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Acid-Base Equilibria in Tertiary Butyl Alcohol*

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ABSTRACT

The dissociation of acids in tertiary butyl alcohol has been studied by potentiometric, spectrophotometric, and conductimetric methods. Values for the over-all dissociation of perchloric and picric acids and several tetrabutylammonium salts were estimated by the Fuoss-Kraus treatment of conductance data. Potentiometric studies were carried out at constant ionic strength in order to minimize activity coefficient variations. An acidity scale was established from potentiometric measurements at a glass electrode, and conductance values of dissociation constants. A method was developed for the evaluation of the over-all dissociation constant of weak acids using potentiometric data for hydrogen ion activities and conductance data for the corresponding anion activities. Over-all dissociation constants are reported for perchloric acid, picric acid, 2,4-dinitrophenol, and benzoic acid. Apparent dissociation constants from potentiometric measurements at a constant ionic strength were determined for hydrobromic, nitric, hydrochloric, picric, and p-toluenesulfonic acids.

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Tertiary butyl alcohol has been shown to be a very useful solvent for the titration of weak acids with tetrabutylammonium hydroxide (14). This solvent is especially useful for differentiating titrations involving carboxylic acids and phenols because of the flat slope in the buffer region of the titration curve. In solvents such as acetone, acetonitrile, and pyridine, the titration curves have a steep slope in the buffered region, owing to the intermolecular association of the acid anion with the free acid (4,10,16,17). Evidently, this association is not appreciable in tertiary butyl alcohol.

Because of its excellent solvent characteristics, fundamental information on acid-base equilibria would be very useful. Taking into account previous investigations of acid-base equilibria in alcoholic solvents (1,2,11,12,13,15) and solvents of low dielectric constant (9,6), we felt that the main reactions involved in the dissociation of an acid HX are: $\text{HX} \rightleftharpoons \text{H}^+\text{X}^-$ (ion-pair formation); $\text{H}^+\text{X}^- \rightleftharpoons \text{H}^+ + \text{X}^-$ (ion-pair dissociation). The corresponding equilibrium constants are: $K_1 = (\text{H}^+\text{X}^-)/(\text{HX})$; $K_d = (\text{H}^+)(\text{X}^-)/(\text{H}^+\text{X}^-)$. Ion-pair formation in tertiary butyl alcohol is undoubtedly significant (6), but probably not extensive. The over-all dissociation of strong electrolytes in dilute solutions (10^{-3}M to 10^{-5}M) was expected to be large on the basis of titration data.

Since it is convenient to interpret potentiometric data in terms of the over-all dissociation of a species, we adopted the use of the over-all constant for our work. This constant is defined (8) for an acid as $K_{HX} = (H^+)(X^-)/(HX) + (H^+X^-)$. In the case of very low dissociation of the solute, $(HX) + (H^+X^-)$ will be very nearly equal to C_{HX} (C_{HX} is the analytical concentration of solute).

The plan of research was to determine K_{HX} for various acids in tertiary butyl alcohol by potentiometric, spectrophotometric, or conductometric methods. We were able to apply the method of Fuoss and Kraus (5) in the determination of dissociation constants from conductance data. Unfortunately, conductance measurements for solutions of weak acids could not be obtained because the solutions were not sufficiently conductive.

Potentiometric measurement was at first believed to be the best method for evaluation of dissociation constants of weak acids. However, K_{HX} values varied with C_{HX} unless a fairly high ($10^{-2}M$) concentration of tetrabutylammonium perchlorate (Bu_4NClO_4) was added to keep the ionic strength constant. This was an indication that the activity coefficients of the ionic species are markedly dependent upon the ionic strength. Subsequent analysis of conductance data did show that activity coefficients varied even at very low ($10^{-5}M$) concentrations of solute.

While the addition of a large amount of Bu_4NClO_4 does keep the activity coefficients constant during the potentiometric measurement of acidity of a weak acid, it complicates the simple equilibrium of HX as shown below:

(For simplicity, ion-pair forms of solutes will be omitted from all subsequent discussion.) A modified constant, K'_{HX} , can be applied to this equilibrium, $K'_{\text{HX}} = \{ [\text{H}^+] + (\text{HClO}_4) \} \{ [\text{X}^-] + (\text{Bu}_4\text{NX}) \} / (\text{HX})$. Here, $[\text{H}^+]$ is the actual concentration of hydrogen ions in solution (and not the activity). For a solution of HX in excess Bu_4NClO_4 , the expression for K'_{HX} becomes $K'_{\text{HX}} = \{ [\text{H}^+] + (\text{HClO}_4) \}^2 / (\text{HX})$. Values of the quantity $\{ [\text{H}^+] + (\text{HClO}_4) \}$ are determined by reference to the concentration-EMF curve for perchloric acid. K'_{HX} may also be evaluated from spectral measurements of the quantity $\{ [\text{X}^-] + (\text{Bu}_4\text{NX}) \}$.

Another expression for the over-all constant K_{HX} can be obtained by substitution of the equations,

$$[\text{H}^+] = \{ [\text{H}^+] + (\text{HClO}_4) \} K_{\text{HClO}_4} / \{ K_{\text{HClO}_4} + (f_{\text{H}^+})(\text{ClO}_4^-) \}$$

$$[\text{X}^-] = \{ [\text{X}^-] + (\text{Bu}_4\text{NX}) \} K_{\text{Bu}_4\text{NX}} / \{ K_{\text{Bu}_4\text{NX}} + (f_{\text{X}^-})(\text{Bu}_4\text{N}^+) \}$$

which hold when the amount of added tetrabutylammonium perchlorate is large compared to the amount of acid present. The resulting expression for the over-all dissociation constant,

$$K_{\text{HX}} = \frac{\{ [\text{H}^+] + (\text{HClO}_4) \} \{ [\text{X}^-] + (\text{Bu}_4\text{NX}) \}}{(\text{HX})} \cdot \frac{K_{\text{HClO}_4} K_{\text{Bu}_4\text{NX}} (f_{\text{H}^+})(f_{\text{X}^-})}{\{ K_{\text{HClO}_4} + (f_{\text{H}^+})(\text{ClO}_4^-) \} \{ K_{\text{Bu}_4\text{NX}} + (f_{\text{X}^-})(\text{Bu}_4\text{N}^+) \}}$$

may be separated into two parts, K'_{HX} and K''_{HX} . The K'_{HX} part is the same as given previously. The other part

$$K''_{HX} = K_{HClO_4} K_{Bu_4NX} (f_{\pm} H^+) (f_{\pm} X^-) / \{ K_{HClO_4} + (f_{\pm} H^+) (ClO_4^-) \} \{ K_{Bu_4NX} + (f_{\pm} X^-) (Bu_4N^+) \}$$

contains constants or constant terms only. In order to calculate the over-all constant from potentiometric measurements, it is necessary then to know, or have estimates of, $K_{Bu_4NClO_4}$, K_{HClO_4} , K_{Bu_4NX} , and the activity coefficients of H^+ and X^- .

In the work reported, values for K'_{HX} for a number of normally strong acids, and values for the over-all constant for picric acid and 2,4-dinitrophenol were determined by a combination of conductance and potentiometric measurements. The constant, K'_{HX} , for picric acid was determined by spectrophotometric measurements and compared to the value obtained by potentiometric measurements.

EXPERIMENTAL

Solutions of perchloric, nitric, hydrochloric, hydrobromic, and sulfuric acids were prepared from commercially available concentrated aqueous solutions. All other acid solutions were prepared from Eastman White Label grade materials. All tetrabutylammonium salts except the perchlorate, bromide, and iodide were prepared from carbonate free tetrabutylammonium hydroxide. Tetrabutylammonium picrate, 2,4-dinitrophenolate and perchlorate were recrystallized from water-methanol solutions. Water was removed from the dinitrophenolate by azeotropic distillation with benzene. The picrate and perchlorate salts were dried at room temperature. Water was evaporated from the benzoate salt at a pressure of 2-3 mm. Hg until the solution crystallized. The bromide (Southwestern Analytical

Chemicals) and iodide salts (Rymark Laboratories) were used without further purification or drying.

The potential variation with acid concentration for "strong" acids was obtained in the following way: the solid or liquid sample was added to 50.0 ml. of 0.00974M Bu_4NClO_4 in tertiary butyl alcohol in the cell compartment. (Details of the reference electrode and salt bridge system are given in a previous paper (14).) After 20 to 30 minutes stirring, a potential measurement was made. Exactly 25 ml. of solution was withdrawn, and 25 ml. fresh 0.00974M Bu_4NClO_4 was added. After 10 to 15 minutes equilibration, the potential was measured again. In most cases, the experiments were performed at room temperature. The dilution process was continued until the acid concentration was approx. 10^{-6} M. Normally, equilibration for 5 to 10 minutes was sufficient to obtain a constant potential reading after a dilution was made. Potential drift did occur upon prolonged equilibration in some cases, but it was on the order of 2 to 3 mv. over a period of several hours.

Tetrabutylammonium iodide, bromide, or perchlorate was used to maintain constant ionic strength in the experiments involving weak acids. The solubility of the bromide salt is greater than that of the other salts, and thus it is the best to use at the higher ionic strengths. The procedure used for the measurement of the acidity of the weak acids was the same as that used for the strong acids, except in the cases where actual titrations were performed.

Conductance measurements were made with an Industrial Instruments Inc. Conductivity Bridge Model RC 16 B2 at 1000 cycles. The electrodes were

platinum black and approximately 1 cm.^2 in area. A cell constant of 0.104 was determined from the conductance of a 0.0100 M KCl solution. The temperature during the measurements was held constant to within 0.2°C . Dilutions were made by removing 50.0 ml. from exactly 75.0 ml. of solution, and replacing the amount taken out with pure tertiary butyl alcohol.

A Cary Model 14 was used for the spectral analysis of picric acid. Solutions of tetrabutylammonium perchlorate were used for reference samples. Silica cells were used throughout.

Conductance of Solutes in Tertiary Butyl Alcohol. Although the dielectric constant of tertiary butyl alcohol is relatively low (11.5 at 26°C.) we assumed that the Fuoss-Kraus (5) method for the determination of dissociation constants would be applicable. Conductance measurements were obtained for solutions of perchloric and picric acids, and several tetrabutylammonium salts.

Preliminary values of the equivalent conductances at infinite dilution were obtained by extrapolation of the λ_0 vs. $C^{\frac{1}{2}}$ curves. Values of α , $(= 8.18 \times 10^5 \lambda_0 / (DT)^{\frac{3}{2}} + 82 / \eta (DT)^{\frac{1}{2}})$, β , $(= \frac{0.4343e^2}{2DkT} (8 Ne^2 / 1000DkT)^{\frac{1}{2}})$, and δ , $(= (8 Ne^2 / 1000DkT)^{\frac{1}{2}} a)$ were calculated using a dielectric constant of 11.5 and a viscosity of 0.0425 poise. The ionic radius, a , used in the calculation of the δ correction terms was calculated from the Stokes-Einstein equation using one half the equivalent conductance at infinite dilution for the equivalent conductance of an ion.

Plots of $fC^{\frac{1}{2}}$ vs. $X^{\frac{1}{2}}$, where $X = (1 - \gamma) / \gamma^2$, were linear in every case when the concentration of the solutions was in the range of 5×10^{-3} to $5 \times 10^{-5} \text{ M}$. A summary of the final values for the equivalent conductance

at infinite dilution that give lines that intercept the origin is given in Table I. Equilibrium constants evaluated from the slope of the $\frac{1}{\kappa c^2}$ vs. $\frac{1}{X^2}$ plots are also given in Table I.

Qualitatively, the dissociation constants are in the order of magnitude expected. The fact that perchloric acid is a stronger acid than picric is in agreement with the behavior of these acids in other non-aqueous systems. We speculated that for the tetrabutylammonium salts the greater the charge distribution of the anion formed by dissociation, the greater would be the extent of dissociation. The data presented in Table I seem to bear out the validity of this speculation.

Table I. Constants for Conductance Curves
for Solutes in Tertiary Butyl Alcohol

Solute	λ_o	T°C.	β	α	σ	K_{HX}
HClO ₄	22	26.4	9.62	122	1.48	1.14×10^{-4}
R ₄ NPi	8	26.5	9.62	65.5	4.08	1.00×10^{-4}
R ₄ NDNP	10	26.0	9.62	74	3.26	8.26×10^{-5}
R ₄ NBz	8	26.0	9.62	65.5	4.08	9.86×10^{-6}
HPi	13	26.6	9.62	86	2.50	8.73×10^{-6}
R ₄ NClO ₄	17	25.2	9.70	102	1.92	5.70×10^{-6}
R ₄ NBr	17	26.0	9.62	102	1.92	4.34×10^{-6}

Activity coefficients were estimated from plots of $fC^{\frac{1}{2}}$ vs. $C^{\frac{1}{2}}$, which were constructed from conductance data. Since we were interested in activity coefficients of species in the presence of a large amount of tetrabutylammonium perchlorate, we evaluated the activity coefficients at $C^{\frac{1}{2}} = (Bu_4NClO_4)^{\frac{1}{2}}$. The error involved in this method should not be too large owing to the similarity of the degree of dissociation of most of the solutes.

Potentiometric Determination of Dissociation Constants. The dissociation of perchloric acids was studied first because it was the strongest of the acids available for examination. Potentials at the glass electrode were obtained as a function of $HClO_4$ content at a constant concentration of Bu_4NClO_4 . The water content, 0.025%, of the solutions was constant at the amount of water in the solvent.

Figure 1 shows the plot of $\log(HClO_4)$ vs. EMF. As was expected, the curve showed a linear portion at the very low concentrations of acid. Although the slope of the linear portion of the curve is 60 mv., no inference can be made on the extent of dissociation of $HClO_4$ owing to the presence of the large concentration of Bu_4NClO_4 .

The amount of undissociated $HClO_4$ in solutions can be evaluated from the dissociation constants of $HClO_4$ and Bu_4NClO_4 . Thus, we calculate that the ratio $(H^+)/ (HClO_4) = K_{HClO_4} / (ClO_4^-)$ is only 0.484. Using $f_{\pm} H^+ = 0.416$ evaluated at $C^{\frac{1}{2}} = 0.00974M$, the calculated H^+ activity is equal to $0.224 C_{HClO_4}$. This activity, combined with the potential for a $10^{-4}M HClO_4$ solution leads to a value of +0.610 volt vs. the SCE reference for the standard H_2/H^+ potential. This value is used in subsequent calculations of H^+ activity since the same electrode was used throughout this study.

The dissociation of p-toluenesulfonic, hydrobromic, nitric, hydrochloric, and picric acids was also studied in perchlorate media. The

potential measurements as a function of acid content are shown in Figure 1. In each case, there is a greater curvature to the line at the higher concentration of acid, than for HClO_4 . The curvature is due mainly to the incomplete dissociation of the acids. Assuming that the change in acid concentration from 10^{-3}M to 10^{-4}M has little effect on the dissociation of the acid by virtue of changes of activity coefficients (this becomes valid as the strength of the acid decreases,) and the junction potentials are constant, one can use the potentiometric data to calculate constants of the type K'_{HX} . Here, $([\text{H}^+] + (\text{HClO}_4))$ is evaluated by reference to the experimentally determined Concentration-EMF curve (Curve A¹, Figure 1) for perchloric acid. A summary of the values obtained for these constants is given in Table II.

Table II. Dissociation Constants K'_{HX} of Acids from Potentiometric Measurements. 0.00974M Bu_4NClO_4 in Tertiary Butyl Alcohol Solvent

Acid	$-\log K'_{\text{HX}}$
Hydrobromic	3.7
Picric	3.65
p-Toluenesulfonic	3.81
Hydrochloric	5.0
Nitric	5.1

A test of the validity of the expression for K'_{HX} was made by calculating the ratio $([\text{H}^+] + (\text{HClO}_4))^2 / (\text{HCl})$ at several concentrations of HCl . Values of this ratio are given in Table III. The constants so calculated

are reasonably constant and do not show any distinct trend. We ascribe what variation there is to the difficulty of making potential measurements more accurate than $\pm 2 - 3$ mv.

Table III. Dissociation Constants K'_{HX} for Hydrochloric Acid at Various Concentrations of Acid. $0.00974M$ Bu_4NClO_4 in Tertiary Butyl Alcohol Solvent

conc. HCl	$\{ [H^+] + HClO_4 \}$	K'_{HCl}
$1.0 \times 10^{-5}M$	$6.1 \times 10^{-6}M$	9.5×10^{-6}
5.0×10^{-5}	1.8×10^{-5}	1.0×10^{-5}
1.0×10^{-4}	2.8×10^{-5}	1.1×10^{-5}
5.0×10^{-4}	6.8×10^{-5}	1.1×10^{-5}

The constants of the type K'_{HX} may also be obtained from spectral measurements. For purposes of comparison, the spectral value of K'_{HPi} was obtained from absorption spectra of picric acid in $0.00974M$ Bu_4NClO_4 . The quantity $([Pi^-] + (Bu_4N Pi))$, where Pi^- is the picrate ion concentration, was calculated from the absorption at $425 m\mu$. The spectrum of pure picrate was obtained by the addition of a slight excess of Bu_4NOH . Picric acid absorption is very slight at this wavelength. The value obtained, 2.16×10^{-4} , is remarkably close to the EMF value of 2.22×10^{-4} . The agreement is particularly good in view of the 5-10% uncertainty of both values.

The over-all dissociation constant for picric acid was estimated by calculation of the constant K''_{HPi} . Mean-ion activity coefficients for

hydrogen ion and picrate ion were obtained from conductance measurements of perchloric acid and Bu_4NPI solutions. Using the values $K_{\text{Bu}_4\text{NPI}} = 1.00 \times 10^{-4}$, $K_{\text{HClO}_4} = 1.14 \times 10^{-4}$ and $K_{\text{Bu}_4\text{NClO}_4} = 5.70 \times 10^{-6}$ gives $K_{\text{HPi}}'' = 5.0 \times 10^{-2}$. Thus, the over-all constant K_{HPi} is 1.1×10^{-5} . This is in good agreement with the conductance value of 8.73×10^{-6} , considering the number of factors involved in the calculation.

If it is assumed that the activity coefficients of ClO_4^- and Bu_4N^+ are constant with small changes in ionic strength, then the change in K_{HPi}' should be calculable from the change in K_{HPi}'' . Comparison of the calculated and observed changes in K_{HPi}'' was made in two ways. In one, perchloric acid was added to picric acid in $9.74 \times 10^{-3}\text{M}$ Bu_4NClO_4 and the picrate absorption at 425 μ used to calculate K_{HPi}'' . In the second, the Bu_4NClO_4 content was changed from 2 to $9.74 \times 10^{-3}\text{M}$.

In the first case, the predicted change of K_{HPi}'' for a change in HClO_4 concentration from zero to $5.85 \times 10^{-4}\text{M}$ is a 1% increase. Verification of this increase was impossible, since the experimental error was much larger. It was interesting to note, however, that the constants K_{HPi}' given in Table IV decrease rather than increase with added HClO_4 . One explanation that accounts for part of this discrepancy is that the spectrum of the picrate shifts to shorter wavelengths with an increase in HClO_4 concentration. It is evident that the absorption at 425 μ must also decrease with added HClO_4 . Unfortunately, any correction for the spectral shift would be very uncertain.

Better results were obtained for the effect of Bu_4NClO_4 on the constant K_{HPi}' . In this case, there was no evidence of a spectral shift

as the amount of perchlorate was varied. The calculated ratio $K' (0.00974M) / K' (0.00200M)$ was 2.75. The observed ratio of the constants was 2.71. Thus, it appears that the expression for K'_{HX} is fairly accurate in predicting changes in acidity with electrolyte concentration.

Table IV. Dissociation Constants K'_{HX} for Picric Acid from Spectral Measurements as a Function of Perchloric Acid and Tetrabutylammonium Perchlorate Content. Tertiary Butyl Alcohol

Solvent			
$2.0 \times 10^{-3} M Bu_4NClO_4$		$9.74 \times 10^{-3} M Bu_4NClO_4$	
conc. $HClO_4$ * moles/liter	K'_{HPi}	conc. $HClO_4$ * moles/liter	K'_{HPi}
0.00	7.95×10^{-5}	0.00	2.16×10^{-4}
1.17×10^{-5}	8.00×10^{-5}	1.17×10^{-4}	1.92×10^{-4}
1.17×10^{-4}	6.6×10^{-5}	5.85×10^{-4}	1.72×10^{-4}

* Concentration of picric acid is $3.7 \times 10^{-5} M$.

The use of potential measurements as a method for determination of dissociation constants of acids considerably weaker than the mineral acids was examined. The measurement of potentials of acid solutions in perchlorate media is, in general, unsatisfactory as a result of the unbuffered nature of the solutions. Thus, most measurements were made in the presence of the tetrabutylammonium salt of the acid.

The acidity of 2,4-dinitrophenol in perchlorate media is shown in Figure 2. Curve A for the acid alone in perchlorate solutions shows that

the acidity is dependent upon the square root of the dinitrophenol concentration. Since this acid is somewhat weaker than nitric acid, a slope of 30 mv. over the accessible concentration range was expected. Calculation of the over-all dissociation constant from the data in Curve A by the same method used for picric acid gave a value of $10^{-10.85}$.

Curve C, Figure 2, shows the results of the measurement of the acidity of 2,4-dinitrophenol solutions in a constant amount ($10^{-3}M$) of tetrabutylammonium 2,4-dinitrophenolate. Here, the acidity varies directly with the dinitrophenol concentration since the dinitrophenolate salt provides a large concentration of dinitrophenolate ion compared to the amount furnished by ionization of dinitrophenol. Calculation of the over-all dissociation constant from the measured activity of hydrogen ion and the calculated activity of dinitrophenolate ion (from conductance measurements) gives a value of $10^{-10.68}$.

The influence of Bu_4NClO_4 on the acidity of 2,4-dinitrophenol solutions containing some dinitrophenolate salt is illustrated by comparison of Curves B and C, Figure 2. The increase in acidity with added Bu_4NClO_4 is a result of the decrease in dinitrophenolate ion activity (common ion effect). This comparison is interesting in that it illustrates the effect that would be observed for the titration of 2,4-dinitrophenol in a mixture containing a stronger acid.

Figure 3 shows the potential variations for benzoic acid in perchlorate and bromide media containing some benzoate salt. The acidity of benzoic acid solutions in the presence of a constant amount of benzoate salt is proportional to the benzoic acid concentration. This same result

was obtained for 2,4-dinitrophenol, and for several other acids of strength comparable to benzoic acid. Here also, the acidity of a benzoic acid solution increases upon the addition of tetrabutylammonium perchlorate, Curves B and C, and varies linearly with acid concentration in the presence of tetrabutylammonium benzoate.

Over-all dissociation constants for benzoic acid were calculated from measured hydrogen ion activities and estimated values for the benzoate ion activity in the various mixtures. A summary of the results is given in Table V. Benzoate ion activities in mixtures containing perchlorate or bromide salts were calculated by setting

$Bu_4N^+ = \{ (Bu_4NBz) K_{Bu_4NBz} + (Bu_4NClO_4) K_{Bu_4NClO_4} \}^{\frac{1}{2}}$, and substituting this value of Bu_4N^+ into the expression for the dissociation constant of Bu_4NBz . Correction for the decrease in (Bu_4NBz) by ionization was made by subtraction of $(a_{Bz^-})/f_{+Bz^-}$ from (Bu_4NBz) . Here, as before, the mean-ion activity coefficient, (0.64), was estimated from conductance measurements.

The variation of potential with benzoate concentration, Curve D, Figure 3, shows that a 10-fold decrease in acidity is obtained for a 10-fold increase in benzoate salt concentration. This result is obtained because the ratio of $(Bz^-)/(Bu_4NBz)$ is constant, and thus a 10-fold dilution results in a 10-fold lowering of (Bz^-) .

Studies with 2,4-dinitrophenol and benzoic acid showed that the glass electrode can be relied on to give good estimates of the hydrogen ion activity as low as 10^{-13} M. At hydrogen ion activities below this level, there are two factors that must be taken into account in order to interpret potential measurements. One is that the solutions must be free of

potassium and sodium salts. The other, which is more difficult to avoid, is that the solutions must be free of carbonate impurities. Unfortunately, it becomes increasingly difficult to prepare tetrabutylammonium salts that are free of carbonate as the strength of the acid decreases.

Table V. Over-all Dissociation Constants of
Benzoic Acid in Tertiary Butyl
Alcohol Solvent

Solution comp.	$-\log K_{\text{HBz}}$
$1.0 \times 10^{-3} \text{ M Bu}_4\text{NBz}$	15.11
$1.0 \times 10^{-3} \text{ M Bu}_4\text{NBz} +$ $9.74 \times 10^{-3} \text{ M Bu}_4\text{NClO}_4$	14.97
$1.0 \times 10^{-3} \text{ M Bu}_4\text{NBz} +$ $9.74 \times 10^{-3} \text{ M Bu}_4\text{NBr}$	15.02

An attempt was made to minimize these problems by making potential measurements during a titration of a weak acid in the presence of a large amount of tetrabutylammonium bromide or iodide. The amount of water formed in the titration should have an insignificant effect on potentials since it is small compared to the amount in the solvent (as long as the acid concentration is less than 10^{-2} M).

Acidities of acid solutions ranging in concentration from $5 \times 10^{-5} \text{ M}$ to $5 \times 10^{-3} \text{ M}$ were studied for p-nitrophenol, o-nitrophenol (in 0.10M bromide media), and phenol (in 0.10M iodide media). Plots of the $\log(\text{acid}/\text{salt})$ ratio as a function of potential for these acids gave straight

lines with slopes of 59 mv. for the ortho and para-nitrophenols, and 66 mv. for phenol. The plot for o-nitrophenol is shown in Figure 4. These results indicate that a constant amount of tetrabutylammonium salt, the principal equilibria that are involved in the dissociation of an acid and its salt lead to the same titration characteristics that are found for a weak acid in aqueous systems. The main difference between tertiary butyl alcohol and water is that in the alcohol solvent, the salts formed in titrations are not highly dissociated. Thus, a common ion effect (Bu_4N^+) is observed in tertiary butyl alcohol, where it is rarely observed in aqueous systems.

The dissociation constants of phenol, ortho- and para-nitrophenols were not evaluated because of the uncertainty in the constancy of the junction potential when the sample solution is changed from 0.00974M Bu_4NClO_4 to 0.10M Bu_4NBr or Bu_4NI . Also, the dissociation constants of the tetrabutylammonium salts of these acids need to be known, and these salts have not been prepared at the present time.

DISCUSSION

Several items of practical interest result from the consideration of the equilibria above. For one, it is evident that the titration curve for a weak acid depends upon the ionic strength of the solution. Thus, the curve for a weak acid will be displaced when it is titrated in a mixture containing a very strong acid such as perchloric or hydrobromic. We have observed (3) that the displacement is not appreciably large when the amount of strong acid is small compared to the amount of weak acid. However, when the amount of strong acid is greater than about 10 times the amount of weak acid, a displacement of the weak acid can be substantial.

It is of interest to speculate on the effect of added Bu_4NClO_4 on the difference in acidity between solution of an acid HX and salt Bu_4NX , and a solution of a salt Bu_4NX and a base Bu_4NOH . These two situations exist in the region of the endpoint of a titration. The potential difference in these two cases, or the potential jump, would increase if the product $K_{\text{Bu}_4\text{NOH}}(\text{Bu}_4\text{NOH}) \approx K_{\text{Bu}_4\text{NClO}_4}(\text{Bu}_4\text{NClO}_4) \gg K_{\text{Bu}_4\text{NX}}(\text{Bu}_4\text{NX})$. Assuming that the potential jump in the interval $\pm 2\%$ of the endpoint is taken as the criterion of the potential break, then a ratio of $K_{\text{Bu}_4\text{NOH}}/K_{\text{Bu}_4\text{NX}} = 50$ would be necessary to observe an increase in the potential break. On the basis of the constants found for the tetrabutylammonium salts used in this study, it seems unlikely that a ratio of 50 would ever be obtained, except for some specific case where there was unusually strong ion-pair formation.

It is possible that a more favorable ratio of $K_{\text{OH}^-}/K_{\text{X}^-}$ (where K_{OH^-} is the dissociation constant of the hydroxide species) could be obtained by the use of another quaternary ammonium base titrant. Harlow (7) has shown that trimethylbutylammonium hydroxide gives better titration curves for weak anionic acids in isopropanol than does tetrabutylammonium hydroxide. The reason for this is presumed to be due to stronger ion-pair formation of the titrant cation with the acid anion. Thus, the use of Me_3BuNOH suggests itself as a good titrant for the determination of very weak acids in tertiary butyl alcohol.

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FIGURE CAPTIONS

Figure 1. Acidity of strong acids in tertiary butanol. Ionic strength maintained by addition of 0.00974M tetrabutylammonium perchlorate.

- A. Perchloric acid
- B. Picric acid
- C. Hydrobromic acid
- D. Para-toluenesulfonic acid
- E. Hydrochloric acid
- F. Nitric acid

Figure 2. Acidity of 2,4-dinitrophenol in tertiary butanol.

- A. 2,4-Dinitrophenol, no added phenolate salt
0.00974M Bu_4NClO_4
- B. 2,4-Dinitrophenol, 0.00100M $\text{Bu}_4\text{N}-2, 4-\text{NO}_2$ Phen.
0.00974M Bu_4NClO_4
- C. 2,4-Dinitrophenol, 0.00100M $\text{Bu}_4\text{N}-2, 4-\text{NO}_2$ Phen.

Figure 3. Acidity of benzoic acid in tertiary butanol. Ionic strength maintained by addition of tetrabutylammonium bromide in B, and by tetrabutylammonium perchlorate in C and D.

- A. Benzoic acid, no added perchlorate, 0.00974M Bu_4Bz
- B. Benzoic acid, 0.00100M Bu_4NBz , 0.00974M Bu_4NBr
- C. Benzoic acid, 0.00100M Bu_4NBz , 0.00974M Bu_4NClO_4
- D. Bu_4NBz , 0.0100M HBz , 0.00974M Bu_4NClO_4

Figure 4. Acidity of o-nitrophenol in tertiary butanol. Ionic strength maintained by addition of 0.100M Bu_4NBr .

Figure 1

Figure 2

Figure 3

Figure 4

END