid in the organic phase for the previously defined temperatures.

THIRD-PHASE STUDY

The object of this work has been to model the surface where the third phase starts and to include a signal in the SEPHIS program to indicate data above this surface. The surface at which third phase occurs is defined by the thorium and acid concentrations in the organic phase and temperature. A plot of the incipient third-phase thorium data given in Tables 1, 2, and 3 is shown in Fig. 11. This plot shows organic thorium versus organic acid for 30°, 40°, and 60°C. The data show that the solubility of the thorium-TBP complex in the normal dodecane increases slightly (∿10% per 10° rise in temperature) and decreases slightly

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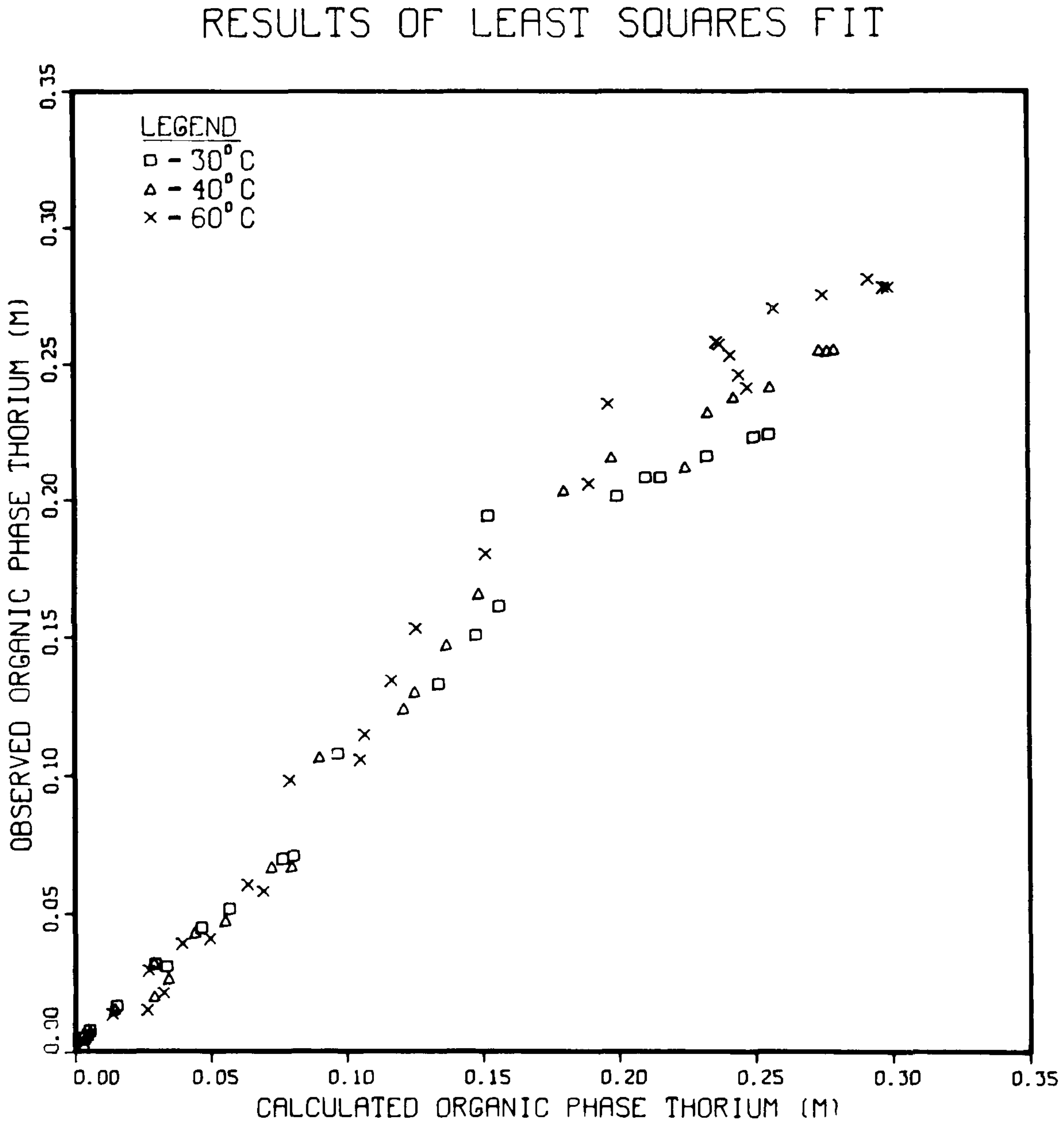

Fig. 9. Observed Versus Calculated Organic Phase Thorium.

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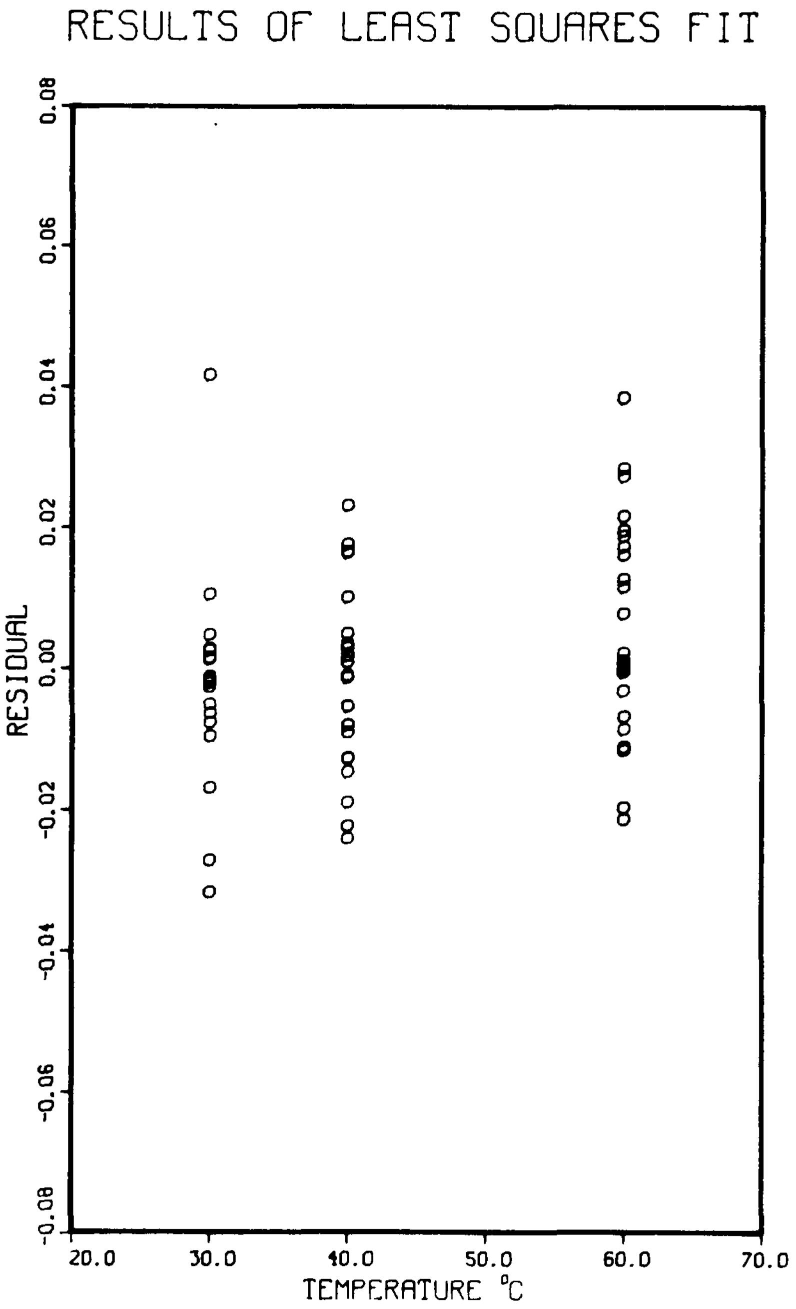

Fig. 10. Residuals (Observed Minus Calculated Organic Phase Thorium) Versus Temperature.

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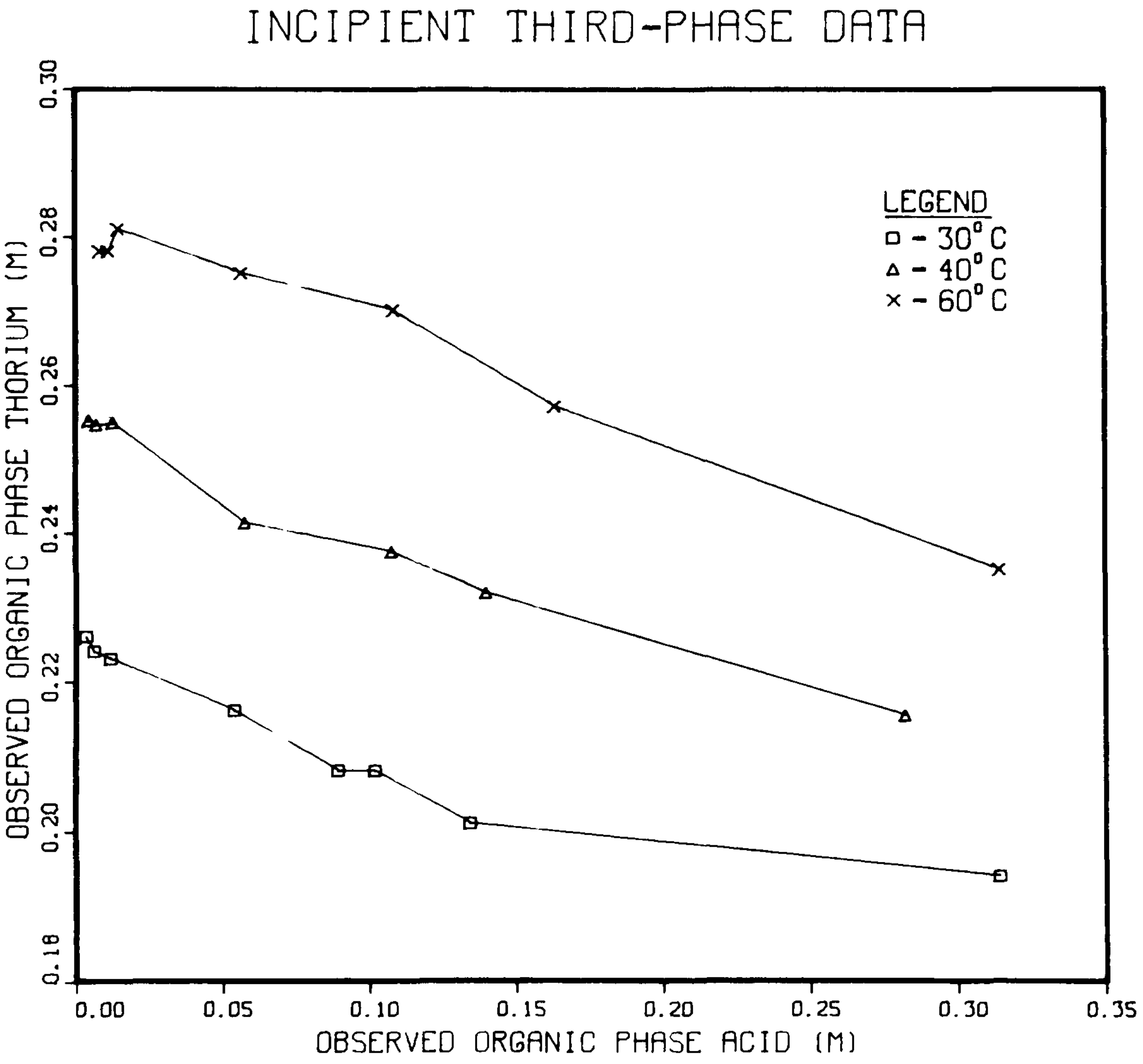

Fig. 11. Observed Incipient Third-Phase Thorium Versus Observed Organic Acid.

with increasing acidity of the organic phase. The model for the third phase, however, is not based on the observed data but on the concentrations of thorium and acid which the SEPHIS code would calculate from the feed composition. The SEPHIS code has the least accuracy at this high concentration range. Figure 12 shows the SEPHIS-calculated organic thorium plotted versus SEPHIS calculated organic acid for the various temperatures.

These calculated values of organic thorium and acid, together with temperature, have been used to model the third-phase surface. The surface is a function of the form

$$Th_o = [0.4312 \times 10^{-1} - 0.3318 \times 10^{-4} (A - 55.032)^2 + 0.3672 (H_0 - 0.3456)^2]^{1/2} \quad , \tag{3}$$

where

Th_o = incipient third-phase organic thorium,

A = temperature in °C,

H_o = calculated organic phase acid.

A plot of the third-phase surface is shown in Fig. 13. This surface is a section of a hyperboloid of one sheet, i.e., the surface intersects the temperature-thorium plane in an ellipse and intersects the two other coordinate planes in hyperboles.

Figure 14 shows the relationship of the three sets of incipient third-phase data which we have discussed. The dashed lines represent the observed organic thorium taken from Fig. 11. The "X" represents the SEPHIS values for organic thorium taken from Fig. 12. The solid lines represent the smoothing of calculated values as defined by Equation (3), in a thorium-acid cross-section of Fig. 13. Though the agreement between the "X" (calculated) and the dashed line (observed) values show the discrepancies discussed in the previous section, this is adequate for estimates in the design of fuel reprocessing plants.

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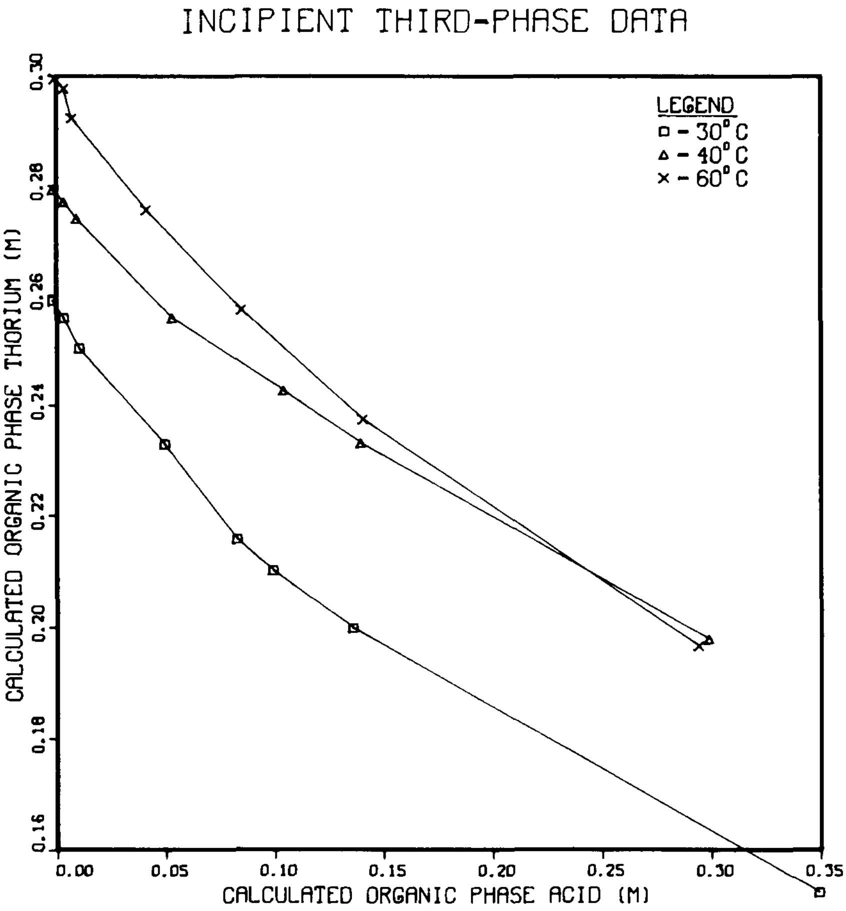

Fig. 12. Calculated Incipient Third-Phase Thorium Versus Calculated Organic Acid.

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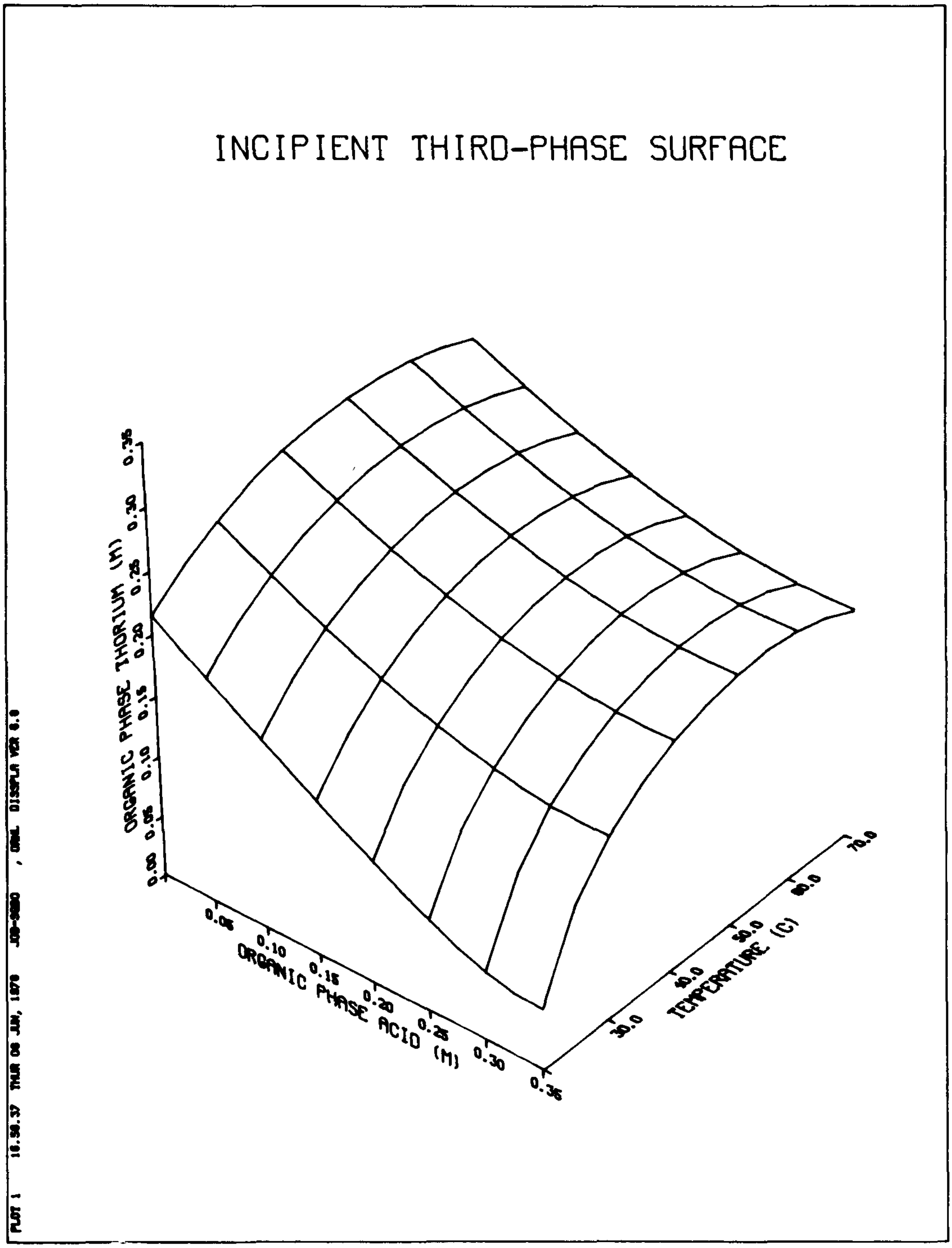

Fig. 13. Incipient Third-Phase Surface-Organic Thorium as a Function of Organic Acid and Temperature.

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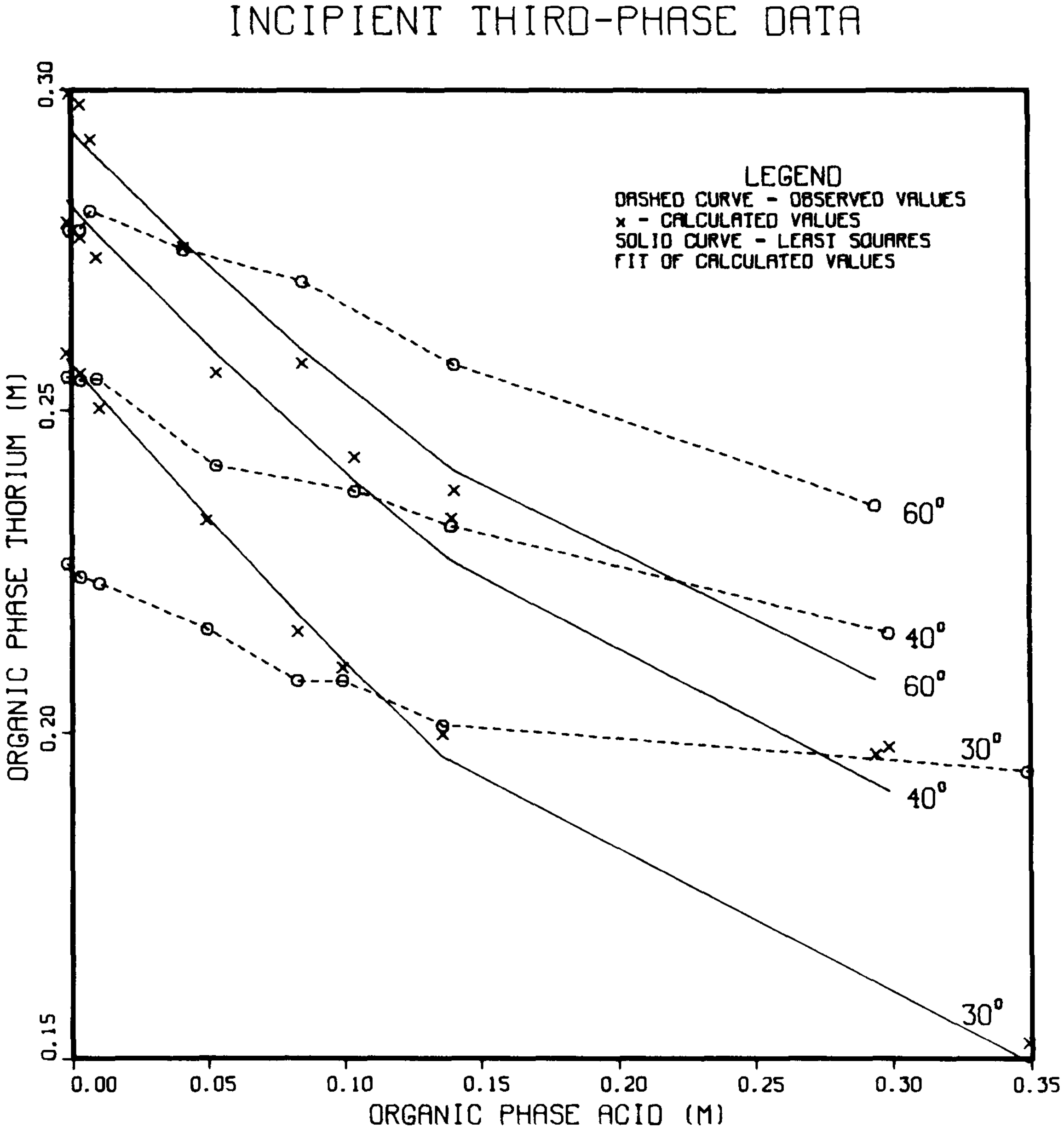

Fig. 14. Relationship of Observed, Calculated and Smoothed Incipient Third-Phase Data.

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