g = gravitational acceleration, LT^{-2}
h = diminution of radius, L
K_L = mass transfer coefficient, LT^{-2}
L = characteristic length, L
r = distance radially from sphere center, L
S = surface area, L^2
t = time interval, T
u = velocity parallel to surface, LT^{-1}
v = velocity normal to surface, LT^{-1}
W = total mass transferred, M
x = distance coordinate along surface, L
y = distance coordinated normal to surface, L

Greek Letters

δ = boundary-layer thickness, L
θ = angle from forward stagnation point
ϵ = angle between normal to surface and the vertical
ν = kinematic viscosity
ρ = density (fluid)
ρ_s = density (solid)

Dimensionless Groups

N_{Gr} = $gd^3\beta\,\Delta T/\nu^2$ = Grashof number
N'_{Gr} = $gd^3\,\Delta\rho/\nu^2\rho$ = modified Grashof number for mass transfer
N_{Nu} = $h'd/D$ = Nusselt number
N_{Pr} = ν/K = Prandtl number
N_{Ra} = $gd^3\beta\,\Delta T/\nu K$ = Rayleigh number
N'_{Ra} = $gd^3\,\Delta\rho/\nu^2\rho\cdot\nu/D$ = modified Rayleigh number for mass transfer
N_{Sc} = ν/D = Schmidt number
N_{Sh} = K_Ld/D = Sherwood number

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The Distribution of Nitric Acid Between Water and Tributyl Phosphate - Hexane Solvents

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The distribution of nitric acid between water and solutions of tributyl phosphate in n-hexane has been measured over a greater range of acid and tributylphosphate concentrations than have been reported previously.

The partitioning of nitric acid between water and tributylphosphate-hexane solvents has been satisfactorily explained on the basis of the commonly accepted equilibrium complexing reaction, with this modification: The over-all aqueous-to-organic reaction is subdivided into the distribution of uncomplexed nitric acid and an organic phase complexing reaction. This alteration is found necessary to account for the behavior of the partitioning data of dilute acid over the entire tributylphosphate-hexane range. The residual discrepancy between the theory and the data can be qualitatively attributed either to modest nonideality of the organic phase or to the effect of the varying water content of the solvent on the distribution coefficient of uncomplexed nitric acid.

The sparse data on water extraction by tributylphosphate-hexane solvents are not amenable to the same type of analysis, even though a type of complexing similar to that found for nitric acid has been previously proposed. The interaction between water and tributylphosphate appears to be stronger than that normally attributed to nonideality but weaker than a true chemical complex.

Like many heavy metal nitrates nitric acid reacts chemically with tributylphosphate to form a stable complex. Although the compound nitric acid-tributylphosphate has never been chemically isolated, its existence has been conclusively demonstrated by the ultraviolet spectral evidence of Collopy and Blum (3). However no analytical method has yet been devised to differentiate quantitatively the small amount of physically dissolved nitric acid from the complex in the organic phase.

Warf (*13*) and Moore (*11*) were the first to point out the competitive effect of nitric acid on the extraction of the lanthanide and actinide nitrates. Alcock (*1*), Fletcher (*4*), and Gruverman (*6*) have done further experimental work on the extraction of pure aqueous nitric acid into tributylphosphate, while Kooi (*7*) and Fletcher (*4*) have investigated the partitioning of nitric acid between water and other organic solvents. Recently Alcock et al. (*1*), McKay and Healy (*10*) and Tuck (*12*) have subjected the nitric acid-water-tributylphosphate diluent system to an exhaustive examination. An excellent summary of the physical chemistry of these complexing reactions has been presented by Glueckauf (*5*), while Baldwin et al. (*2*) have investigated the distribution of a large number of monovalent electrolytes between water and tributylphosphate.

Nitric acid, unlike the heavy metal nitrates, does not have a coordination number to be fulfilled; yet there is strong evidence that it forms only one complex with tributylphosphate, namely nitric acid-tributylphosphate. First the spectrum of nitric acid tributylphosphate solutions indicates no higher complexes (3). Secondly there is a tendency for the organic phase to saturate at a 1-to-1 mole ratio of nitric

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acid to tributylphosphate as the aqueous acidity is increased (*1*, *5*). Thirdly using the dilution technique* Glueckauf (*5*), McKay and Healy (*10*), and Moore (*11*) claim that the distribution coefficient is proportional to the first power of the tributylphosphate concentration. Finally at low tributylphosphate concentrations Alcock (*1*) has shown that the distribution data fit the theoretical expression:

$$K = \frac{C_c}{a_{\pm}^2 C_{TBP_f}} \qquad (1)$$

K is the equilibrium constant for the over-all reaction:

$$HNO_3(aq) + TBP(org) \rightleftarrows HNO_3 \cdot TBP(org)$$

In Alcock's work the concentration of the complex in the organic phase is identified with the total acid concentration in the organic phase, and the free tributylphosphate concentration is obtained by the material-balance equation:

$$C_{TBP_f} = C_{TBP} - C_c \qquad (2)$$

where

$$C_{TBP} = \frac{1{,}000\, d_{TBP}}{M_{TBP}\, f_w} \qquad (3)$$

Equation (3) is applicable only if there is no volume change on mixing of the pure tributylphosphate and inert diluent, as is true for hexane and kerosene solvents.

Alcock (*1*) has employed Equation (1) in treating partitioning data up to 7 molar aqueous acidity. The correlation is excellent at 1.9% tributylphosphate. Deviations at higher tributylphosphate concentrations (apparent in the low and high acidity regions) are attributed to nonideality of the organic phase. Physical dissolution of the acid is assumed to begin discontinuously at 7 molar aqueous acidity. For pure tributylphosphate, Tuck (*12*) has observed a discontinuity in the volume change upon extraction at 3.6 molar organic acidity. This is attributed to the formation of the complex below this concentration and physical dissolution of uncomplexed acid at higher acidities.

Glueckauf (*5*) has also interpreted the nitric acid-tributylphosphate system by the over-all equilibrium concept, with the organic-phase activities replaced by volume fractions instead of molar concentrations. However the molecular weights and densities of the species involved are such that the resulting mass action expression reduces to Equation (1).

Baldwin et al. (*2*) have proposed a modified over-all equilibrium relation which however does not directly consider the complexing reaction.

If the activity coefficients of the species in the organic phase are not unity, Equation (1) can be rewritten as the product of concentrations and activity coefficients:

$$K = \frac{C_c}{a_{\pm}^2 C_{TBP_f}} \cdot \frac{y_c}{y_{TBP}} \qquad (4)$$

Figure 1 has been constructed by the use of Equation (4) and the data of this work, Fletcher (*4*), and Gruverman (*6*). The product of *K* and y_{TBP}/y_c has been plotted against the molar concentration of aqueous nitric acid to illustrate the apparent nonideal behavior of the organic phase at different aqueous acidities. The system appears to approach ideality at 5% initial tributylphosphate.

TABLE 1. DISTRIBUTION OF NITRIC ACID BETWEEN WATER AND TRIBUTYLPHOSPHATE-HEXANE SOLVENTS AT 25°C.

Nitric acid molarity Aqueous	Nitric acid molarity Organic
5% TBP, $C_{TBP} = 0.18$	
0.118	0.0005
0.240	0.0015
0.516	0.0065
1.01	0.0298
2.06	0.071
5.16	0.164
9.73	0.194
10.5	0.212
15.5	0.335
10% TBP, $C_{TBP} = 0.36$	
0.125	0.0013
0.238	0.0038
0.515	0.0159
0.991	0.0548
2.00	0.141
4.96	0.312
9.10	0.382
10.4	0.406
15.6	0.617
20% TBP, $C_{TBP} = 0.72$	
0.102	0.0020
0.208	0.0079
0.487	0.0396
0.950	0.109
1.37	0.192
1.74	0.250
1.87	0.270
2.62	0.382
3.53	0.489
4.76	0.590
5.98	0.648
7.62	0.695
9.31	0.743
10.9	0.803
12.6	0.904
13.8	1.05
15.3	1.27
30% TBP, $C_{TBP} = 1.08$	
0.321	0.040
0.499	0.083
0.625	0.117
0.874	0.184
0.976	0.217
40% TBP, $C_{TBP} = 1.43$	
0.132	0.011
0.242	0.032
0.435	0.085
1.65	0.491
4.29	1.09
8.65	1.42
11.5	1.73
14.6	2.31
50% TBP, $C_{TBP} = 1.78$	
0.089	0.0097
0.167	0.0296
0.215	0.0442
0.297	0.0735
0.549	0.188
0.661	0.250
0.761	0.291
0.941	0.391
1.48	0.633
2.83	1.06
60% TBP, $C_{TPB} = 2.13$	
0.125	0.019
0.212	0.052
1.38	0.642
3.87	1.47
8.11	2.04
10.5	2.32
13.8	3.06
70% TBP, $C_{TBP} = 2.46$	
0.107	0.021
0.152	0.039
0.263	0.100
0.399	0.190
0.485	0.248
0.667	0.375
0.752	0.426
100% TBP, $C_{TBP} = 3.43$	
0.079	0.021
0.116	0.042
0.139	0.059
0.194	0.100
0.237	0.143
0.302	0.205
0.335	0.238
0.411	0.316
0.526	0.409
0.576	0.478
1.02	0.840
1.22	1.01
2.04	1.46
3.22	2.08
3.83	2.30
6.91	3.16
9.96	3.82
12.6	4.76
13.1	4.78

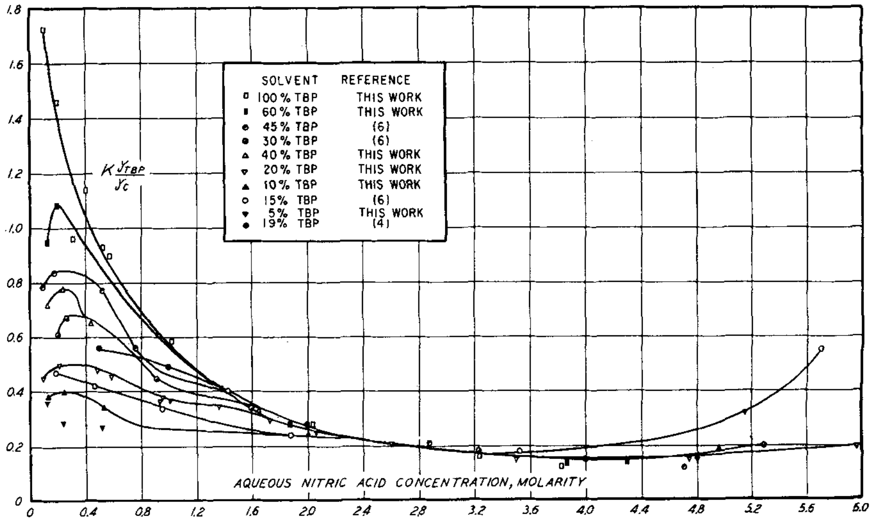

Fig. 1. Variation of Ky_{TBP}/y_c as defined by Equation (4) with aqueous nitric acid concentration for various tributylphosphate-hexane solvents, 25°C.

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* The composition of the aqueous phase is maintained at a constant (trace) value of the ionic solute, and the organic phase is progressively reduced in tributylphosphate content by addition of inert diluent. The measured distribution coefficient is then proportional to the number of tributylphosphate molecules per molecule of nitric acid in the complex.

Equation (4) is based on the assumption that uncomplexed nitric acid does not dissolve in the organic phase. If this is incorrect, then the spread of the curves in Figure 1 is due at least in part to the omission of a second equilibrium expression representing the physical dissolution of the acid. Moreover Equations (1) and (4) are expressions of an over-all, two-phase equilibrium. If the mass action law were applied to the organic phase alone, then the $a_\pm^2$ term of Equation (1) would be replaced by the activity of the uncomplexed acid in the organic phase. This latter activity would depend not only upon the aqueous-phase activity but on the physical distribution coefficient of the acid as well. Furthermore the partitioning of uncomplexed acid would probably depend upon the tributylphosphate content (or, more generally, the polarity) of the solvent, and it will be shown in this study that the large discrepancies of Figure 1 can be attributed to the omission of the distribution of uncomplexed acid in the development of Equations (1) and (4).

EXPERIMENTAL RESULTS

Partitioning measurements were made by shaking equal volumes of the aqueous-acid and water-saturated solvent in a 250-cc. glass-stoppered cylinder. Pure grade *n*-hexane was employed without further purification. The tributylphosphate was vacuum distilled at 125°C. before use. The acidity of both phases was determined by direct titration with aqueous potassium hydroxide to a phenolphthalein end point. In the organic-phase analysis a two-phase titration resulted but did not impair the precision of the results. Partitioning data at 25°C. are shown in Table 1. The mean ionic molal activity of aqueous nitric acid has been measured quite precisely, and the values presented in the Landolt-Börnstein Tables (*8*) have been employed.

The water content of the organic phase was determined by Karl Fischer titration. These results are presented in Table 2.

Volume changes on extraction were measured in a device which consisted of the top section of a separatory funnel, a 30-cc. section of a 100-cc. buret, the bulb of a 100-cc. pipette, and a two-way stopcock, joined in that order. Volume changes are reported as the ratio of the volume of the equilibrated organic phase divided by its initial volume; this ratio is denoted by f_w for the extraction of water into initially dry tributylphosphate-hexane solvent and f_A for acid extraction into initially water-saturated but acid-free solvent. Values of f_w are presented in Table 2 and f_A in Figure 8, with a precision estimated at ± 0.005.

CORRELATION OF RESULTS

Previous thermodynamic analyses of this system have been designed to justify the saturation effect*, and the equilibrium constants have been fitted to the data in this region. As a result the correlations are generally poor in the extreme regions of low and high acidity (*1, 6*). In this work an attempt will be made to correlate the distribution data over the concentration range bracketing aqueous acidities between 0 and 11 molar.

The distribution of nitric acid between the two phases is assumed to be governed by the following equilibria:

$$H^+(aq) + NO_3^-(aq) \rightleftarrows HNO_3(aq) \qquad (A)$$

$$HNO_3(aq) \rightleftarrows HNO_3(org) \qquad (B)$$

$$HNO_3(org) + TBP(org) \rightleftarrows HNO_3 \cdot TBP(org) \qquad (C)$$

The mass-action constants for these three reactions are:

For reaction (A)

$$K_D = \frac{a_\pm^2}{a_{wA}} \qquad (5)$$

For reaction (B)

$$p = \frac{a_{oA}}{a_{wA}} \qquad (6)$$

For reaction (C)

$$K_R = \frac{C_c}{a_{oA}\, C_{TBP_f}} \qquad (7)$$

Note that Equation (7) contains the organic phase acid activity rather than the aqueous activity of Equation (1).

These relations assume the organic phase to behave ideally. This is not entirely the case but should be reasonably accurate in dilute tributylphosphate-hexane solvents. The effect of nonideality of the organic phase will be considered in a later section. It has also been tacitly assumed that both tributylphosphate and hexane are negligibly soluble in the aqueous phase, which can then be considered simply a solution of nitric acid in water. Alcock (*1*) and Baldwin (*2*) have shown this to be essentially correct.

If the total acidity of the organic phase is C_o

$$C_o = C_c + C_{oA} \qquad (8)$$

It will be assumed that in Equation (8) C_{oA} can be replaced by a_{oA} if the amount of physically dissolved nitric acid is sufficiently small. This assumption can be justified for the following reasons:

1. If C_{oA} is small, the sum $C_c + C_{oA}$ will not be greatly affected even by a fairly large percentage change in the second term, which might be caused by employing a_{oA} instead of C_{oA}.
2. Since C_{oA} is small, its high dilution probably means thermodynamic behavior close to ideality, in which case $C_{oA} = a_{oA}$ (if the standard state is chosen at infinite dilution). Thus

$$C_o = C_c + a_{oA} \qquad (9)$$

Substituting Equations (2), (5), (6), and (9) into Equation (7) one gets $K_R =$

$$\frac{C_o - \left(\frac{p}{K_D}\right) a_\pm^2}{\left(\frac{p}{K_D}\right) a_\pm^2 \left[C_{TBP} - C_o + \left(\frac{p}{K_D}\right) a_\pm^2\right]} \qquad (10)$$

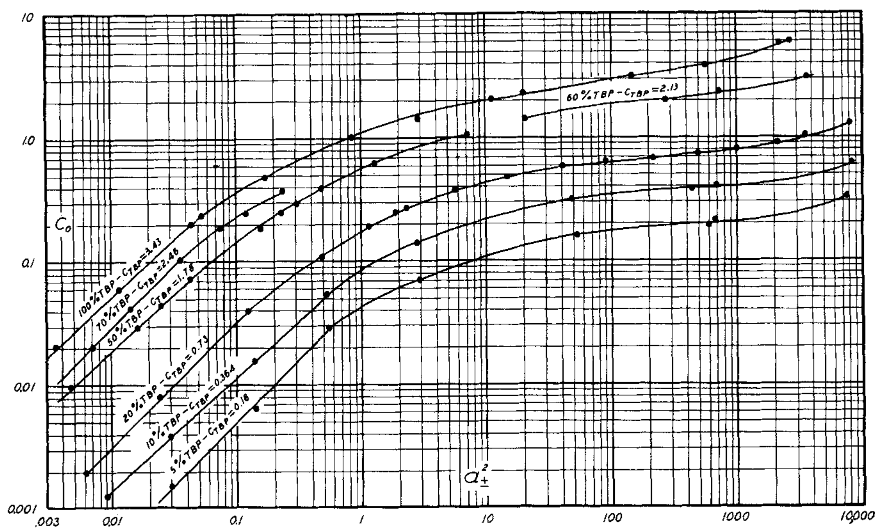

Fig. 2. Total acidity of organic phase as a function of aqueous nitric acid acidity for various tributylphosphate-hexane solvents, 25°C.

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* Throughout this work the term "saturation" denotes complete conversion of the free tributylphosphate to the complex nitric acid-tributylphosphate.

or rearranging Equation (10) one obtains

$$C_o = \frac{(K_R C_{\mathrm{TBP}} + 1)\left(\frac{p}{K_D}\right) a_{\pm}^2 + K_R \left(\frac{p}{K_D}\right)^2 a_{\pm}^4}{1 + K_R \left(\frac{p}{K_D}\right) a_{\pm}^2} \tag{11}$$

Because of the highly paraffinic and nonpolar nature of hexane (the diluent used in these studies) compared with the high degree of polarity of tributylphosphate, the physical distribution coefficient would be expected to increase with increasing tributylphosphate content of the solvent. A simple quantitative relationship between the two has been assumed as

$$p = P\, C^n_{\mathrm{TBP}} \tag{12}$$

when one substitutes Equation (12) into Equation (11)

$$C_o = \frac{(K_R C_{\mathrm{TBP}} + 1)\left(\frac{P}{K_D}\right) C^n_{\mathrm{TBP}} a_{\pm}^2 + K_R \left(\frac{P}{K_D}\right)^2 C^{2n}_{\mathrm{TBP}} a_{\pm}^4}{1 + K_R \left(\frac{P}{K_D}\right) C^n_{\mathrm{TBP}} a_{\pm}^2} \tag{13}$$

The constants in Equation (13) must now be determined from the distribution data, which have been plotted in Figure 2 in the form of C_o vs. $a_{\pm}^2$. Several regimes can be visually discerned:

1. A saturation region for which $C_o \approx C_{\mathrm{TBP}}$ does exist for $10 < a_{\pm}^2 < 1{,}000$, or $3 < C_{\mathrm{HNO_3}} < 11$ molar. However, the plateau is never truly horizontal, and its upward slope becomes greater as the tributylphosphate concentration increases.
2. At aqueous acidities, $a_{\pm}^2 > 1{,}000$, or $C_{\mathrm{HNO_3}} > 11$ molar, the curves begin to rise again (owing to physically dissolved acid, in accordance with this theory).
3. In the region of low acidity, $a_{\pm}^2 < 0.1$ or $C_{\mathrm{HNO_3}} < 0.5$ molar, the curves become linear. Moreover the slopes of these linear portions are all about unity. The region for which C_o is proportional to $a_{\pm}^2$ extends to greater aqueous-acid activities the lower the tributylphosphate content. For 5% tributylphosphate the linear range extends to $a_{\pm}^2 = 0.5$, while for pure tributylphosphate curvature begins at $a_{\pm}^2 = 0.06$.
4. All of the curves are parallel over the entire region. However the spacing between them is greater at low acidities than at high ones. In particular the spacing is constant for $a_{\pm}^2 < 0.1$, goes through a transition for $0.1 < a_{\pm}^2 < 10$, and is again constant in the region $10 < a_{\pm}^2 < 1{,}000$.

It will be shown that all of these effects are predicted by Equation (13).

For purposes of the following analysis four regions will be identified:

$a_{\pm}^2 < 0.1$,	$C_{\mathrm{HNO_3}} < 0.5$	— Low-acidity region
$0.1 < a_{\pm}^2 < 10$,	$0.5 < C_{\mathrm{HNO_3}} < 3$	— Transition region
$10 < a_{\pm}^2 < 1{,}000$,	$3 < C_{\mathrm{HNO_3}} < 11$	— Saturation region
$1{,}000 < a_{\pm}^2$	$11 < C_{\mathrm{HNO_3}}$	— High-acidity region

The spacing between the curves in the saturation region will be examined, to see if it can be related to the tributylphosphate concentration. Figure 3 is a plot of C_o against C_{TBP} on logarithmic coordinates for constant values of $a_{\pm}^2$. The straight lines which result indicate that C_o is proportional to $C^{0.97}_{\mathrm{TBP}}$ over the entire $a_{\pm}^2$ range, substantiating the visual observation that the spacing was constant in this region. With reference to Equation (13) this region is identified with

$$K_R \left(\frac{P}{K_D}\right)^2 C^{2n}_{\mathrm{TBP}}\, a_{\pm}^4 \approx 0$$

and

$$K_R \left(\frac{P}{K_D}\right) C^n_{\mathrm{TBP}}\, a_{\pm}^2 >> 1$$

Equation (13) then reduces to

$$C_o = \frac{(K_R C_{\mathrm{TBP}} + 1)\left(\frac{P}{K_D}\right) C^n_{\mathrm{TBP}} a_{\pm}^2}{K_R \left(\frac{P}{K_D}\right) C^n_{\mathrm{TBP}} a_{\pm}^2} = \frac{K_R C_{\mathrm{TBP}} + 1}{K_R} \tag{14}$$

Furthermore since the log-log plot of Figure 3 would not be linear if there were additive terms to C_{TBP}, it can be concluded that $K_R C_{\mathrm{TBP}} >> 1$.

An examination of the derivation of Equation (13) shows that 1 in the $K_R C_{\mathrm{TBP}} + 1$ term on the left-hand side of the numerator and the entire $K_R (P/K_D)^2 C^{2n}_{\mathrm{TBP}} a_{\pm}^4$ term represents the contribution of physically dissolved nitric acid in the material balance, Equation (8). The fact that both of these terms can simultaneously be considered negligible indicates that the total acidity of the organic phase up to ~ 11 molar aqueous acidity is primarily due to the complex. However the small concentration of physically dissolved nitric acid is still of prime importance in the equilibrium expression, Equation (7).

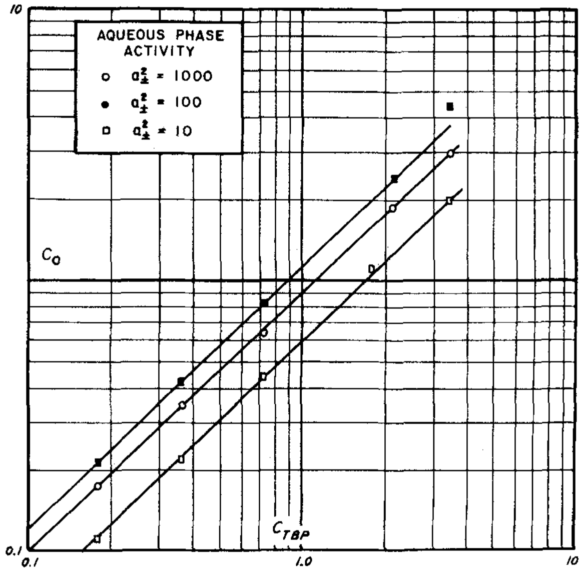

Fig. 3. Variation of total organic-phase acidity as a function of the tributylphosphate concentration of the water-saturated solvent for three constant aqueous-phase activities in the saturation region.

TABLE 2. SOLUBILITY OF WATER IN TRIBUTYLPHOSPHATE-HEXANE SOLVENTS AT 25°C.

Volume*, % TBP	C_{TBP}	C_{H_2O}	f_w
0	0	0.006	1.000
10	0.36	0.081	—
20	0.72	0.238	1.007
30	1.08	0.439	1.011
40	1.43	0.703	1.017
50	1.78	1.028	1.023
60	2.13	1.37	1.030
70	2.46	1.82	1.037
100	3.43	3.55	1.065

* Based on water-free materials.

With this simplification Equations (13) or (14) for the saturation region reduce to

$$C_o = C_{TBP} \qquad (15)$$

The experimental curves of Figure 2 show that at the beginning of this region $a_\pm^2 = 10$, C_o is below C_{TBP}, but approaches this value at $a_\pm^2 = 1{,}000$. This is presumably due in part to the fact that unity is not negligible compared with $K_R(P/K_D)C^n_{TBP}\,a_\pm^2$, especially for the low values of $a_\pm^2$. However the agreement between the experimental exponent from Figure 3, 0.97, and the theoretical value of unity is important. As a further illustration of the effectiveness of the correlation for this region $C_o/C^{0.97}_{TBP}$ is plotted against $a_\pm^2$ for $10 < a_\pm^2 < 1{,}000$ in Figure 4. The points for all tributylphosphate concentrations from 5% ($C_{TBP} = 0.18$) to 100% ($C_{TBP} = 3.43$) lie on a single curve. If Equation (15) were followed, the curve should be a horizontal line at $C_o/C_{TBP} = 1$. This value is reached only at $a_\pm^2 = 600$. It is below it at low $a_\pm^2$ values, since unity is not negligible compared to $K_R(P/K_D)C^n_{TBP}\,a_\pm^2$.

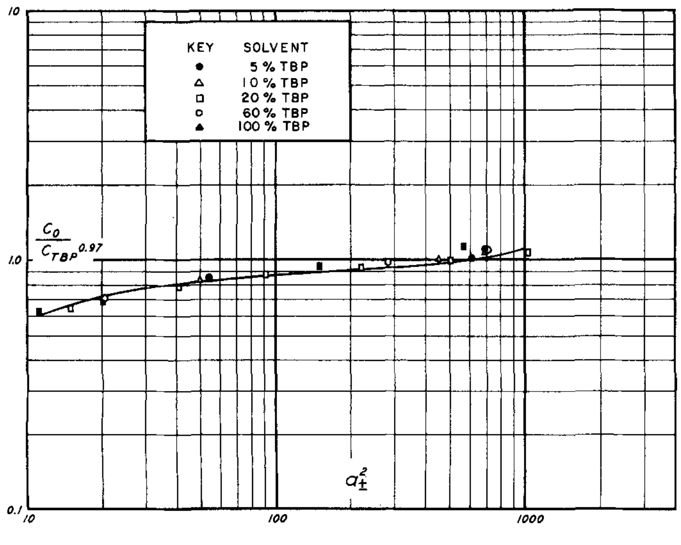

Fig. 4. $C_o/c_{TBP}^{0.97}$ as a function of aqueous-phase activity in the saturation region.

In Figure 5, C_o has again been plotted against C_{TBP} on logarithmic coordinates, for constant values of $a_\pm^2$ in the low-acidity region. The results are again straight lines, each with a slope of 1.6. With reference to Equation (13) the low-acidity region can be considered as one in which $a_\pm^2$ is so small that

$$K_R\left(\frac{P}{K_D}\right)^2 C^{2n}_{TBP}\,a_\pm^4 = 0$$

$$1 >> K_R\left(\frac{P}{K_D}\right) C^n_{TBP}\,a_\pm^2$$

Since it has been shown that $K_R C_{TBP} >> 1$, Equation (13) for the low-acidity region becomes

$$C_o = K_R C^{n+1}_{TBP}\left(\frac{P}{K_D}\right) a_\pm^2 \qquad (16)$$

It should be noted that Figure 5 is at variance with the data reported by Glueckauf (5), which suggest that a logarithmic plot of $(C_o/a_\pm^2)$ against C_{TBP} [which, by Equation (3), is approximately proportional to the volume fraction of tributylphosphate] has a slope of unity. It is not known whether this anomaly is due to the relatively few data points presented by Glueckauf, or to the difference in tributylphosphate concentration used in the dilution experiments ($0.01 < A < 0.10$ for Glueckauf; $0.05 < A < 1.00$ for this work). However the points on Figure 5 corresponding to 5 and 10 volume % tributylphosphate ($C_{TBP} = 0.18$ and 0.36 respectively) overlap those of Glueckauf; yet the slope does not appear to be decreasing from 1.6 to unity.

Thus it can be concluded from Equation (16) and Figure 5 that $n + 1 = 1.6$, or $n = 0.6$. Equation (16) further predicts that $C_o/C^{1.6}_{TBP}$ should be linear in $a_\pm^2$ with a slope of $K_R P/K_D$. Figure 6 shows that the data for all tributylphosphate concentrations do in fact lie on a single straight line when plotted in this manner, up to $a_\pm^2 \approx 0.05$. From the slope of this line

$$\frac{K_R P}{K_D} = 0.67$$

The determination of this constant permits the equilibrium expression for the entire range from 0 to 11 molar aqueous acidity to be written as

$$C_o = \frac{0.67\,C^{1.6}_{TBP}\,a_\pm^2}{1 + 0.67\,C^{0.6}_{TBP}\,a_\pm^2} \qquad (17)$$

For comparison Equation (1) can be rewritten (with the tributylphosphate material balance and $C_o = C_c$) as

$$C_o = \frac{K\,C_{TBP}\,a_\pm^2}{1 + K\,a_\pm^2} \qquad (18)$$

which is the special case of Equation (17) for n arbitrarily set equal to zero, that is the physical distribution coefficient assumed independent of the tributylphosphate content.

The effect of physical dissolution of the acid, although accounted for by the right-hand term of the numerator in Equation (13), has not been numerically evaluated since independent values of K_R and P/K_D cannot be determined with sufficient accuracy from the data.

The data for all tributylphosphate concentrations can be brought into a single curve only for the low-acidity and saturation regions, since the equation for these cases permits the C_{TBP} term to be extracted from the right-hand member of Equation (17). These correlations are represented by Figures 4 and 6. For the transition region however Equation (17) does not permit the separation of C_{TBP} and $a_\pm^2$, so that each tributylphosphate concentration must be treated individually.

To compare the predicted values of C_o with the experimental data Equation (17) was plotted in Figure 7 for 5, 20, and 100 volume % tributylphosphate. The agreement is good for all tributylphosphate concentrations at low aqueous acidities. This is to be expected, since the constants $n = 0.6$ and $(K_R P/K_D) = 0.67$ were determined from the data in this region.

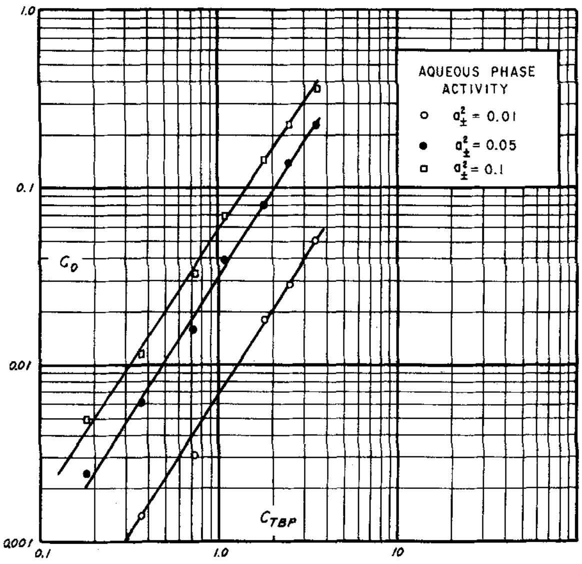

Fig. 5. Variation of total organic-phase acidity as a function of the tributylphosphate concentration of the water-saturated solvent for three constant aqueous-phase activities in the low-acidity region.

However the excellent agreement for 5% tributylphosphate over the entire acidity range indicates that the assumptions are sound if the organic phase is sufficiently dilute in tributylphosphate. The deviation of the calculated and experimental curves increases with tributylphosphate content and is greatest for 100% tributylphosphate. This is presumably due to the onset of nonideal behavior of the organic phase.

EFFECT OF ORGANIC PHASE VOLUME CHANGES ON ACID EXTRACTION

The tributylphosphate material balance, Equation (2), tacitly assumes that in the course of acidifying the water-saturated solvent no tributylphosphate is transferred to the aqueous phase and the volume of the organic phase remains at its acid-free value. The first assumption is quite good, owing to the extremely low solubility of tributylphosphate in water. The second assumption however is far from true. To account for the change in volume on acid extraction the ratio f_A equal to the final volume divided by the initial volume must be introduced. The C_{TBP} term in Equation (2) then becomes C_{TBP}/f_A. When one carries the f_A term through the derivation, the C_o of Equation (17) becomes $f_A C_o$, which in turn should have been plotted as the ordinate of Figure 7.

However the magnitude of f_A, presented in Figure 8, is small compared with the twofold discrepancy between the experimental and semitheoretical curves for 100% tributylphosphate (Figure 7). The inclusion of this volume change on extraction correction would not have eliminated the necessity of assuming substantial nonideality of the organic phase.

EFFECT OF ORGANIC PHASE NONIDEALITY

If the organic phase complexing equilibrium is expressed entirely in terms of activities [by multiplying the right-hand side of Equation (7) by y_c/y_{TBP}], then the 1 in the denominator of Equation (17) should be replaced by y_c/y_{TBP}. This revised relation can be solved for the activity coefficient ratio to yield

$$\frac{y_c}{y_{TBP}} = 0.67\, C_{TBP}^{0.6}\, a_\pm^2 \left[\frac{C_{TBP}}{C_o} - 1\right] \qquad (19)$$

As computed for the data on extraction into pure tributylphosphate y_c/y_{TBP} is unity up to $a_\pm^2 \cong 0.5$, passes through a maximum of 25 at $a_\pm^2 \cong 100$, becomes zero at $a_\pm^2 = 250$, and is negative thereafter.*

That the ratio is unity at low acidities implies standard states corresponding to infinite dilution for the complex and the pure (but water-saturated) substance for tributylphosphate. If the observed variation of water content with acidity and the possible existence of uncomplexed nitric acid are both momentarily neglected, then this idealized organic phase reduces to a binary mixture of tributylphosphate and nitric acid-tributylphosphate (or nitric acid-tributylphosphate-water). For the above mentioned standard states y_c/y_{TBP} should approach the ratio $(P_c^\circ P^\circ_{TBP})/(k_c k_{TBP})$ in the saturation region, where the organic phase consists of dilute tributylphosphate in a medium of essentially pure complex. Thus the left-hand term in the denominator of Equation (17) instead of remaining at unity for all $a_\pm^2$ need only be 1 in the low-acidity region and approach the vapor pressure—Henry's Law constant ratio at high acidities. In the transition region however any positive value of y_c/y_{TBP} is permissible, including ratios

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* It should be noted that the calculation of the activity-coefficient ratio is very sensitive to the C_{TBP}/C_o term at high $a_\pm^2$, since a small difference between two numbers close to unity is involved (in addition f_A has not been considered in the calculation). Hence the estimated ratio is most reliable at small $a_\pm^2$.

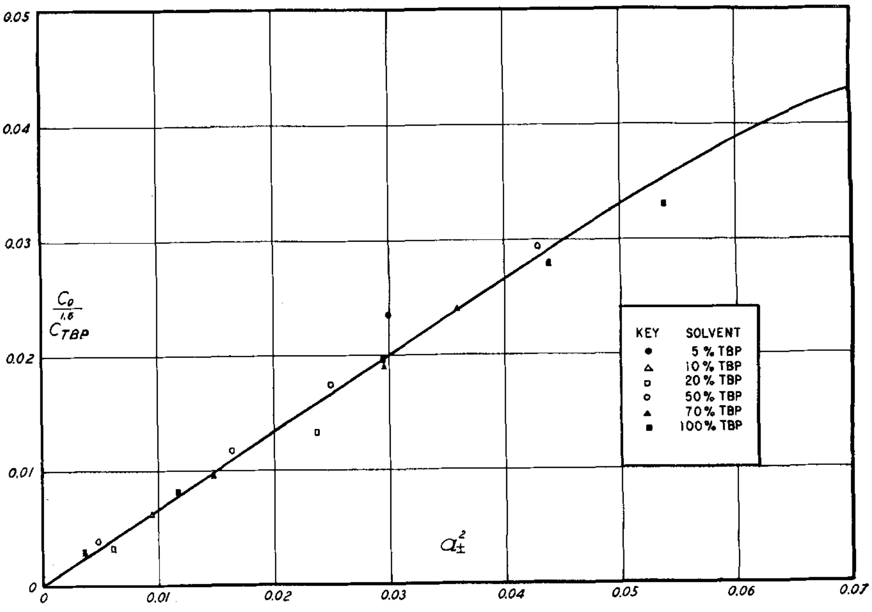

Fig. 6. $C_o/C_{TBP}^{1.6}$ as a function of aqueous-phase activity in the low-acidity region.

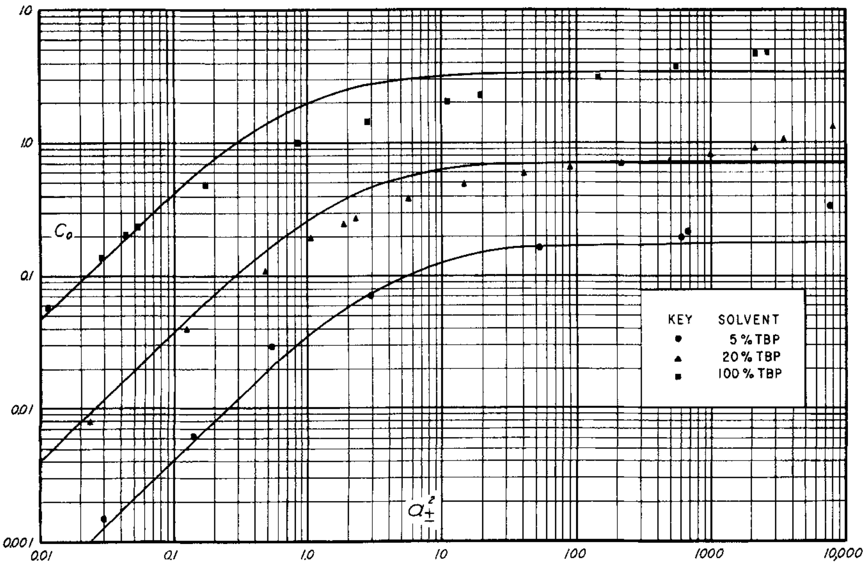

Fig. 7. Comparison of experimental equilibrium data with values calculated from Equation (17).

greater than $(P_c^\circ P^\circ_{TBP})/(k_c k_{TBP})$; the calculated maximum value of 25 could arise for instance from $y_c = 5$ and $y_{TBP} = 0.2$, a not improbable combination in view of Alcock's (*1*) activity coefficient measurements. Thus the magnitude of the discrepancies between the experimental and theoretical curves of Figure 7 can be quite adequately attributed to nonideality of the organic phase rather than to some basic defect in the complexing theory. That the calculated y_c/y_{TBP} unrealistically pass through zero and assume negative values is a direct result of neglecting the existence of uncomplexed nitric acid in the organic phase. At high acidities the presence of a third component destroys the postulated binary nature of the organic phase. Consequently the assumptions underlying Equation (19) and its ramifications are no longer valid.

EFFECT OF VARIABLE WATER CONTENT OF THE ORGANIC PHASE

In the preceding discussion the root of the discrepancies between the semitheoretical and experimental curves of Figure 7 was attributed solely to the nonideal interactions of the tributylphosphate and the complex molecules. The role of the dissolved water was neglected, even though in pure tributylphosphate it accounts for nearly one half of the organic phase (on a mole basis). This omission is of no consequence if it is assumed, as with Glueckauf (*5*), that the complexing reaction merely converts the species tributylphosphate-water to the complex nitric acid-tributylphosphate-water (thereby maintaining constant water concentration). However the data of Alcock (*1*) and Baldwin (*2*) clearly show that the water concentration of the organic phase is far from constant. The drop in water content with increasing acidity cannot be simply attributed to a decrease in the aqueous-phase activity of the water; up to the acidity corresponding to the minimum water content the aqueous activity of water has decreased less than half as much as the organic phase water concentration (or mole fraction).

However the deviations exhibited in Figure 7 begin in approximately the same region in which the water concentration starts to decrease from its value in the acid-free solvent. This observation suggests either that the water content markedly affects the tributylphosphate-complex interactions and consequently their activity coefficient ratio or that the amount of dissolved water partially determines how much uncomplexed nitric acid the organic phase can accept from the aqueous phase. These two possibilities are not directly related; even if tributylphosphate and the complex did not interact, the second effect might alter the value of p in Equation (6) and thus account for the deviations of Figure 7 without requiring that the y_c/y_{TBP} ratio depart from unity. Undoubtedly both of these effects contribute to the over-all behavior of the system, but since there is no way of estimating how the presence of water alters the force fields around tributylphosphate and complex molecules, the following discussion will be restricted to a qualitative description of the second possibility.

It has been assumed that the physical distribution of uncomplexed nitric acid depended solely upon the tributylphosphate content of the organic phase, that is Equation (12). The reason behind this assumption was that the relatively polar nature of tributylphosphate (compared with hexane) created a more favorable environment for simple dissolution of nitric acid. However the polarity of the organic phase is not uniquely determined by the total tributyl phosphate content; the presence of the dissolved water might also augment the physical dissolution of nitric acid.

As the acidity of the organic phase increases, the water content decreases. The rejection of this polar species may reduce the affinity of the organic phase for uncomplexed nitric acid, which in turn would decrease the value of p

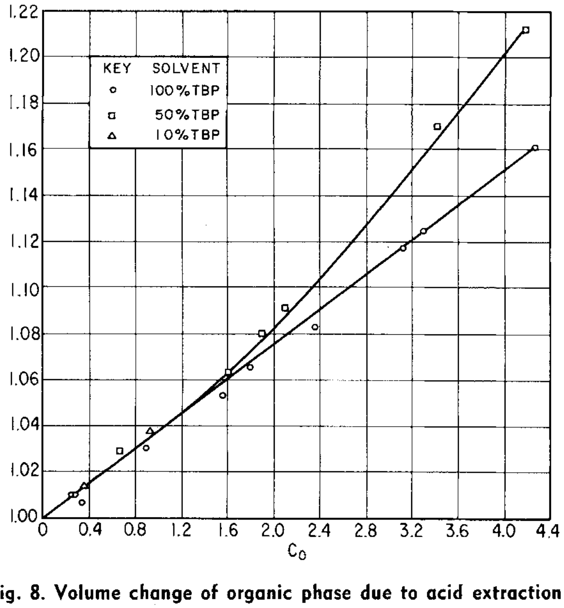

Fig. 8. Volume change of organic phase due to acid extraction into initially water-saturated tributylphosphate-hexane solvents, 25°C.

from that in the low-acidity region. Consequently the omission of this possible effect in the derivation of Equation (17) should and does predict curves which lie above the experimental data.

COMPLEXING OF WATER AND TRIBUTYLPHOSPHATE

Although tributylphosphate dissolves in water only to the extent of 0.0015 molar, saturated solutions of diluent-free tributylphosphate contain practically as much water, on a mole basis, as tributylphosphate. This implies the existence of the complex tributylphosphate-water, an inference which has some support from infrared spectral measurements (*1*). Glueckauf (*5*) cites the observation that the water content of the organic phase is almost independent of the water partial pressure as evidence of a strong water-tributylphosphate interaction.

However in accordance with the data obtained in this work and those of Alcock (*1*) the 1-to-1 mole correspondence of tributylphosphate and water is true only for pure tributylphosphate. From Table 2 it can be seen that as the tributylphosphate content of the solvent decreases, this stoichiometric correspondence vanishes; at saturation not all of the tributylphosphate has been consumed by the supposed complexing reaction.

The water concentration of acid-free tributlyphosphate-hexane solvents can be expressed empirically as

$$C_{H_2O} = 0.4\,C^{1.67}{}_{TBP} \qquad (20)$$

Alcock's (*1*) measurements indicated that the water concentration was proportional to the 1.6 power of the tributylphosphate concentration.

The striking similarity between the form and power dependence of Equations (16) (with $n = 0.6$) and (20) suggests that the water-tributylphosphate complexing reaction might be amenable to the same treatment as the nitric acid system.

However if the derivation which produced Equation (16) is applied to the water-tributylphosphate system, it becomes apparent that the magnitudes of the quantities involved do not permit the desired reduction to be made. Hence it appears that the close similarity of the exponents in the water and nitric acid distribution expressions is coincidental and that water does not form a distinct complex with tributylphosphate.

An additional indication that the mechanisms of nitric acid and water partitioning are not identical is provided by the heats of solution, which have been measured as −3,800 cal./mole and −1,050 cal./mole respectively. Lewis (*9*) reports a heat of solution of −3,620 cal./mole for the extraction of uranyl nitrate into 20% tributylphosphate. Thus although the heat of solution of water is larger in tributylphosphate than in most other organic solvents, it is only one quarter as exothermic as the cases of known complex formation. (The near equality of the heats of solution for uranyl nitrate and nitric acid suggests that the formation of the complex, and not the particular electrolyte involved, controls the energetics.) The water-tributylphosphate system appears to lie in the limits between the physical interaction normally characterized by activity coefficients and the bona fide chemical combination of complex formation.

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NOTATION

$a_\pm$ = mean molal ionic activity of aqueous nitric acid
a_{wA} = molar activity of undissociated nitric acid in the aqueous phase
a_{oA} = molar activity of physically dissolved (uncomplexed) nitric acid in the organic phase
A = nominal volume fraction of tributylphosphate in the water-free solvent
C_c = complex concentration in the organic phase, moles/liter
C_{oA} = concentration of physically dissolved (uncomplexed) nitric acid
C_o = total acid concentration of organic phase, moles/liter
C_{TBP} = total concentration of all tributylphosphate bearing species in the organic phase, equal to the tributylphosphate concentration of the acid-free, water-saturated solvent, moles/liter
C_{TBP_f} = concentration of the free or uncomplexed tributylphosphate in the organic phase, moles/liter
C_{H_2O} = concentration of water in the organic phase, moles/liter
C_{HNO_3} = concentration of nitric acid in the aqueous phase, mole/liter
d = density, g./cc.
f_A = fractional volume change on acid extraction, equal to the volume of the acidified solvent divided by the initial volume of the water-saturated solvent
f_w = fractional volume change on water extraction, equal to the volume of the water-saturated solvent divided by the initial volume of the dry solvent
k_c, k_{TBP} = Henrys law constant for the complex and tributylphosphate respectively, atm./moles/liter
K = mass action constant for the over-all complexing reaction
K_D = thermodynamic dissociation constant of nitric acid
K_R = mass action constant for the organic phase complexing reaction of nitric acid
M = molecular weight
n = power dependence of the distribution coefficient of uncomplexed nitric acid on the total tributylphosphate concentration of the solvent, Equation (12)
p = distribution coefficient of uncomplexed nitric acid, Equation (6)
P = constant in Equation (12)
$P^\circ{}_c, P^\circ{}_{TBP}$ = vapor pressure of complex and tributylphosphate respectively, atm.
y_c = molar-activity coefficient of the complex in the organic phase
y_{TBP} = molar-activity coefficient of the uncomplexed tributylphosphate organic phase

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