

567. *Solvent Extraction Studies. Part II.*¹ *The System Nitric Acid-Water-Tri-n-butyl Phosphate.*

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The extraction of nitric acid from aqueous solution by tri-*n*-butyl phosphate has been investigated. From the volume changes it has been shown that up to $\sim 3.6M$ -acid in the organic phase the extraction is due to the formation of $Bu_3PO_4 \cdot HNO_3$ by addition at the strongly polar $P \rightarrow O$ group. When this donor oxygen is saturated, further addition takes place at the less basic oxygen atom of a $P-O-C$ bond; in this case, the acid is shown to be extracted as $H_2O \cdot HNO_3$. The experimental results are discussed in relation to mass-action equations derived for these two types of equilibrium.

IN Part I¹ it was shown that the species extracted from aqueous nitric acid by an organic solvent could be identified by a quasi-dilatometric method in which changes in the volumes of the two phases were measured. In the work described below, this technique has been used as the starting point for an investigation of the interaction of aqueous nitric acid with the solvent tri-*n*-butyl phosphate. Some of the features of this system have already been discussed by Alcock, Grimley, Healy, Kennedy, and McKay.² The present work has removed some of the anomalies in their treatment and revealed factors not discussed

¹ Part I, Tuck, *J.*, 1957, 3202.

² Alcock, Grimley, Healy, Kennedy, and McKay, *Trans. Faraday Soc.*, 1956, 52, 39.

by them. As these authors emphasise, tri-*n*-butyl phosphate is a good extractant for many inorganic nitrates, and a full understanding of its reactions with nitric acid is essential for a complete interpretation of its behaviour in multicomponent systems.

EXPERIMENTAL

Reagents.—Analytical-grade nitric acid was suitably diluted some time before use; acid concentrations were determined by titration against standard alkali. Aliquot parts of the organic phase were dissolved in an excess of aqueous acetone before titration.

A solution of potassium nitrate was made up from "AnalaR" material.

Commercial tri-*n*-butyl phosphate (100 ml.) was refluxed with 0.5% aqueous sodium hydroxide (500 ml.) for 10 min. and the mixture then distilled in a slow stream of air, to prevent excessive "bumping;" this distillation was continued until about 200 ml. had been collected. The remaining material was washed at least six times with its own volume of water. Excess of water was removed by addition of anhydrous magnesium sulphate and filtration under suction. Infrared spectroscopy showed that the final product contained no dibutyl hydrogen phosphate.

Extraction Measurements.—Determinations of acidity in the organic phase, extraction coefficient, and volume change arising from extraction of nitric acid followed those outlined in Part I. Since tri-*n*-butyl phosphate has a relatively high specific gravity, mixtures of the solvent and weak aqueous solutions of nitric acid took a considerable time to settle after mixing. All solutions were centrifuged to ensure complete separation of the phases before determination of the nitric acid concentration in each. In the present experiments, no detectable change in the total volume of the system occurred as a result of the extraction.

For measurements of the extraction of nitric acid from aqueous nitric acid-potassium nitrate mixtures, equal volumes of the two phases were stirred together for 10 min., then centrifuged.

Infrared Spectra.—The infrared absorption spectra of certain solutions of nitric acid in tri-*n*-butyl phosphate were examined, as liquid films, in a Perkin-Elmer double-beam spectrometer.

Density Measurements.—The density of solutions of nitric acid in the organic phase was determined by weighing, by difference, the amount of solution contained in a graduated micro-pipette (capacity ~0.5 ml.). After being weighed, the solution was quantitatively removed from the pipette and the acid concentration determined as described earlier.

RESULTS AND DISCUSSION

Volume Changes.—Fig. 1 shows the change in volume of the organic phase plotted against the amount of nitric acid extracted. Since it has been shown that tri-*n*-butyl phosphate is essentially insoluble in aqueous nitric acid,² these changes lead directly to the identification of the extracted species.

It should first be noted that the value of ΔV for the transfer of water only (*i.e.*, zero nitric acid concentration) is in good agreement with the postulated formation of a $\text{Bu}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ complex.^{2,3} Five ml. of tri-*n*-butyl phosphate⁴ (d 0.973) contain 18.3 mmoles, so one should find a volume change of 0.329 ml. (18.3 mmoles of water) on saturation; the solubility of tri-*n*-butyl phosphate in water is negligible compared with that of water in the ester. The experimental result ($\Delta V = 0.31$ ml.) is in good agreement with this argument, within the limits of the measurements in this region where, as noted previously, the very similar densities of the two phases cause some difficulty.

It is clear from Fig. 1 that two distinct types of interaction are responsible for the extraction of nitric acid, and that the region in which both can occur simultaneously is small. Extrapolation of the two straight portions of the curve shows that the point of intersection is at 18.7 mmoles of nitric acid extracted, equivalent to the complete formation of a complex $\text{Bu}_3\text{PO}_4 \cdot \text{HNO}_3$. Below this point it is suggested that effectively

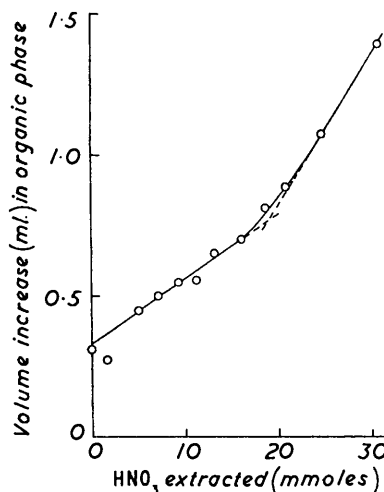
³ Moore, AECD-3196.

⁴ Scheffan and Roberts, "Handbook of Solvents," MacMillan and Co. Ltd., London, 1953, p. 658.

all the tri-*n*-butyl phosphate is present as either $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$ or $\text{Bu}_3\text{PO}_4, \text{HNO}_3$. In terms of the change in volume of the organic phase in relation to increasing extraction of nitric acid, this implies the replacement of water in the organic phase by nitric acid, with an overall volume change of $(41.5 - 18.0)$ ml. per mole of nitric acid extracted. The experimental slope of 0.0237 ml. per mmole is in good agreement. In the region of higher acidity, the slope of the curve is 0.055 ml. per mmole of nitric acid extracted, or 18.2 mmoles per ml. This is almost identical with the value found previously¹ for the extraction of nitric acid into diethylene glycol dibutyl ether, where the extracted species was shown to be $\text{H}_2\text{O}, \text{HNO}_3$.

These results suggest the following scheme for the interaction of tri-*n*-butyl phosphate with aqueous nitric acid. At low acidities, up to about 7M (equilibrium) aqueous nitric

FIG. 1. Volume changes in tri-*n*-butyl phosphate due to the extraction of nitric acid.



acid, the extraction is entirely due to the strongly polar $\text{P} \rightarrow \text{O}$ group, which can form a complex directly with a nitric acid molecule. When all the tri-*n*-butyl phosphate is in the form of $\text{Bu}_3\text{PO}_4, \text{HNO}_3$, further addition takes place on the weakly basic oxygen atom of one of the butoxy-groups. The argument implies that there are no hydrated nitric acid complexes of the type $\text{Bu}_3\text{PO}_4, \text{HNO}_3, \text{H}_2\text{O}$ postulated by McKay and his group. Their results on the water content of tributyl phosphate solutions of nitric acid are in qualitative agreement with the present theory, showing a fall in water content with increasing nitric acid concentration up to an $\text{HNO}_3 : \text{Bu}_3\text{PO}_4$ ratio of about 1, followed by an increase above this value. However, in the low acidity region, they find that the sum of the water and the nitric acid concentration is greater than the available moles of solvent. This may be due to take-up of some water by a butoxy-oxygen atom, although this is difficult to reconcile with the good straight line found in the present work for the volume change.

Partition Data.—The experimental results for nitric acid partitions up to an aqueous phase equilibrium concentration of 14M are given in Table 1. There is a maximum value of E_{HNO_3} at $\sim\text{M}$ -nitric acid (aqueous phase); at higher concentrations the extraction coefficient reaches a fairly constant value of approximately 0.35 . The latter change occurs at $\sim 3.4\text{M}$ -nitric acid in the organic phase, corresponding to saturation of the $\text{P} \rightarrow \text{O}$ group and the beginning of addition at a butoxy-group, as suggested above.

It has been shown² that for dilute (2%) solutions of tri-*n*-butyl phosphate in an inert solvent, the law governing the partition is:

$$[\text{Bu}_3\text{PO}_4, \text{HNO}_3] / [\text{Bu}_3\text{PO}_4(f)] \cdot a_{\text{HNO}_3} = \text{Constant}$$

where a_{HNO_3} is the activity of nitric acid in the equilibrium aqueous phase; $\text{Bu}_3\text{PO}_4(\text{f})$ and $[\text{Bu}_3\text{PO}_4, \text{HNO}_3]$ are the concentrations of uncomplexed ester and of nitric acid in the organic phase. It appears, however, from McKay's paper (ref. 2, fig. 4) that this is far from valid for 100% ester. Further, deviations are appreciable for all concentrations of ester in the organic phase once the HNO_3 : ester ratio exceeds unity; this point will be discussed below. The importance of extraction of water in the low acidity region

TABLE 1. Partition of nitric acid between tri-*n*-butyl phosphate and aqueous solution.

Aqueous phase HNO_3 concn. (M)	Organic phase HNO_3 concn. (M)	E_{HNO_3}	Aqueous phase HNO_3 concn. (M)	Organic phase HNO_3 concn. (M)	E_{HNO_3}
0.098	0.031	0.32	2.41	1.68	0.699
0.150	0.069	0.47	3.21	2.00	0.624
0.270	0.175	0.66	4.12	2.31	0.560
0.41	0.33	0.81	5.75	2.83	0.493
0.535	0.46	0.86	7.49	3.21	0.429
0.765	0.685	0.895	9.69	3.50	0.362
1.10	0.93	0.845	11.55	4.06	0.353
1.70	1.32	0.778	13.73	4.84	0.352

has been emphasised earlier, suggesting that any law governing the system 100% Bu_3PO_4 - HNO_3 - H_2O must take account of this. Two mass-action equations of the type quoted above can be set up for the formation of the $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$ and $\text{Bu}_3\text{PO}_4, \text{HNO}_3$ complexes:

$$K_1 = [\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}] / [\text{Bu}_3\text{PO}_4(\text{f})] \cdot a_{\text{H}_2\text{O}}$$

$$K_2 = [\text{Bu}_3\text{PO}_4, \text{HNO}_3] / [\text{Bu}_3\text{PO}_4(\text{f})] \cdot a_{\text{HNO}_3}$$

Combining these, one should have:

$$[\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}] / [\text{Bu}_3\text{PO}_4, \text{HNO}_3] = K_1 \cdot a_{\text{H}_2\text{O}} / K_2 \cdot a_{\text{HNO}_3} \quad \dots \quad (1)$$

where the activities are again those in the equilibrium aqueous phase. Complex formation in this low-acid region is concerned exclusively with the polar P→O group so that, in testing equation (1), the amount of water has been calculated as:

$$\text{mmoles of H}_2\text{O} = \text{mmoles of ester(p)} - \text{mmoles of HNO}_3(\text{org})$$

where ester(p) implies pure tri-*n*-butyl phosphate (*i.e.*, 18.3 mmoles per 5 ml.). This is based on the volume changes discussed above; it does not exclude presence of additional water in the organic phase, but implies rather that any such water, which must be small in quantity, is not concerned in the extraction mechanism in this concentration region. The results of these simple calculations are given in Table 2, along with the relevant values⁵ of a_{HNO_3} and $a_{\text{H}_2\text{O}}$.

TABLE 2. Water in tri-*n*-butyl phosphate solutions of nitric acid.

HNO_3 , mmoles (expt.)	H_2O , mmoles (by subtraction)	a_{HNO_3}	$a_{\text{H}_2\text{O}}$	HNO_3 , mmoles (expt.)	H_2O , mmoles (by subtraction)	a_{HNO_3}	$a_{\text{H}_2\text{O}}$
0.163	18.1 ₅	0.006	0.997	5.02	13.3	0.685	0.965
0.368	17.9	0.015	0.995	7.13	11.2	1.89	0.943
0.935	17.3 ₅	0.040	0.991	9.32	9.0	4.71	0.914
1.71	16.6	0.091	0.987	11.20	7.1	10.9	0.873
2.46	15.8	0.152	0.983	13.1	5.2	24.5	0.818
3.70	14.6	0.312	0.974	16.1	2.2	76.4	0.710

Equation (1) has been tested against the data in Table 2 by plotting a_{HNO_3} (*i.e.*, $m_{\pm}^2 \gamma_{\pm}^2$) against $a_{\text{H}_2\text{O}} [\text{Bu}_3\text{PO}_4, \text{HNO}_3] / [\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}]$. The resultant curve (Fig. 2) shows that below about 0.4M (aqueous) nitric acid equation (1) is indeed valid. The limiting slope of 1 on this log-log plot is in agreement with the low degrees of dissociation estimated by McKay and his co-workers² on the basis of the semi-empirical relation proposed by Walden,⁶ and with conductivity measurements.⁷

⁵ Data from Landolt-Börnstein's "Tabellen."

⁶ Walden, "Acids, Bases and Salts," McGraw-Hill, New York, 1929, pp. 283 *et seq.*

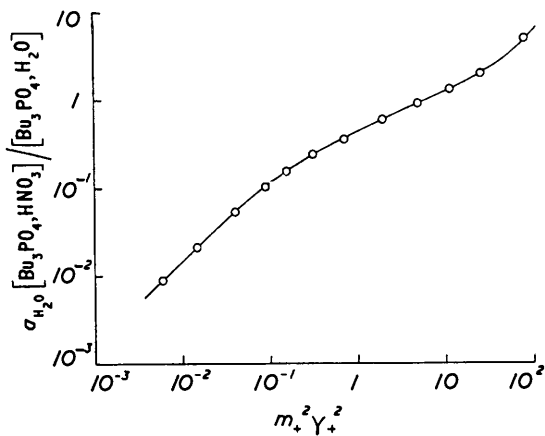
⁷ Healy and McKay, *Trans. Faraday Soc.*, 1956, **52**, 633.

Above this region of linearity one finds lower values of the term

$$a_{\text{H}_2\text{O}}[\text{Bu}_3\text{PO}_4, \text{HNO}_3]/[\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}]$$

than would be predicted from the nitric acid activity in the equilibrium aqueous phase. A tentative explanation is the following. In writing the mass-action equations on which equation (1) is based, it has been assumed that the activity coefficients for the species $\text{Bu}_3\text{PO}_4, \text{HNO}_3$ and $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$ can be neglected. This is probably quite justified for the former in the absence of dissociation, since attractive interactions appear unlikely; this supposition is certainly confirmed for nitric acid species in dibutylcarbitol,¹ and in the high acidity region of the present system, where the results are explained satisfactorily

FIG. 2. Nitric acid extraction into tri-*n*-butyl phosphate as a function of aqueous nitric acid activity.



without the introduction of activity coefficients for the organic phase. For $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$, however, one can envisage the formation of weak association complexes, reducing the activity of the monomeric species. Re-writing equation (1) in the form plotted in Fig. 2, one has

$$a_{\text{H}_2\text{O}}[\text{Bu}_3\text{PO}_4, \text{HNO}_3]/f_1[\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}] = \text{Constant} \times a_{\text{HNO}_3}$$

where f_1 is the activity coefficient for $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$. At sufficiently low nitric acid concentrations in the organic phase, the amount of $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$ is effectively constant and few of the postulated $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$ dimers would be affected by changes in the amount of nitric acid extracted. Under these conditions, f_1 would be constant. With increasing replacement of $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$ by $\text{Bu}_3\text{PO}_4, \text{HNO}_3$, the possibility of dimer formation is reduced and so the activity coefficient of the monomer rises, leading to the type of change observed. For an organic phase such as 2% of ester in kerosene, in which water is essentially insoluble, consideration of the behaviour of water in the organic phase is unnecessary. Under these conditions, equation (1) reduces to the form proposed by McKay *et al.*², which is a limiting case of the more general equation. Organic phases of intermediate composition will behave as the appropriate mean of these two sets of conditions.

Alternatively, or additionally, one might suppose that deviations from ideality are due to attractive interactions between $\text{Bu}_3\text{PO}_4, \text{H}_2\text{O}$ and $\text{Bu}_3\text{PO}_4, \text{HNO}_3$. Again, such interactions would have little effect at low nitric acid concentrations or in systems of negligibly small water content. It is hoped to investigate this problem later.

When the nitric acid concentration in tri-*n*-butyl phosphate is such that the donor activity of the P→O group is approaching saturation, the slope of the curve in Fig. 2 begins to rise and one might believe that the slope is again approaching unity. The situation is complicated, however, at these acidities by the onset of extraction of nitric

acid by addition of a butoxy-group, as shown by the results in Fig. 1, so that it is difficult to ascribe any significance to this change of slope.

Infrared Spectra.—Although the results show that the $\text{Bu}_3\text{PO}_4\cdot\text{HNO}_3$ complex is not dissociated into free ions to any extent, the highly polar nature of tri-*n*-butyl phosphate should produce significant ion-pair formation. The infrared spectra are in agreement with this; the spectrum of a solution of the approximate composition $\text{Bu}_3\text{PO}_4\cdot\text{HNO}_3$ shows absorption bands at 1400 and 810 cm^{-1} , characteristic of ionic organic nitrates.⁸ One also finds a broad band with a maximum at about 2550 cm^{-1} , arising from a hydrogen-bonded $\text{P}\rightarrow\text{O}$ group.⁹ These results suggest that the complex is actually $(\text{BuO})_3\text{P}\rightarrow\text{O}\cdots\text{H}^+\text{NO}_3^-$.

The System Bu_3PO_4 -Aqueous $\text{HNO}_3 + \text{KNO}_3$.—The extraction of nitric acid by tri-*n*-butyl phosphate from aqueous solutions containing both nitric acid and potassium nitrate has been briefly studied. This salt was chosen because of its low solubility in the organic phase.⁷ The results (Table 3) show a marked "salting out"; unfortunately the activity coefficients a_{H^+} , $a_{\text{NO}_3^-}$, and $a_{\text{H}_2\text{O}}$ are not available for mixed solutions of nitric acid and potassium nitrate, so that a complete analysis of the results is not possible.

Density Measurements.—The density of a series of solutions of nitric acid in tri-*n*-butyl phosphate is shown in Fig. 3. The value for zero nitric acid is in fact that for water-saturated tri-*n*-butyl phosphate. For the low-acidity region, Fig. 3 shows a smooth curve,

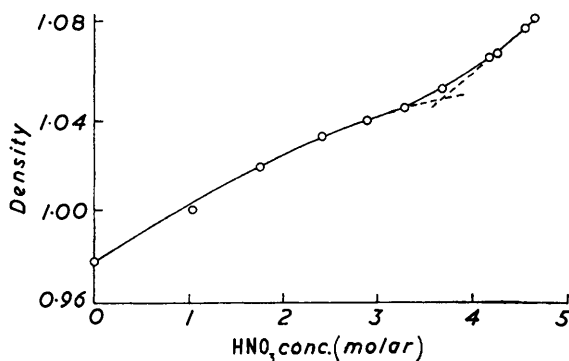


FIG. 3. Density of solutions of nitric acid in tri-*n*-butyl phosphate.

in general agreement with the theory advanced above of non-ideal behaviour. In the high-acidity region, there is a linear increase of density, d , with increasing nitric acid concentration, given by $d = \text{Constant} + 0.034c$, where c is the molar concentration of nitric acid. This slope can be compared with the value 0.0338 found for solutions of nitric acid monohydrate in diethylene glycol dibutyl ether.¹ The point at which the two

TABLE 3. Extraction of nitric acid by tri-*n*-butyl phosphate from aqueous solutions of $\text{HNO}_3 + \text{KNO}_3$.

Original aq. HNO_3 concn. (M)	0.60	0.60	0.60	0.60	0.60
Original aq. KNO_3 concn. (M)	0	0.30	0.45	0.60	1.20
Final organic phase HNO_3 concn. (M) ...	0.274	0.315	0.330	0.342	0.382

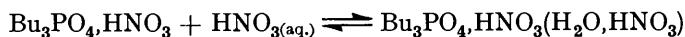
portions of the curve intercept on extension corresponds to a $\text{Bu}_3\text{PO}_4 : \text{HNO}_3$ ratio of unity, equivalent to complete formation of $\text{Bu}_3\text{PO}_4\cdot\text{HNO}_3$.

High-acidity Region.—From the evidence of the volume changes and of the density relation, it is clear that in the high-acidity region one is observing the addition of

⁸ Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London, 1954, p. 255.

⁹ Bellamy, *loc. cit.*, p. 257.

$\text{H}_2\text{O}, \text{HNO}_3$ to the weakly basic oxygen of a butoxy-group. This should then obey the equation



in which case there should be a relation of the type:

$$\frac{[\text{Nitric acid in ester as } \text{H}_2\text{O}, \text{HNO}_3]}{[\text{"Free"} \text{ Bu}_3\text{PO}_4, \text{HNO}_3]} \propto a_{\text{HNO}_3} \quad (2)$$

The total amount of nitric acid present in the organic phase as $\text{H}_2\text{O}, \text{HNO}_3$ is given by (total $\text{HNO}_3 - 18.3$) and that of "free" $\text{Bu}_3\text{PO}_4, \text{HNO}_3$ by $[18.3 - (\text{H}_2\text{O}, \text{HNO}_3)]$. A rough quantitative test of equation (2) has been made by using the two results at highest nitric concentration (Table 1); Fig. 1 shows that only at these concentrations is the species extracted uniquely $\text{H}_2\text{O}, \text{HNO}_3$.

TABLE 4. Extraction of nitric acid by $\text{Bu}_3\text{PO}_4, \text{HNO}_3$.

Total HNO_3 in ester phase (mmoles)	HNO_3 as $\text{H}_2\text{O}, \text{HNO}_3$ (mmoles)	"Free" $\text{Bu}_3\text{PO}_4, \text{HNO}_3$ (mmoles)	Ratio	HNO_3 concn., aq. phase (M)	$m_{\pm}^2 \gamma_{\pm}^2$
24.8	6.5	11.8	0.55	11.55	1430
30.9	12.6	5.7	2.21	13.73	3550

These values agree with the writing of equation (2) as

$$\left[\frac{[\text{Nitric acid in ester as } \text{H}_2\text{O}, \text{HNO}_3]}{[\text{"Free"} \text{ Bu}_3\text{PO}_4, \text{HNO}_3]} \right] = 8.0 \times 10^{-4} (m_{\pm}^2 \gamma_{\pm}^2 - 700)$$

where the term in the square bracket is the mole ratio. The value of 700 found for the constant by graphical extrapolation is the value of $m_{\pm}^2 \gamma_{\pm}^2$ for zero extraction of nitric acid as $\text{H}_2\text{O}, \text{HNO}_3$; this corresponds to an equilibrium aqueous phase of 9.9M-nitric acid, which would be in equilibrium with an organic phase of 3.5M-nitric acid. This is again in agreement with the scheme proposed above, according to which addition of $\text{H}_2\text{O}, \text{HNO}_3$ does not begin until the $\text{Bu}_3\text{PO}_4, \text{HNO}_3$ complex is completely formed. The exactness of this agreement is perhaps fortuitous, since there is some uncertainty in the interpolation of the activities in this concentration region.

There remains the difference in the interaction of nitric acid with the two different donor groups of tri-*n*-butyl phosphate. It appears that the strong polarity of the $\text{P} \rightarrow \text{O}$ bond allows this oxygen atom to solvate a hydrogen ion (or atom) directly, but that the less basic ester-oxygen is unable to do this and so can only form a hydrogen bond with (effectively) H_3O^+ . Another interesting consequence of the strongly basic nature of the $\text{P} \rightarrow \text{O}$ bond is that tri-*n*-butyl phosphate extracts hydrochloric acid from aqueous solution, whereas ethereal or ketonic solvents extract this acid only slightly.¹⁰

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¹⁰ Tuck, unpublished results.