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ORNL-TM-43

COPY NO. - 25

DATE November 1, 1961

THERMODYNAMICS OF EXTRACTION OF NITRIC ACID BY TRI-n-BUTYL PHOSPHATE--HYDROCARBON DILUENT SOLUTIONS

1. Distribution Studies with TBP in Amsco 125-82 at Intermediate and Low Acidities

Wallace Davis, Jr.

ABSTRACT

The distribution of 0-8 M HNO_3 between aqueous and 5-100 vol % solutions of TBP in Amsco 125-82 has been measured and used to obtain a quantitative description of this extraction process. Up to ~ 5 M aqueous HNO_3 , a limit arbitrarily chosen because of uncertainties in HNO_3 activity coefficients, the data of this report at any particular concentration of TBP in Amsco are accurately described by the equation $\log \frac{(\text{HNO}_3)_{\text{org}}}{\{[\text{HNO}_3]_{\text{aq}}(3.75493 - (\text{HNO}_3)_{\text{org}})\}} = A + B (\text{HNO}_3)_{\text{org}}$, where parentheses refer to concentrations, square brackets to activities, and subscripts org and aq to organic and aqueous phases.

The antilogarithms of the constants A for the six TBP-diluent solutions studied can be described as a linear function of $(Y_{\text{H}_2\text{O}}^{\circ} + Y_{\text{TBP}}^{\circ})$, the sum of the mole fractions, $Y_{\text{H}_2\text{O}}^{\circ}$ and Y_{TBP}° , of water and TBP in the acid-free water-saturated organic phase. These antilogarithms were interpreted as the product $K_1 \gamma_T$, where K_1 is the thermodynamic equilibrium constant for the extraction reaction and γ_T is the mean activity coefficient of TBP and $\text{TBP} \cdot \text{H}_2\text{O}$ in the acid-free, water-saturated organic phase. As the concentration of TBP in Amsco 125-82 increases from 0 to 100%, $K_1 \gamma_T$, in molal units, varies from 0.2 to 1.5. The quantities B of the above equation are proportional to $(Y_{\text{TBP}}^{\circ} + Y_{\text{H}_2\text{O}}^{\circ})^{1/2}$ while the product $B(\text{HNO}_3)_{\text{org}}$ is interpreted as $\log \gamma_{\text{TN}}$, where γ_{TN} is the mean activity coefficient of the species $\text{TBP} \cdot \text{HNO}_3$ and $\text{TBP} \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$. The organic phase water and acidity values are consistent with formation of the complexes $\text{TBP} \cdot \text{H}_2\text{O}$, $\text{TBP} \cdot \text{HNO}_3$, $\text{TBP} \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$, and $\text{TBP} \cdot 2\text{HNO}_3$.

This paper is for review by Nuclear Science and Engineering.

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THERMODYNAMICS OF EXTRACTION OF NITRIC ACID BY TRI-*n*-BUTYL
PHOSPHATE--HYDROCARBON DILUENT SOLUTIONS

I. Distribution Studies with TBP in Amsco 125-82 at Intermediate
and Low Acidities

by

Wallace Davis, Jr.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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THERMODYNAMICS OF EXTRACTION OF NITRIC ACID BY TBP

I. Distribution Studies with TBP in Amsco 125-82

Wallace Davis, Jr.
Chemical Technology Division
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee

ABSTRACT

The distribution of 0-8 M HNO_3 between aqueous and 5-100 vol % solutions of TBP in Amsco 125-82 has been measured and used to obtain a quantitative description of this extraction process. Up to $\sim 5 M$ aqueous HNO_3 , a limit arbitrarily chosen because of uncertainties in HNO_3 activity coefficients, the data of this report at any particular concentration of TBP in Amsco are accurately described by the equation $\log (HNO_3)_{org} / \left\{ [HNO_3]_{aq} (3.75493 - (HNO_3)_{org}) \right\} = A + B (HNO_3)_{org}$, where parentheses refer to concentrations, square brackets to activities, and subscripts org and aq to organic and aqueous phases.

The antilogarithms of the constants A for the six TBP-diluent solutions studied can be described as a linear function of $(Y_{H_2O}^o + Y_{TBP}^o)$, the sum of the mole fractions, $Y_{H_2O}^o$ and Y_{TBP}^o , of water and TBP in the acid-free water-saturated organic phase. These antilogarithms were interpreted as the product $K_1 Y_T$, where K_1 is the thermodynamic equilibrium constant for the extraction reaction and Y_T is the mean activity coefficient of TBP and $TBP \cdot H_2O$ in the acid-free, water-saturated organic phase. As the concentration of TBP in Amsco 125-82 increases from 0 to 100%, $K_1 Y_T$, in molal units, varies from 0.2 to 1.5. The quantities B of the above equation are proportional to $(Y_{TBP}^o + Y_{H_2O}^o)^{1/2}$ while the product $-B(HNO_3)_{org}$ is interpreted as $\log Y_{TN}$, where Y_{TN} is the mean activity coefficient of the species $TBP \cdot HNO_3$ and $TBP \cdot HNO_3 \cdot H_2O$. The organic phase water and acidity values are consistent with formation of the complexes $TBP \cdot H_2O$, $TBP \cdot HNO_3$, $TBP \cdot HNO_3 \cdot H_2O$, and $TBP \cdot 2HNO_3$.

INTRODUCTION

The purpose of the work described here was to deduce an equation, based primarily on standard thermodynamic concepts, to describe the distribution of nitric acid between an aqueous and a tributyl phosphate organic phase under the certain stated limitations.

Tributyl phosphate, TBP, is widely used in small- and large-scale recovery of uranium, thorium, plutonium, and other elements from spent nuclear reactor fuels and of uranium in its original purification from ore concentrates. Primarily as a result of such uses, the extraction of various inorganic materials has been studied extensively, most frequently with nitrate systems because these are the ones of practical importance.

The complexities of the multicomponent process solutions are so great that no serious efforts have been made to provide quantitative interpretations. Instead, there has been a concerted effort (1-15) to obtain a quantitative description of the simplest solvent extraction system, namely, TBP-diluent-HNO₃-H₂O. With some exceptions (4,7,8,11,15) these studies were further simplified by elimination of the diluent. Data on HNO₃ extraction by TBP have been interpreted in terms of the formation in the organic phase of a series of addition compounds, the quantity of each changing as the aqueous nitric acid concentration changes. Thus at 0 M HNO₃, the compound TBP·H₂O is formed; as the aqueous HNO₃ concentration increases to ~15 M, it has been postulated that compounds such as TBP·HNO₃, TBP·HNO₃·H₂O, TBP·2HNO₃, TBP·3HNO₃ and TBP·4HNO₃ are formed successively, although evidence for complexes containing more than 2 moles of HNO₃ per mole of TBP is very sketchy (12).

The present study of the extraction of nitric acid is limited to the regions of aqueous acidity, primarily 5 M or less, that are used in the pilot plant and production facilities

described in the Geneva papers (16-17). Experiments were performed with 5 to 100 vol % solutions of TBP in the diluent Amsco 125-82, which is an odorless mineral spirits.

EXPERIMENTAL

Materials

Technical grade tributyl phosphate and Amsco 125-82 were used as starting materials. The TBP was partially purified (freed of acid) by two or three contacts with equal volumes of 2.5% aqueous sodium carbonate; any traces of the latter were removed with three equal-volume distilled-water washes. Before being stored, the resulting TBP was degassed and dehydrated under vacuum to a water content of 1.8 mg/ml. Diluent was used after two or three water washes.

Procedures

TBP-Amsco stock solutions were synthesized by weight and then vigorously agitated, in 25-50 ml portions, with equal volumes of the various HNO_3 solutions for 5-20 min. These mixtures were allowed to settle until the two phases appeared to be water clear, the minimum settling time being 15 min and the maximum 3 days. After separation of the two phases density, acidity, and, in some cases, nitrate were determined in the aqueous phase and density, water content, acidity, and, in some case, nitrate in the organic phases. Densities were determined with 10-ml pycnometers, usually at 25°C. Acidity was determined by electrometric titration with appropriate sodium hydroxide solutions. Water was added to the organic samples to make their titrations in essentially aqueous media. Water in the organic solutions was determined by the Karl Fisher method as

described by Kelley et al. (18). Nitrate was determined by reaction with 2,6-dimethylphenol and subsequent colorimetric measurement in a manner similar to the method based on phenoldisulfonic acid (19). The limit of detection of nitrate in the TBP-Amsco solutions was approximately 5 μg .

RESULTS

Original analytical data on the extraction of nitric acid by nominally 5, 10, 15, 30, and 65 vol % solutions of TBP in Amsco 125-82 and by diluent-free, i.e., 100 vol %, TBP are presented in Tables I-VI.* In addition to analytical data there are included values of the mean molar stoichiometric activity coefficients of nitric acid in water calculated from the 25°C molal data of Hartmann and Rosenfeld (20). Some of the extraction data were not used in the mathematical analyses described below either because differences between nitrate and acidity determinations, in the low-acidity region, in the organic phase were large enough to suggest the presence of other acids, perhaps dibutyl phosphoric, or because adequate nitric acid activity coefficient data are not available. Hartmann and Rosenfeld (20) corrected the activity coefficients they calculated from their freezing point measurements to values at 25°C only at concentrations up to 3 m. Some extrapolation of their 25°C values was made as indicated in Tables I-VI.

In common with the presentations of many workers in the field, the mathematical description of the present report is based on the extraction of nitric acid by TBP solutions according to the reaction

* The first experiments were performed with 30% TBP in Amsco 125-82, Table IV. Thus, the analytical difficulties indicated in this table were not encountered in subsequent experiments.

Table I. Distribution of HNO₃ Between Aqueous and 5%^a TBP-Amsco 125-82 Phases

Experimental Data

Aqueous Phase			Organic Phase			
HNO ₃ Conc, C _s ^d Anal. H ⁺	Activity Coef. y _s	Density (25°), g/ml	HNO ₃ Conc, M		H ₂ O Conc, M	Density (25°), g/ml
			Anal. H ⁺	Anal. NO ₃ ⁻		
0.098	----	1.0002	0.0004 ^c	0.00014 ^c	0.0250	0.7609
0.198	0.758	1.0031	0.0011	0.00103	0.0222	0.7608
0.405	0.733	1.0102	0.00382	0.00305	0.0261	0.7611
0.591	0.731	1.0162	0.0077	0.00814	0.0211	0.7611
0.793	0.735	1.0231	0.0133	0.01312	0.0239	0.7617
0.983	0.746	1.0288	0.0196	0.0213	0.0217	0.7615
1.49	0.784	1.0457	0.0390	0.0406	0.0283	0.7624
1.91	0.845	1.0590	0.0587		0.0289	0.7629
2.41	0.923	1.0756	0.0805		0.0244	0.7636
2.87	1.016	1.0902	0.100		0.0289	0.7638
3.92	1.342	1.1228	0.130		0.0211	0.7649
4.83 ^b	----	1.1515	0.149		0.0167	0.7651
6.35 ^b	----	1.1936	0.164		0.0111	0.7660
8.41 ^b	----	1.2532	0.178		0.0094	0.7662

^a0.06378 g TBP/g Amsco, or 0.172₂ M TBP, on the dry basis. This is ~5 vol % TBP.

^bData were not used in the mathematical analyses because of the absence of HNO₃ activity coefficient data.

^cData were not used in mathematical analyses because of large difference between H⁺ and NO₃⁻ determinations.

^dUnits of C_s are moles/liter.

Table II. Distribution of HNO₃ Between Aqueous and 10%^a TBP-Amsco 125-82 Phases

Experimental Data						
Aqueous Phase			Organic Phase			
HNO ₃ Conc, C _s ^c Anal. H ⁺	Activity Coef. Y _s	Density (25°), g/ml	HNO ₃ Conc, <u>M</u>		H ₂ O Conc, <u>M</u>	Density (25°), g/ml
			Anal. H ⁺	Anal. NO ₃ ⁻		
0.0986	0.793	1.0003	0.00073	0.00058	0.0594	0.7721
0.196	0.758	1.0003	0.00293	0.00303	0.0605	0.7719
0.398	0.734	1.0102	0.0101	0.0115	0.0566	0.7722
0.580	0.730	1.0156	0.0201	0.0206	0.0583	0.7727
0.774	0.735	1.0224	0.0331	0.0329	0.0710	0.7732
0.958	0.744	1.0279	0.0462		0.0727	0.7734
1.44	0.785	1.0443	0.0884		0.0816	0.7746
1.84	0.834	1.0564	0.129		0.0810	0.7755
2.32	0.910	1.0734	0.167		0.0672	0.7769
2.80	1.004	1.0876	0.210		0.0699	0.7778
3.76	1.287	1.1197	0.264		0.0555	0.7800
4.72 ^b	----	1.1481	0.311		0.0400	0.7814
6.10 ^b	----	1.1887	0.336		0.0222	0.7821
8.31 ^b	----	1.2490	0.368		0.0139	0.7825

^a0.1383 g TBP/g Amsco, or 0.3518 M TBP, on the dry basis. This is ~ 10 vol % TBP.

^bData were not used in the mathematical analyses because of the absence of HNO₃ activity coefficient data.

^cUnits of C_s are moles/liter.

Table III. Distribution of HNO₃ Between Aqueous and 15%^a TBP-Amsco 125-82 Phases

Experimental Data

Aqueous Phase			Organic Phase			
HNO ₃ Conc, C _s ^c Anal. H ⁺	Activity	Density (25°), g/ml	HNO ₃ Conc, <u>M</u>		H ₂ O Conc, <u>M</u>	Density (25°), g/ml
	Coef. γ _s		Anal. H ⁺	Anal. NO ₃ ⁻		
0.098	0.794	0.9998	0.0022	0.0020	0.0949	0.7827
0.194	0.758	1.0034	0.0056	0.0057	0.1110	0.7826
0.390	0.734	1.0098	0.0179	0.0200	0.1121	0.7829
0.570	0.730	1.0152	0.0339	0.0406	0.1182	0.7829
0.764	0.734	1.0217	0.0546	0.0606	0.1182	0.7845
0.940	0.743	1.0272	0.0763		0.1260	0.7847
1.40	0.780	1.0427	0.145		0.1421	0.7867
1.80	0.829	1.0551	0.198		0.1504	0.7883
2.27	0.896	1.0707	0.244		0.1371	0.7902
2.72	0.992	1.0849	0.294		0.1266	0.7912
3.67	1.250	1.1157	0.390		0.0844	0.7944
4.58 ^b	----	1.1435	0.430		0.0594	0.7957
5.98 ^b	----	1.1857	0.498		0.0472	0.7964
8.12 ^b	----	1.2465	0.526		0.0372	0.7974

^a0.2163 g TBP/g Amsco, or 0.5219 M TBP, on the dry basis. This is ~ 15 vol % TBP.

^bData were not used in the mathematical analyses because of the absence of HNO₃ activity coefficient data.

^cUnits of C_s are moles/liter.

Table IV. Distribution of HNO₃ Between Aqueous and 30% TBP-Amsco 125-82 Phases

Experimental Data

Aqueous Phase				Organic Phase				
HNO ₃ Conc, C _s ^c		Activity Coef. Y _s	Density (23°C), g/ml	HNO ₃ Concentration, M			H ₂ O Conc, M	Density (23°), g/ml
Anal. H ⁺	Anal. NO ₃ ⁻			Anal. H ⁺	Anal. NO ₃ ⁻	Anal. NO ₃ ⁻ Recheck		
0.0087	0.0087	----	0.9981	0.00098 ^b	0.00021 ^b	0.00016 ^b	0.287	0.8209
0.0186	0.0181	----	0.9992	0.0012 ^b	0.00050 ^b	0.00016 ^b	0.353	0.8190
0.0379	0.0381	----	1.0001	0.0020 ^b	0.00121 ^b	0.00087 ^b	0.363	0.8203
0.0569	0.0558	----	0.9991	0.0032 ^b	0.0023 ^b	0.0023 ^b	0.377	0.8192
0.0741	0.0698	0.810	0.9953	0.0047 ^b	0.0055 ^b	0.0032 ^b	0.379	0.8204
0.0915		0.798	1.0009	0.0062 ^b		0.0044 ^b	0.379	0.8187
0.174		0.763	0.9998	0.0172 ^b		0.0158 ^b	0.353	0.8208
0.359		0.737	1.0082	0.0451			0.388	0.8214
0.517		0.730	1.0154	0.0872			0.402	0.8230
0.685		0.732	1.0204	0.126			0.369	0.8237
0.843		0.738	1.0261	0.171			0.443	0.8262
1.24		0.763	1.0372	0.279			0.398	0.8276
1.60		0.803	1.0516	0.367			0.390	0.8317
2.03		0.861	1.0647	0.465			0.372	0.8339
2.43		0.925	1.0783	0.548			0.337	0.8369
3.35		1.146	1.1080	0.707			0.322	0.8400
4.14		1.430	1.1345	0.835			0.221	0.8438

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^a0.5540 g TBP/g Amsco, or 1.094_g M TBP, on the dry basis. This is ~ 30 vol % TBP.

^bData were not used in mathematical analyses because of large difference between H⁺ and NO₃⁻ determinations in the organic phase.

^cUnits of C_s are moles/liter.

Table V. Distribution of HNO₃ Between Aqueous and 65% TBP-Amsco 125-82 Phases

Experimental Data

Aqueous Phase					Organic Phase				
Anal. H ⁺		Anal. NO ₃ ⁻			Density (25°), g/ml	HNO ₃ Conc, M		H ₂ O Conc, M	Density (25°C), g/ml
HNO ₃ Conc, C _s ^c	Activity Coef. Y _s	HNO ₃ Conc, C _s	Activity Coef. Y _s	Anal. H ⁺		Anal. NO ₃ ⁻			
0.0888	0.789	0.0888	0.798	1.0000	0.0117	0.0115	1.354	0.8957	
0.166	0.767	0.1775	0.763	1.0019	0.0364	0.0342	1.310	0.8963	
0.307	0.741	0.314	0.740	1.0073	0.105	0.101	1.321	0.8985	
0.423	0.733	0.379	0.735	1.0107	0.176	0.156	1.343	0.9001	
0.570	0.730	0.527	0.730	1.0157	0.264	0.240	1.282	0.9026	
0.690	0.732	0.645	0.731	1.0188	0.334	0.300	1.277	0.9043	
1.01	0.747	1.038	0.748	1.0302	0.530	0.483	1.160	0.9099	
1.30	0.769	1.28	0.768	1.0391	0.670		1.160	0.9128	
1.70	0.815	1.63	0.807	1.0516	0.840		1.121	0.9175	
2.01	0.859	1.935	0.849	1.0625	0.960		1.082	0.9206	
2.82	1.005	2.73	0.983	1.0886	1.24		0.944	0.9280	
3.54	1.210	3.42	1.166	1.1109	1.46		0.788	0.9320	
4.68 ^b	----	4.74 ^b	----	1.1475	1.73		0.672	0.9380	
6.72 ^b	----	6.57 ^b	----	1.2069	2.10		0.436	0.9446	

^a2.297 g TBP/g Amsco, or 2.334 M TBP, on the dry basis. This is ~65 vol % TBP.

^bData were not used in the mathematical analyses because of the absence of HNO₃ activity coefficient data.

^cUnits of C_s are moles/liter.

Table VI. Distribution of HNO₃ Between Aqueous and 100% TBP Phases

Experimental Data

Aqueous Phase				Organic Phase		
HNO ₃ Conc., Anal. H ⁺	C _s ^b	Activity Coef. Y _s	Density (25°), g/ml	HNO ₃ Conc., Anal. H ⁺	H ₂ O Conc., M	Density (25°), g/ml
0.080		0.805	0.9997	0.0202	3.21	0.9765
0.146		0.773	1.0017	0.0585	3.28	0.9772
0.257		0.747	1.0055	0.151	3.12	0.9801
0.360		0.737	1.0083	0.245	3.03	0.9821
0.457		0.732	1.0120	0.359	2.86	0.9850
0.558		0.730	1.0147	0.460	2.66	0.9872
0.837		0.737	1.0243	0.711	2.71	0.9935
1.07		0.751	1.0319	0.914	2.58	0.9977
1.39		0.778	1.0423	1.12	2.68	1.0036
1.68		0.813	1.0518	1.29	2.59	1.0063
2.40		0.920	1.0751	1.66	2.24	1.0139
3.05		1.061	1.0959	1.94	2.03	1.0196
4.10		1.412	1.1294	2.39	1.80	1.0272
5.93 ^a		----	1.1835	2.87	1.26	1.0359

^aData were not used in the mathematical analyses because of the absence of HNO₃ activity coefficient data.

^bUnits of C_s are moles/liter.



from which is formulated the equilibrium equation

$$K_1 = \frac{[\text{TBP}\cdot\text{HNO}_3]_{\text{org}}}{[\text{HNO}_3]_{\text{aq}} [\text{TBP}]_{\text{org}}} \quad (2)$$

In these and subsequent equations the following nomenclature applies:

Brackets refer to activities and parentheses to concentrations;

Subscripts "org" and "aq" refer to the organic and aqueous phases, respectively;

Y, m, c are mole fraction, molality, and molarity, respectively; the second two letters are also used to differentiate dimensions of quantities; e.g., K^m is an equilibrium constant with molal units;

266.316 = molecular weight of TBP, g/mole;

ρ = density, g/ml;

γ = activity coefficient, molal scale;

y = activity coefficient, molar scale;

y_s and C_s = stoichiometric activity coefficient and concentration of HNO_3 in the aqueous phase, molar scale;

$W_{\text{Dil}}/W_{\text{TBP}}$ = weight ratio of diluent to TBP in the extraction solution.

Of the three chemical species of eq. 2, the activity only of nitric acid is known from other work. Activities of the other two species, TBP and $\text{TBP}\cdot\text{HNO}_3$, are unknown, but their concentrations may be approximated by equating the concentration of $\text{TBP}\cdot\text{HNO}_3$ to total nitric acid in the organic phase, i.e., by assuming

$$(\text{TBP}\cdot\text{HNO}_3)_{\text{org}} = (\text{HNO}_3)_{\text{org}} \quad (3)$$

Similarly, the concentration of "free" TBP may be equated to that not complexed as $\text{TBP}\cdot\text{HNO}_3$, i.e., by assuming

$$(\text{TBP})_{\text{org}} = (\text{TBP}_s)_{\text{org}} - (\text{TBP}\cdot\text{HNO}_3)_{\text{org}} \quad (4)$$

where $(\text{TBP}_s)_{\text{org}}$ is the stoichiometric concentration of TBP in the organic phase, which equals 1000/266.316 or 3.75493 moles/kg TBP in the molal scale of this report or which in the molar scale is calculated as

$$(\text{TBP}_s)_{\text{org}} = \frac{1000 \rho_{\text{org}} - 63.016(\text{HNO}_3)_{\text{org}}^c - 18.016(\text{H}_2\text{O})_{\text{org}}^c}{266.316 (1 + W_{\text{Dil}}/W_{\text{TBP}})} \quad (5)$$

With the definitions given above and the usual replacement of activities by the product of concentration times activity coefficient, eq. 2 becomes, in molal units,

$$K_1 = \frac{(\text{HNO}_3)_{\text{org}}^m}{[\text{HNO}_3]_{\text{aq}}^m \left\{ 3.75493 - (\text{HNO}_3)_{\text{org}}^m \right\}} \frac{\gamma_{\text{TN}}}{\gamma_{\text{T}}}, \quad (6)$$

where γ_{TN} is an activity coefficient of the nitric acid-TBP complex and γ_{T} the activity coefficient of "free" TBP. By rearranging eq. 6 we obtain the relation in eq. 7, which also defines F_4 ,

$$F_4 = K_1 \frac{\gamma_T}{\gamma_{TN}} = \frac{(\text{HNO}_3)_{\text{org}}^m}{[\text{HNO}_3]_{\text{aq}}^m \left\{ 3.75493 - (\text{HNO}_3)_{\text{org}}^m \right\}} \quad (7)$$

the numerical value of which can be obtained from analytical data as given in Tables I-VI and the equations

$$(\text{HNO}_3)_{\text{org}}^m = 3.75493 (\text{HNO}_3)_{\text{org}}^c / (\text{TBP})_{\text{s org}} \quad (8)$$

$$[\text{HNO}_3]_{\text{aq}}^c = (\gamma_s C_s)^2 \quad (9)$$

$$[\text{HNO}_3]_{\text{aq}}^m = (1.00294 \gamma_s C_s)^2 = \gamma_s^2 m_s^2 \quad (10)$$

Previous workers using eq. 7 plotted the numerical value of F_4 , or its logarithm, against the aqueous nitric acid concentration in showing the effects of acidity and the TBP/diluent ratio. The mathematics of the present report are based on acidity in the organic phase, not the aqueous phase, being the independent variable since both the dependent variables γ_T and γ_{TN} in the ratio $K_1 \gamma_T / \gamma_{TN}$, eq. 7, refer to the organic phase. In contrast to the curves of plots of $\log F_4$ vs. aqueous acidity, plots of $\log F_4$ vs. organic acidity are straight lines in all cases, as shown by the three examples of Fig. 1, expressible for a fixed TBP/diluent ratio and organic acidities from 0 to 3 m, corresponding to aqueous acidities of 0 to 5 M, by the equation

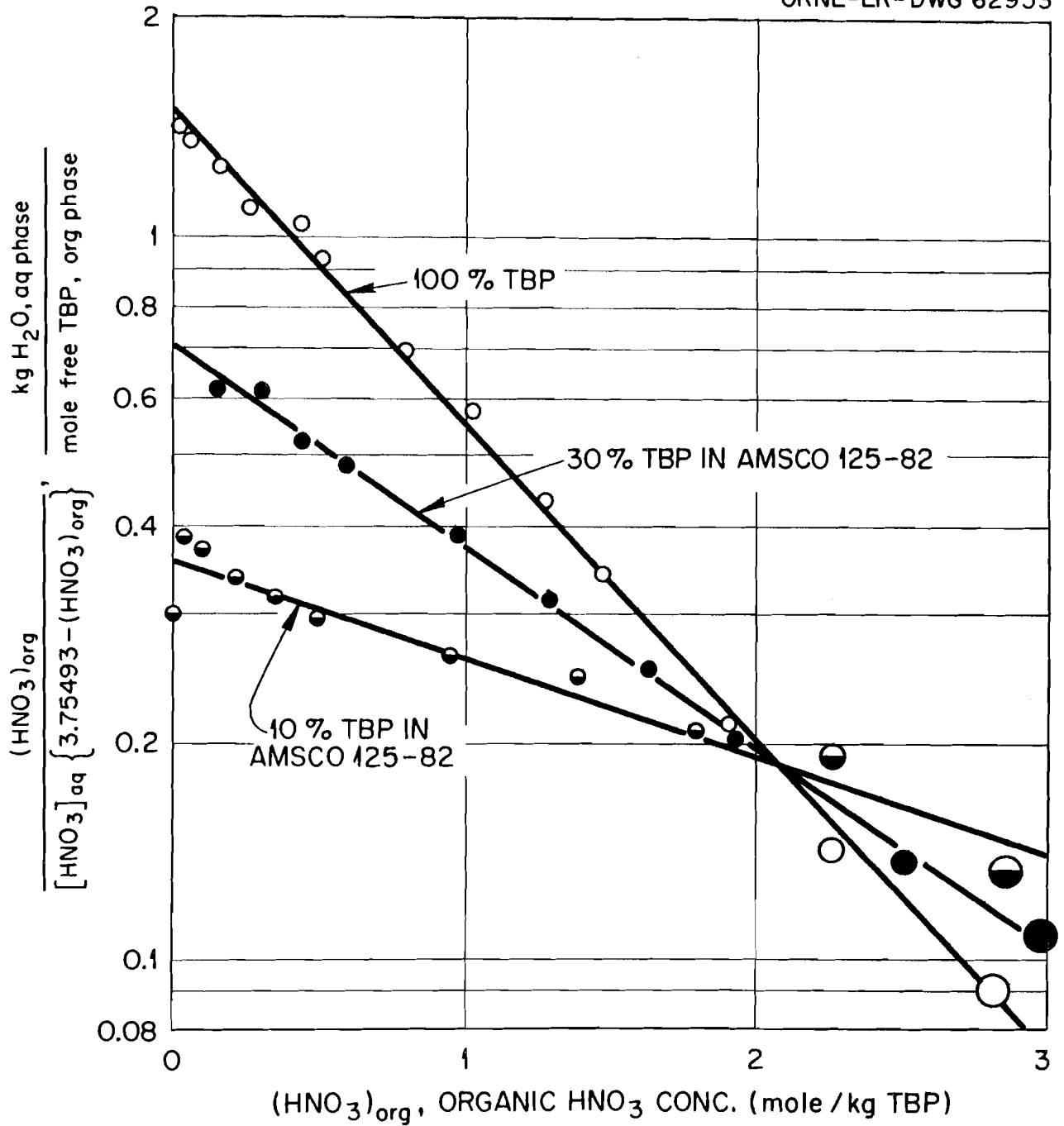


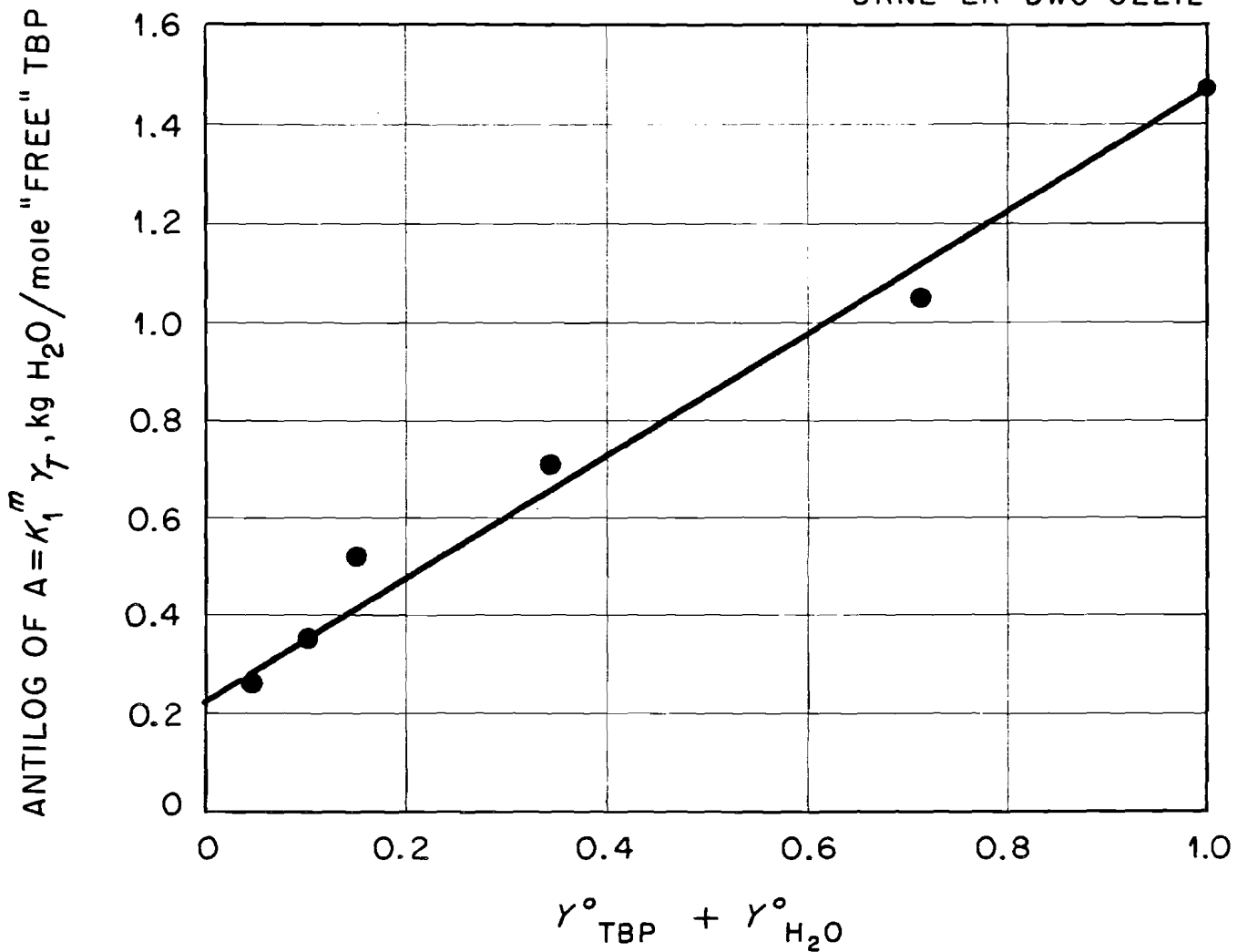
Fig. 1. Correlation of HNO₃ Extraction by 10 and 30 % TBP in Amsco 125-82 and by 100% TBP. Change in Circle Size is used to Indicate Change in Uncertainty in HNO₃ Activity Coefficients in the Aqueous Phase. Lines were Determined by "Least Squares" Analysis.

$$\log \frac{(\text{HNO}_3)_{\text{org}}^m}{[\text{HNO}_3]_{\text{aq}}^m \left\{ 3.75493 - (\text{HNO}_3)_{\text{org}}^m \right\}} = A + B(\text{HNO}_3)_{\text{org}}^m \quad (11)$$

Relative deviations of the arguments of the logarithm in eq. 11, i.e., $100 \left[\text{antilog} (\text{std. dev. of data from eq. 11}) - 1 \right]$, are 9.7, 10.5, 13.7, 3.1, 10.8, and 5.0%, respectively, for 5, 10, 15, 30, 65, and 100 vol % TBP in Amsco 125-82. Each of these is the result of propagation of errors due to ρ_{org} , $(\text{HNO}_3)_{\text{org}}^c$, C_s , and $(\text{H}_2\text{O})_{\text{org}}^c$ and to uncertainties in the extrapolation of nitric acid activity coefficient data of Hartmann and Rosenfeld (20).

Each of the constants A and B of eq. 11 varies regularly with the concentration of TBP in the hydrocarbon diluent (Table VII). Various plots of A, B, and the anti-logarithms of these vs. concentrations of TBP, diluent, and H₂O content of the water-saturated acid-free TBP-diluent solution were made (Figs. 2 and 3) in an effort to obtain the best representation. These parameters are not functions of the nitric acid concentration since the quantity A is an intercept corresponding to $(\text{HNO}_3) = 0$, while the quantity B is experimentally independent of nitric acid concentration for a fixed TBP/diluent ratio (Fig. 1 or eq. 11). Of the functions tested, the best and simplest fit of all the data is given by eq. 12.

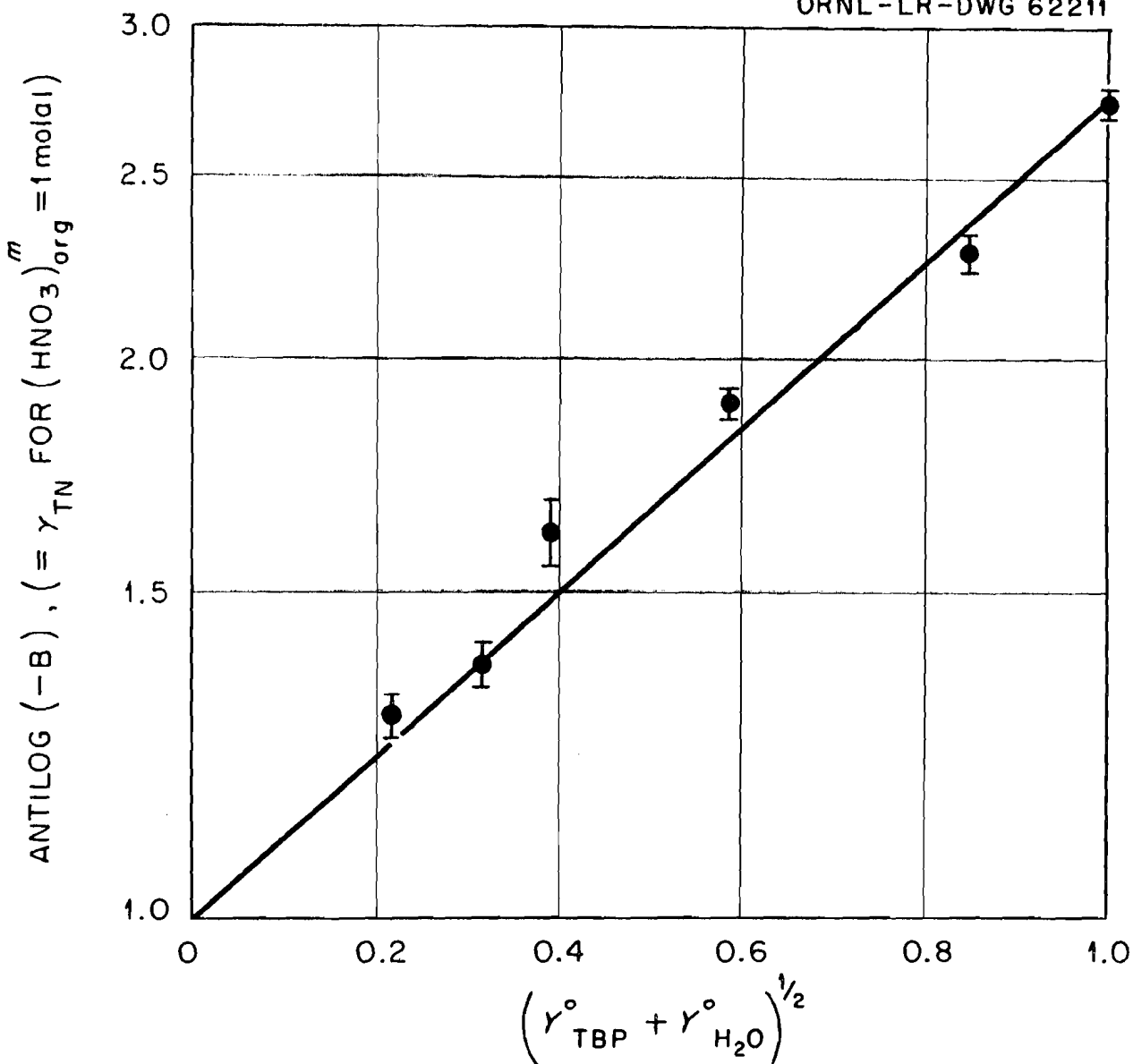
$$\log F_4 = \log \left\{ \frac{(\text{HNO}_3)_{\text{org}}^m}{[\text{HNO}_3]_{\text{aq}}^m \left\{ 3.75493 - (\text{HNO}_3)_{\text{org}}^m \right\}} \right\} = \log \left\{ B_1 + B_2 (Y_{\text{TBP}}^{\circ} + Y_{\text{H}_2\text{O}}^{\circ}) \right\} + B_3 \left(Y_{\text{TBP}}^{\circ} + Y_{\text{H}_2\text{O}}^{\circ} \right)^{1/2} \left(\text{HNO}_3 \right)_{\text{org}}^m \quad (12)$$



Correlation of $K_1^m \gamma_T$ With the Sum of the Mole Fractions of TBP and H₂O in the H₂O-Saturated TBP--Amsco 125-82 Organic Phase.

Fig. 2.

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Correlation of Parameter B With the Sum of the Mole Fractions of TBP and H₂O in the H₂O - Saturated TBP--Amsco 125 - 82 Organic Phase.

Fig. 3.

where Y_{TBP}° is the mole fraction of TBP in the water-saturated acid-free TBP-Amsco*-
 H_2O solution,

$Y_{\text{H}_2\text{O}}^{\circ}$ is the corresponding mole fraction of H_2O .

The "goodness" of the fit of all the 109 sets of data to eq. 12 is shown in Figs. 2 and 3, where the data points correspond to antilog A and antilog (-B) from Table VII, while the lines correspond to the least-squares fit to eq. 12.

Values of the various constants, their standard deviations, and the standard deviation of $\log F_4$, i.e., the logarithm on the left-hand side of eq. 12 are:

$$\begin{array}{ll} B_1 = 0.2282 & \sigma_{B_1} = 0.0076 \\ B_2 = 1.2397 & \sigma_{B_2} = 0.0402 \\ B_3 = 0.4393 & \sigma_{B_3} = 0.0098, \text{ kg TBP/mole HNO}_3 \end{array}$$

$$\sigma_{\log F_4} = 0.05582$$

The standard deviation of $\log F_4$, i.e., $\sigma_{\log F_4}$, corresponds to a standard deviation of F_4 of 13.7% of its value; each of the three constants B_i has a relative standard deviation of 2.2-3.3% of its value.

Complex Formation

Two basically different interpretations of data on the extraction of nitric acid by TBP-diluent solutions have been published. The first, as represented by workers at Harwell (1-4,6), ascribes much of the deviation of the system from ideality to changes in activity coefficients of species in the organic phase as well as in the aqueous phase. A second interpretation (9,10,12,13) postulates the formation of complexes of the type $\text{TBP} \cdot 2\text{HNO}_3$,

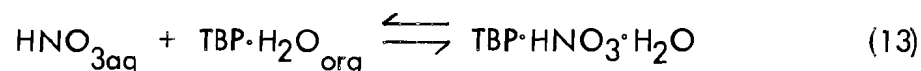
* The molecular weight of Amsco 125-82 is assumed to be 185.0 for the purpose of calculations in this report unless otherwise stated.

Table VII. Fit of HNO₃ Extraction Data to Equation 1

Nominal TBP Conc in Amsco, Vol %	Coefficient A	Std. Dev. of A	Coefficient B, $\frac{\text{kg TBP}}{\text{mole HNO}_3}$	Std. Dev. of B, $\frac{\text{kg TBP}}{\text{mole HNO}_3}$	Number of Sets of Points	Std. Dev. of Data from Eq. 1	Antilog A
5	-0.5800	0.0134	-0.1098	0.0121	16	0.0402	0.2630
10	-0.4468	0.0139	-0.1354	0.0124	16	0.0434	0.3574
15	-0.2831	0.0182	-0.2053	0.0164	16	0.0556	0.5211
30	-0.1512	0.0073	-0.2767	0.0046	10	0.0134	0.7060
65	+0.01973	0.0101	-0.3586	0.0100	38	0.0445	1.0465
100	+0.1732	0.0089	-0.4353	0.0067	13	0.0210	1.490

TBP·3HNO₃, and TBP·4HNO₃, in addition to complexes such as TBP·H₂O, TBP·HNO₃, and TBP·HNO₃·H₂O, without consideration of changes in activity coefficients.

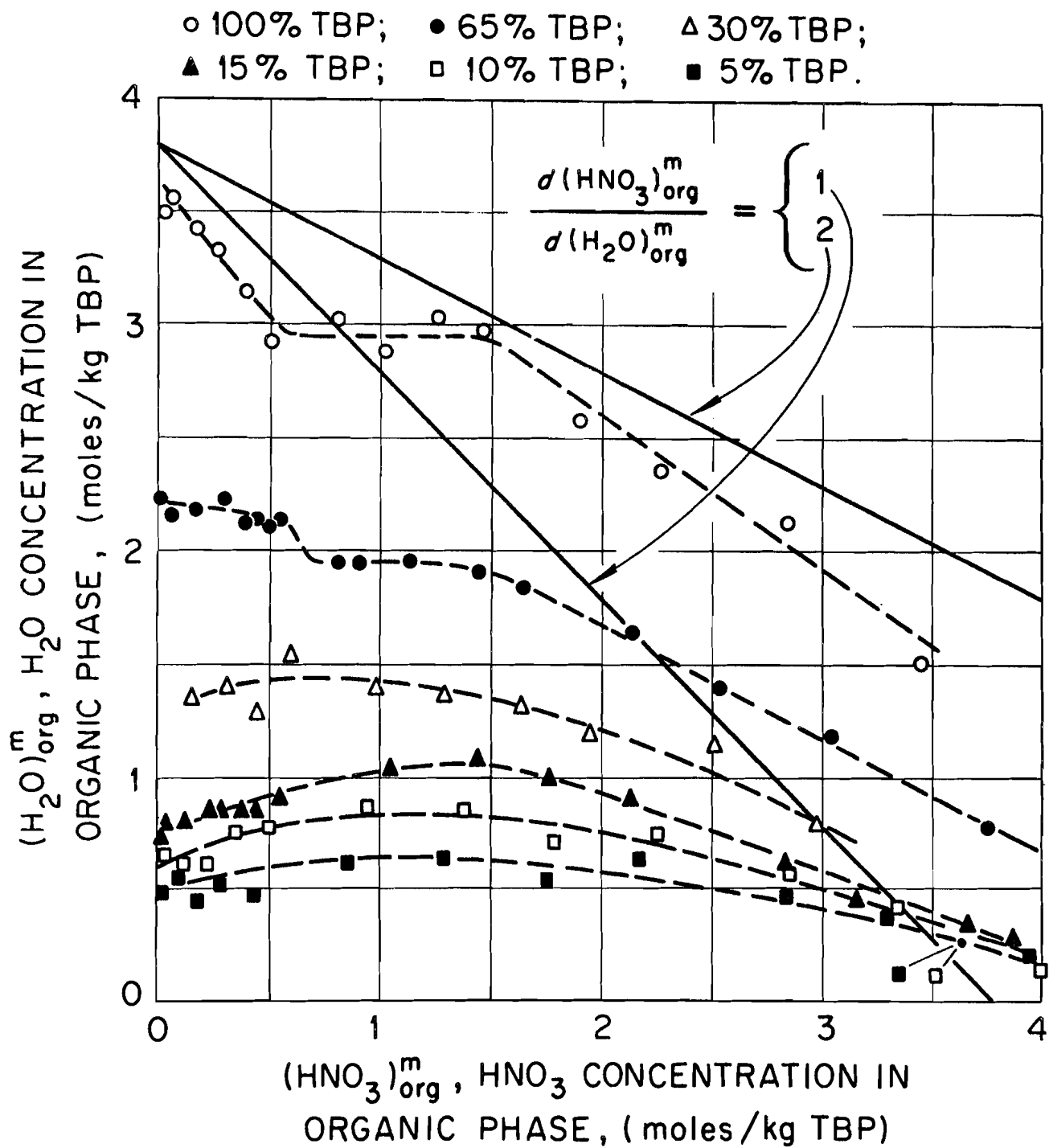
Measurement of the densities and water contents, as well as acidities, of the organic solutions (Tables I-VI) provide a partial basis for determining the mechanism of HNO₃ extraction. First, solutions containing 5 to >30 vol % TBP in Amsco show an increase in water content as the organic phase acidity increases from 0 to 0.5 m or higher; second, solutions containing ~60 to 100 vol % TBP in Amsco initially show a decrease in water content as the acidity increases from 0; third, all solutions gain approximately 2 moles of HNO₃ for each mole of H₂O lost when the organic phase acidity is in the region 1.5 to 4 m (Fig. 4). The relation between H₂O concentration and HNO₃ concentration in the organic phase at low values of the latter suggests, in addition to reaction 1, the reactions*



The initial slopes of the (HNO₃)_{org}^m vs. (H₂O)_{org}^m plots for 10 and 15 vol % TBP in Amsco, for example (Fig. 4), indicate an increase of ~0.15 mole H₂O/kg TBP as the HNO₃ concentration increases from 0 to 0.5 mole/kg TBP. This corresponds to relative extents of reactions 1 and 13 of about 2 to 1. However, as the TBP concentration in the diluent increases, reactions 1 and 13 become less important while reaction 14 becomes predominant.

* The term HNO_{3aq} is used in equations of this report rather than H_{aq}⁺ + NO_{3aq}⁻ for convenience since the two representations are identical. The nitric acid activity can be calculated only one way, that is by eq. 9 or 10. Since undissociated and dissociated components of nitric acid are related by an equilibrium constant, the only difference in the use of HNO_{3aq} and H_{aq}⁺ + NO_{3aq}⁻ is the interpretation of the thermodynamic extraction constant.

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Effects of HNO₃ and Diluent on the Distribution of H₂O into the Organic Phase.

Fig. 4.

The slopes of the curves in Fig. 4 in the range 1.4 to 4 m acid in the organic phase suggest reaction 15:



which does not appear to have been proposed previously. In the case of 65 vol % TBP in Amsco, for which the maximum sets of data are available, eq. 15 applies in this higher acidity region within the small limits of uncertainty of the analytical methods.

Between about 0.4 and 1.4 m HNO_3 in the diluent-free TBP case, acidity increases without a change in the water concentration, corresponding to reaction 13.

DISCUSSION

The argument of the logarithm of eq. 11 has been described frequently in the literature, as indicated earlier in this report, as representing, except for organic-phase activity coefficients, the equilibrium of reaction 1; i.e., in the notation of the present report,

$$K_1^m = \frac{(\text{TBP}\cdot\text{HNO}_3)_{\text{org}}^m}{[\text{HNO}_3]_{\text{aq}}^m \{3.75493 - (\text{TBP}\cdot\text{HNO}_3)_{\text{org}}^m\}} \frac{\gamma_{\text{TN}}}{\gamma_{\text{T}}} \quad (16)$$

However, since the present and other work have presented strong evidence for formation of the compound $\text{TBP}\cdot\text{HNO}_3\cdot\text{H}_2\text{O}$ in addition to $\text{TBP}\cdot\text{HNO}_3$ at low acidities and $\text{TBP}\cdot 2\text{HNO}_3$ at higher acidities, and since the quantity $\{3.75493 - (\text{HNO}_3)_{\text{org}}^m\}$ is defined by eq. 17 provided the aqueous acidity does not exceed ~ 5 M,

$$3.75493 - (\text{HNO}_3)_{\text{org}}^m = (\text{TBP})_{\text{org}}^m + (\text{TBP}\cdot\text{H}_2\text{O})_{\text{org}}^m - (\text{TBP}\cdot 2\text{HNO}_3)_{\text{org}}^m \quad (17)$$

interpretation of eq. 11 in terms of reaction 1 is an oversimplification. Therefore, until the acidity is high enough for the quantity $(\text{TBP}\cdot 2\text{HNO}_3)_{\text{org}}^m$ in eq. 17 to be significant, the argument of eq. 11 is equivalent to

$$\frac{(\text{TBP}\cdot\text{HNO}_3)_{\text{org}}^m + (\text{TBP}\cdot\text{HNO}_3\cdot\text{H}_2\text{O})_{\text{org}}^m}{[\text{HNO}_3]_{\text{aq}}^m \left\{ (\text{TBP})_{\text{org}}^m + (\text{TBP}\cdot\text{H}_2\text{O})_{\text{org}}^m \right\}}$$

When equating this to a term $K_1^m \gamma_T / \gamma_{\text{TN}}$ in which K_1^m is a constant, presumably representing the combined reactions 1, 13, and 14, it is appropriate to consider γ_T as a mean activity coefficient for the species TBP and $\text{TBP}\cdot\text{H}_2\text{O}$ and γ_{TN} as a mean activity coefficient for the species $\text{TBP}\cdot\text{HNO}_3$ and $\text{TBP}\cdot\text{HNO}_3\cdot\text{H}_2\text{O}$ in the organic phase. There does not appear to be any way of calculating the quantity of each of these species under any conditions since only three quantities are known, namely, $(\text{TBP}_s)_{\text{org}}^m = 3.75493$, $(\text{HNO}_3)_{\text{org}}^m$, and $(\text{H}_2\text{O})_{\text{org}}^m$, in equations involving four species plus four activity coefficients.

On the basis of this model, the plot of Fig. 1 is, except for the constant K_1^m , a plot of $(\log \gamma_T - \log \gamma_{\text{TN}})$ vs. $(\text{HNO}_3)_{\text{org}}^m$, giving a correlation of activity coefficients in the organic phase reminiscent of the well known Setschenow correlation for aqueous solutions (21,22). In addition, intercepts of plots such as in Fig. 1, or antilogarithms of values A of Table VII, give $K_1^m \gamma_T / \gamma_{\text{TN}}$ at $(\text{HNO}_3)_{\text{org}}^m = 0$. Since we can choose $\gamma_{\text{TN}} = 1$ when $(\text{HNO}_3)_{\text{org}}^m = 0$, the intercepts correspond to $K_1^m \gamma_T$, not to the equilibrium constant itself. As shown in Table VII, experimental values of this quantity vary from 0.263 for 5% TBP in Amsco 125-82 to 1.49 (moles HNO_3 /kg "free" TBP) (moles HNO_3 /kg H_2O)⁻² in the diluent-free TBP. The extrapolated value corresponding to 0% TBP, i.e., B_1 , equals

0.2282 with a standard deviation of 0.0076. The quantity B_1 of this report is approximately equivalent to the value 0.16 of Alcock et al. (1) which, in terms of the present report, equals $K_1^C y_T$, where K_1^C is a molar equilibrium constant and y_T the molar activity coefficient of TBP + TBP·H₂O infinitely dilute in Amsco 125-82 and saturated with water. The quantity B_1 of this report should not be equated to the value of ~0.2 of Rozen and Khorkhorina (14) since the latter is considered to apply at all concentrations of TBP in the diluent. The quantity $K_1^m y_T$ for diluent-free TBP, i.e., 1.49 in molal units or 1.499 in molar units, corresponds to the K_1 of Damiani and Fattore (13), who state its value to be about unity when the aqueous nitric acid concentration is 0-0.5 M.

Equation 12 contains two independent variables, namely $(\text{HNO}_3)_{\text{org}}$ and $(Y_{\text{TBP}}^{\circ} + Y_{\text{H}_2\text{O}}^{\circ})$, the organic phase concentration of nitric acid and the sum of the mole fractions of TBP and water in the acid-free water-saturated organic phase. The latter variable can be replaced by its equivalent $(1 - Y_{\text{Dil}}^{\circ})$, where Y_{Dil}° is the mole fraction of the diluent in the acid-free water-saturated organic phase. The significance of this variable is that it is a constant for any particular solution of TBP in Amsco 125-82, and that it is basically a measure of the solubility of water in the TBP-Amsco solution.

The interpretation of the data, as given above, corresponds to representing the activity coefficients γ_T and γ_{TN} by eqs. 18-20,

$$\log K_1^m \gamma_T / \gamma_{\text{TN}} = \log [B_1 + B_2(Y_{\text{TBP}}^{\circ} + Y_{\text{H}_2\text{O}}^{\circ})] + B_3(Y_{\text{TBP}}^{\circ} + Y_{\text{H}_2\text{O}}^{\circ})^{1/2} (\text{HNO}_3)_{\text{org}}^m \quad (18)$$

$$K_1^m \gamma_T = B_1 + B_2 (Y_{TBP}^o + Y_{H_2O}^o) \quad (19)$$

$$\log \gamma_{TN} = -B_3 (Y_{TBP}^o + Y_{H_2O}^o)^{1/2} (HNO_3)_{org}^m \quad (20)$$

the last of which represents the mean activity coefficient of the complexes $TBP \cdot HNO_3$ and $TBP \cdot HNO_3 \cdot H_2O$. The value of γ_{TN} tends to unity as the concentration of TBP and of HNO_3 in the diluent tend to zero. Thus γ_T and γ_{TN} have different standard states: that of the former is pure anhydrous TBP, that of the latter is infinite dilution of $TBP \cdot HNO_3 \cdot H_2O$ in the diluent. The relation between the alternative standard state for TBP, namely, infinite dilution in diluent, and the one chosen for use in this report, namely, pure anhydrous TBP, cannot be given at the present time since the value of γ_T for water-saturated TBP is not known. Efforts to obtain this quantity have been started in this laboratory by Faure and Davis (23), who found the vapor pressures of TBP over water-saturated and nearly dry TBP to be ~ 0.51 and $\sim 0.8 \mu$, respectively.

CONCLUSIONS

The distribution of nitric acid between TBP--Amsco 125-82 solutions and aqueous solutions, up to $\sim 5 \text{ M}$ in the latter phase, is accurately described by eq. 11 for any particular weight ratio, $W_{\text{Dil}}/W_{\text{TBP}}$, of Amsco to TBP. All data in all TBP-Amsco solutions are quantitatively described by eq. 12. These equations should prove useful for interpreting solvent extraction data and evaluating the effects of the diluents, which are not described by "regular" solution theory. The data are consistent with the existence of the complexes $\text{TBP}\cdot\text{H}_2\text{O}$, $\text{TBP}\cdot\text{HNO}_3$, $\text{TBP}\cdot\text{HNO}_3\cdot\text{H}_2\text{O}$, and $\text{TBP}\cdot 2\text{HNO}_3$, the last of which is possibly formed by reaction 15. Unless it is assumed that the activity coefficient of each of these species and that of uncomplexed TBP is unity and independent of any concentration, there are not enough measurable variables to allow calculation of the quantities of each species present.

ACKNOWLEDGMENTS

The author wishes to thank P. S. Lawson, C. T. Thompson, and C. G. Hill, Jr. for performing most of the experimental work described in this report. Analyses were performed by members of the groups of W. R. Laing, P. F. Thomason, and G. R. Wilson of the Analytical Chemistry Division of ORNL. Thanks are also extended to M. W. Davis and P. B. Wood of the Central Data Processing Facility of the Oak Ridge Gaseous Diffusion Plant and to M. H. Lietzke of the ORNL Chemistry Division for assistance in performing computer programming and statistical analyses of the data.

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