

Apart from the fact that the high-precision value for propylene carbonate and the relatively low-precision value for benzonitrile deviate from linearity, an average value for R_{∞} of 3.82 Å. adequately accounts for the results. This value is a little above the range of 3.35 to 3.70 Å. found by Fuoss, *et al.*, for Bu_4NBPh_4 in polar-nonpolar solvent mixtures. Obviously the ions of this electrolyte are reasonably ideal.

The relative ideality of a number of ions in acetonitrile, nitromethane, and nitrobenzene is illustrated by the Stokes radii listed in Table VII. These three solvents have similar dielectric constants (36.0, 35.9, and 34.7, respectively), so that the frictional force experienced by a moving ion owing to dielectric relaxation should be similar in these solvents. Hence, those ions which do not experience specific solvation effects should have constant Walden products and Stokes radii in these solvents. That this is the case for $(i\text{-Am})_4\text{B}^-$ and Ph_4B^- , as well as for quaternary ammonium ions

larger than Me_4N^+ , is shown in Table VII. It should be noted that the difference in Walden products previously obtained for Ph_4B^- in acetonitrile (0.199) and nitromethane (0.203) on the basis of an earlier scale of single ion conductivities⁸ virtually disappears on our scale. However, for the majority of anions considerable variations occur in different solvents, as is well known. Finally, for the series of quaternary ammonium ions, the Stokes radii in water increase more rapidly and finally approach the effective crystallographic radii more closely than they do in the three nonaqueous solvents.

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Hydrogen Bonding and the *ortho* Effect in Acetonitrile. Reaction of *ortho*-Substituted Benzoic Acids with Amines

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*In acetonitrile, which has little capacity to solvate anions, the effect of ortho substitution by hydroxyl or nitro groups on the properties of benzoic acids and phenols is more marked than in water. In order to obtain information about the ortho effect and other structural factors in acetonitrile, we have titrated conductometrically *n*-butyl-, dibutyl-, and tributylamine with benzoic, salicylic, and 2,6-dihydroxybenzoic acids, as well as aniline with picric acid. The titration curves are quite different from those in water, and several equilibria must be considered. The necessary single ion conductivities were evaluated, and all titration curves, except those of benzoic acid, could be interpreted quantitatively.*

Introduction

It is well known that the simple electronic theory of organic chemistry has been of limited success in predicting the influence of *ortho* substituents on the strength of benzoic acids and phenols. The problem is a complex one, because in addition to factors such as inductive, field, resonance, and steric effects, several implications of hydrogen bonding must be considered, including solvation and intramolecular (chelation) effects, as well as intermolecular association (dimerization in the case of carboxylic acids). Consequently, it is to be expected that the so-called *ortho* effect may vary markedly in different solvents. Nevertheless little systematic information is available for solvents other

than water, with the notable exception of the thorough study of Davis and Hetzer in benzene as solvent.³

Acetonitrile is a logical choice for studies that are intended to provide improved resolution of the factors mentioned above. Its dielectric constant is sufficiently high (36.0) to allow precise and technically simple conductometry and potentiometry, yet it is more inert than hydroxylic solvents in that it solvates the majority of cations and particularly anions much more weakly. One consequence of this weak solvation is that in the presence of their conjugate acids, certain anions derive stability by resorting to hydrogen bonding ("homoconjugation") with the acid to produce the species $(\text{A} \cdots \text{HA})^-$,⁴ while ammonium ions form corresponding complexes such as $(\text{BH} \cdots \text{B})^+$.⁵ These homoconjugated complexes are sufficiently stable to produce striking differences between acid-base reactions in acetonitrile and in water.

A second consequence of the weak solvation of anions by acetonitrile is that one would expect a clearer picture in acetonitrile than in water of the extent to which different *ortho*-substituted benzoate and phenolate ions are stabilized by intramolecular hydrogen bonding. Considerable information about such stabilization and also other factors of interest can be obtained by following the reaction of these acids with appropriate bases conductometrically, as described in

(3) M. M. Davis and H. B. Hetzer, *J. Res. Natl. Bur. Std.*, **60**, 569 (1958).

(4) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **66**, 1675 (1962).

(5) J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, *Talanta*, **11**, 93 (1964).

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(2) From the Ph.D. thesis of this author, University of Pittsburgh, 1964.

this communication. The results are of analytical interest as well, since the titration curves obtained in nonhydrogen-bonding solvents often have unexpected shapes,^{6,7} unrecognizable by an aquocentric analyst. Numerous such empirical titrations have been carried out.⁸

A quantitative explanation of the conductometric titration of two relatively strong acids, sulfuric and 3,5-dinitrobenzoic acids, with *n*-butylamine and triethylamine, respectively, was given by Kolthoff and Chantooni.⁷ The present investigation is concerned primarily with the influence of structural factors on titration curves and involves mainly the titration of one example each of a primary, secondary, and tertiary aliphatic amine with benzoic, salicylic, and 2,6-dihydroxybenzoic acids. Although our systems are not directly comparable, the results indicate the formation of species similar to those invoked by Kolthoff and Chantooni.

Experimental

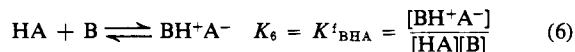
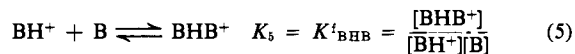
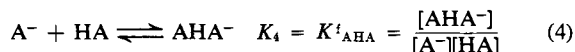
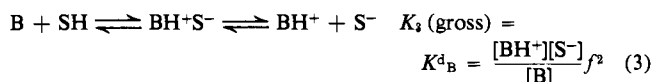
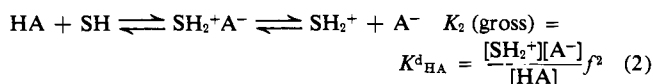
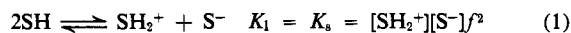
Solvent Purification. Practical grade acetonitrile (Sohio) was purified as described elsewhere,⁹ the main and final step being fractional distillation from calcium hydride through a 4-ft. column packed with 1/8-in. glass helices. The water content was below 1 mM and the conductivity below 2×10^{-7} ohm⁻¹ cm.⁻¹.

Solute Purification. National Bureau of Standards acidimetric grade benzoic acid was dried *in vacuo* at 100°. Salicylic acid (Fisher Certified reagent grade) and 2,6-dihydroxybenzoic acid (K and K Laboratories) were recrystallized from water and dried *in vacuo* at 85° and 65°, respectively. Baker and Adamson picric acid was recrystallized twice from acetone and dried *in vacuo* at 45°. The purification of the amines and ammonium salts used in this investigation are described elsewhere.¹⁰

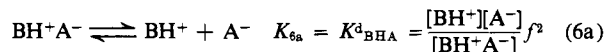
Conductivity Measurements. Conductivities were measured in two Fisher low conductivity cells, No. 9-366, with lightly platinized electrodes and cell constants of 0.1168 and 0.1725 cm.⁻¹, respectively, using a calibrated Leeds and Northrup conductivity bridge, No. 4866. Calibration of the bridge showed it to be accurate to better than 0.2%, which is sufficient for the present purpose. Measurements were made in an oil bath at $25 \pm 0.05^\circ$. The peculiar "shaking effect" described by Prue¹¹ was observed and allowed for.

Results and Discussion

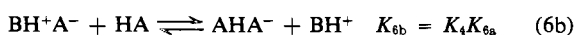
Equilibria Involved. In order to account quantitatively for the reaction of a Brønsted acid (HA) with a base (B) in acetonitrile (SH), it is necessary to consider the following nine independent equilibria (eq. 1 through 6a), where all activity coefficients (*f*) refer to the standard state: $f \rightarrow 1$ as $x_{SH} \rightarrow 1$.



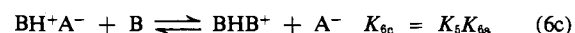
Reaction 6 represents the primary acid-base reaction. Secondary electrolytic dissociation of the ion pair produced is represented by



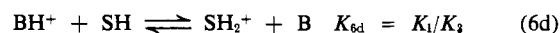
or, if excess HA is present, by



or, if excess B is present, by



Finally, combination of eq. 1 and 3 yields the dissociation constant of BH⁺



In the context of the present investigation, the contributions of reactions 1, 2, and 3 to the conductance are negligible; the value of pK₁ is 28.5 and typical values for the acids and bases titrated are 18 and 11, respectively. Also, formation of BH⁺AHA⁻ and BHB⁺A⁻ ion pairs is a second-order effect which can be ignored for dilute solutions.

Measurements were carried out at sufficiently low ionic strength values (*S*) to allow calculation of activity coefficients from the reduced Debye-Hückel equation, which for a 1:1 electrolyte in acetonitrile (*D* = 36.0) at 25° reduces to

$$-\log f = 1.64S^{1/2} \quad (7)$$

Evaluation of Single Ion Conductivities. Quantitative interpretation of conductometric titration curves requires a knowledge of the conductivities of all major ionic species involved. Consequently the conductivities of the perchlorates and picrates of the bases, and of the tetraethylammonium salts of the acids involved, were determined. The results are reported in Table I, which also contains information for four other salts, included for different reasons. Since the single ion conductivities of perchlorate, picrate, and tetraethylammonium ions are known,¹² the corresponding values for the ions of interest can be calculated, as listed in Table II. The perchlorates were more difficult to crystallize and more hygroscopic than the picrates. Consequently the values for the picrates were used to calculate conductivities for ammonium ions. A reliable value for benzoate ion could not be obtained since our preparations of tetraethyl- and tetrabutylammonium benzoates were extremely hygroscopic and in fact had a "gummy" consistency. Silver benzoate had limited

(6) P. J. R. Bryant and A. W. H. Wardrup, *J. Chem. Soc.*, 895 (1957).

(7) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, 85, 426 (1963).

(8) For a summary, see G. R. Padmanabhan, Ph.D. Thesis, University of Pittsburgh, 1963.

(9) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, 34, 1139 (1962).

(10) J. F. Coetzee and G. R. Padmanabhan, to be published.

(11) J. E. Prue, *J. Phys. Chem.*, 67, 1152 (1963).

(12) J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, 87, 2529 (1965).

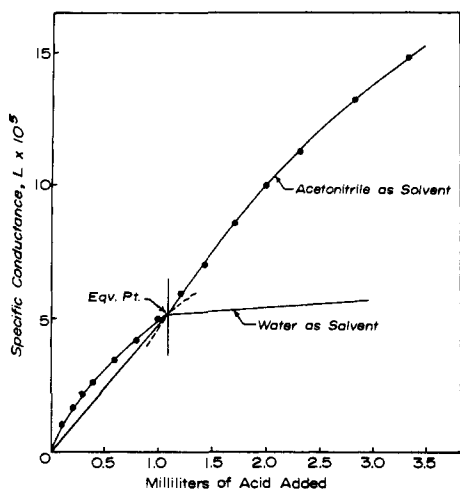


Figure 1. Conductometric titration of 20 ml. of 0.0151 *M* *n*-butylamine with 0.275 *M* benzoic acid in acetonitrile (schematic for corresponding titration in water superimposed, using arbitrary coordinate system).

solubility and in addition proved to be relatively weakly dissociated.¹³ From the fact that the conductivity of 2,6-dihydroxybenzoate is considerably larger than that of salicylate ion, it is evident that the stability derived from intramolecular hydrogen bonding

Table I. Conductivity of Substituted Ammonium Salts in Acetonitrile

Salt	Λ_0^a	$K_{BHA} \times 10^3^a$
Butylammonium perchlorate	194	15
Butylammonium picrate	167.8	3.4
Dibutylammonium perchlorate	185	14
Dibutylammonium picrate	158.5	3.4
Tributylammonium perchlorate	177	9.5
Tributylammonium picrate	149.0	4.6
Tetraethylammonium perchlorate	189	56
Tetraethylammonium salicylate	176.0	21
Tetraethylammonium 2,6-dihydroxybenzoate	189	15
Tetraethylammonium <i>p</i> -nitrophenolate	166	23
Pyridinium perchlorate	202	15
Hydrazonium monopерchlorate	193	18

^a Limiting equivalent conductivity, Λ_0 , and dissociation constant of ion pair, K_{BHA} , both obtained from Shedlovsky plot.

Table II. Approximate Single Ion Conductivities in Acetonitrile

Cation	λ_0	Anion	λ_0
Butylammonium	90 ^a	Benzoate	80–85 ^d
Dibutylammonium	81 ^a	Salicylate	91 ^e
Tributylammonium	72 ^a	2,6-Dihydroxybenzoate	104 ^e
Tetrabutylammonium	61.93 ^b	Picrate	77.32 ^b
Pyridinium	99 ^c	<i>p</i> -Nitrophenolate	81 ^e
Hydrazonium	90 ^c		

^a Assuming picrate = 77.32 (see ref. 12). ^b See ref. 12. ^c Assuming perchlorate = 103.38 (see ref. 12). ^d Estimated value (see text). ^e Assuming tetraethylammonium = 85.05 (see ref. 12).

(13) This fact was unexpected since silver is one of the few ions that coordinate relatively strongly with acetonitrile [see I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957)]. It follows that the absolute activity of benzoate ion in acetonitrile must be unusually high.

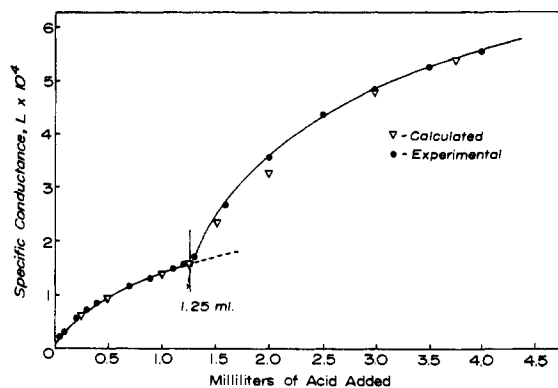


Figure 2. Titration of 0.0159 *M* dibutylamine with 0.250 *M* salicylic acid in acetonitrile.

is much greater, and therefore solvation is less extensive for the former ion than for the latter. It therefore is reasonable to assume that the conductivity of benzoate should be considerably lower than that of salicylate ion, but it probably will be somewhat larger than that of *p*-nitrophenolate ion. On this basis we estimate an approximate value of 80 to 85 for benzoate ion in acetonitrile.

Quantitative Interpretation of Titration Curves. Representative conductometric titration curves are given in Figures 1–6. It will be shown that the striking differences between the curves for water and acetonitrile as solvents (Figure 1) are caused mainly by reactions 6a and 6b.

Sample Calculation. Titration of 20 ml. of 0.0159 *M* dibutylamine with 0.250 *M* salicylic acid (Figure 2).

a. Calculation of K_{BHA} . It was shown before⁵ that in the case of dibutylamine BHB^+ formation is slight (K_b is small). Hence, up to the equivalence point the only current-carrying species will result from reaction 6a (unless K_{bb} is very large and/or K_b is not large; neither is the case here, as will be shown below). Also, it is found that reaction 6 goes to virtual completion.

At the equivalence point, the total (analytical) concentration of acid, C_a , and of base C_b , is given by

$$C_a = C_b = C = [BH^+A^-] + [BH^+] = [BH^+A^-] + [A^-] \\ = 1.59 \times 10^{-2} \times \frac{20}{21.25} = 1.50 \times 10^{-2}$$

while the observed conductivity, L , is given by

$$L = l_{BH^+} + l_{A^-} = 1.70 \times 10^{-4}$$

Hence

$$\Lambda_c = \frac{10^3 L}{C} = 11.3$$

It will be seen below that the ionic strength of the solution is sufficiently low to represent the degree of dissociation, α_c , of the ion pairs, BH^+A^- , by

$$\alpha_c = \frac{\Lambda_c}{\Lambda_0} = \frac{11.3}{81 + 91} = 6.6 \times 10^{-2} \text{ (see Table II)}$$

Since the ionic strength, S , of the solution is given by

$$S = \alpha C = 9.9 \times 10^{-4}$$

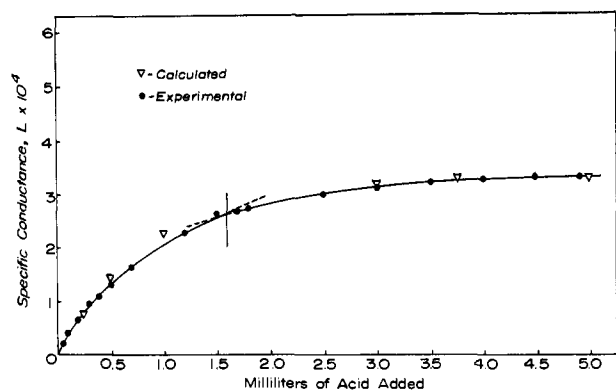


Figure 3. Titration of 0.00403 *M* *n*-butylamine with 0.050 *M* 2,6-dihydroxybenzoic acid in acetonitrile.

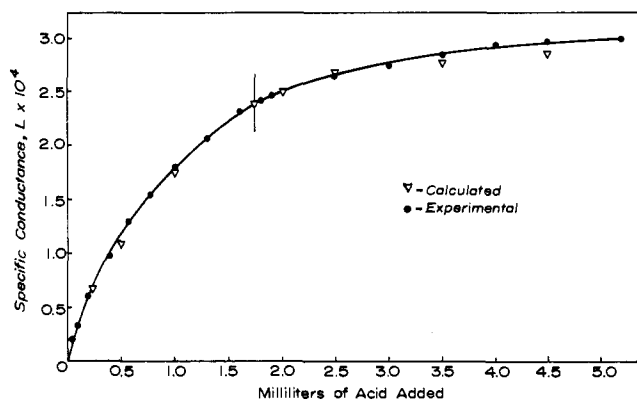


Figure 4. Titration of 0.00432 *M* tributylamine with 0.050 *M* 2,6-dihydroxybenzoic acid in acetonitrile.

it follows from eq. 7 that $f = 0.888$, and from eq. 6a that

$$K_{\text{BHA}}^d = \frac{\alpha^2 C}{1 - \alpha} f^2 = 5.5 \times 10^{-5}$$

b. Calculation of K_{AHA}^f . At the equivalence point, as calculated above

$$[\text{BH}^+] = [\text{A}^-] = \alpha C = 9.9 \times 10^{-4}$$

$$L = 1.70 \times 10^{-4}$$

The contribution of A^- to the total conductivity is given by

$$I_{\text{A}^-} = \frac{\lambda_0^-}{\Lambda_0} L = \frac{91}{172} \times 1.70 \times 10^{-4} = 9.0 \times 10^{-5}$$

Similarly

$$I_{\text{BH}^+} = L - I_{\text{A}^-} = 8.0 \times 10^{-5}$$

Beyond the equivalence point, the increase in conductivity is caused by reaction 6b. For example, after addition of exactly 3 moles of acid per mole of base (3.75 ml. of titrant), the observed conductivity was 5.45×10^{-4} . Assuming that the mobility of the "homoconjugated" complex AHA^- is one-half that of the simple anion A^- ,¹⁴ the calculation is most easily carried

(14) The limiting equivalent conductivity of the complex AHA^- can be determined for solutions containing BH^+A^- and a sufficiently large excess of HA, correcting for the increase in viscosity of acetonitrile on adding HA. An uncertainty arises from the fact that the acids under discussion are extensively hydrogen bonded to acetonitrile (results of R. Lok of this laboratory), with the result that addition of HA changes

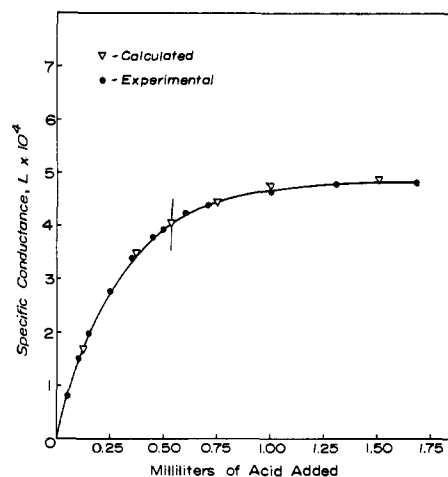


Figure 5. Titration of 0.0108 *M* aniline with 0.402 *M* picric acid in acetonitrile.

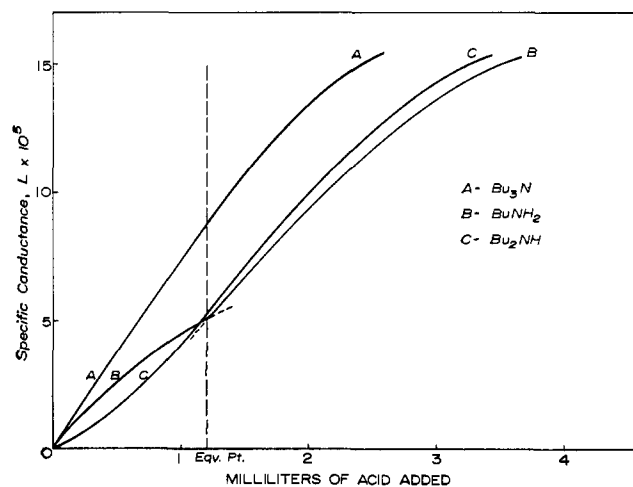


Figure 6. Titration of 0.015 *M* *n*-butyl-, dibutyl-, and tributylamine with 0.25 *M* benzoic acid in acetonitrile.

out by trial and error. It is found that the concentration of BH^+ must be increased by a factor of 4.30 beyond the equivalence point to account for the observed increase in the conductivity by a factor of 3.21. Hence

$$[\text{BH}^+] = 4.30 \times 9.9 \times 10^{-4} = 4.26 \times 10^{-3}$$

and, since the concentration of BH^+A^- ion pairs does not vary unduly

$$[\text{A}^-] \sim \frac{9.9 \times 10^{-4}}{4.30} = 2.3 \times 10^{-4}$$

Consequently

$$[\text{AHA}^-] = [\text{BH}^+] - [\text{A}^-] = 4.03 \times 10^{-3}$$

The following calculation was done as a check.

$$L = I_{\text{BH}^+} + I_{\text{A}^-} + I_{\text{AHA}^-} = (4.30 \times 8.0 \times 10^{-5}) + \left(\frac{9.0 \times 10^{-5}}{4.30}\right) + \frac{1}{2} \left(9.0 \times 10^{-5} \times \frac{4.03 \times 10^{-3}}{9.9 \times 10^{-4}}\right) = 5.5 \times 10^{-4}$$

not only the viscosity of the medium. Kolthoff and Chantooni⁷ reported for 3,5-dinitrobenzoate $\lambda_{\text{AHA}^-}^0 = 0.46\lambda_{\text{A}^-}^0$. We find that the relationship $\lambda_{\text{AHA}^-}^0 = 0.5\lambda_{\text{A}^-}^0$ accounts for our titration curves, which are not unduly sensitive to the exact value chosen. Nevertheless the $K_{\text{AHA}^-}^f$ values are less reliable than the K_{BHA}^d values reported.

The observed value was 5.45×10^{-4} . Hence

$$[\text{BH}^+\text{A}^-] = C_b - [\text{BH}^+] = \left(1.59 \times 10^{-2} \times \frac{20}{23.75} \right) - 4.26 \times 10^{-3} = 9.1 \times 10^{-3}$$

$$[\text{HA}] = C_a - [\text{BH}^+\text{A}^-] - [\text{A}^-] - 2[\text{AHA}^-] = 2.29 \times 10^{-2}$$

It is found that $S = 4.26 \times 10^{-3}$ and $f = 0.782$. Hence, from eq. 6b

$$K_4 K_{6a} = \frac{(4.03 \times 10^{-3})(4.26 \times 10^{-3})}{(9.1 \times 10^{-3})(2.29 \times 10^{-2})} (0.782)^2 = 5.0 \times 10^{-2}$$

Hence

$$K_{\text{AHA}}^f = K_4 = \frac{K_4 K_{6a}}{K_{6a}} = \frac{K_4 K_{6a}}{K_{\text{BHA}}^d} = \frac{5.0 \times 10^{-2}}{5.5 \times 10^{-5}} = 910$$

Preliminary values of K_{BHA}^d and K_{AHA}^f , calculated as above, then were used to compute the conductivity at various points on the titration curve, and, if necessary, minor adjustments in the values of the constants were made to provide the best over-all fit. Figures 2 through 5 show that fair to good agreement could be obtained between calculated and experimental curves. The best values of the calculated equilibrium constants are summarized in Table III.

Table III. Equilibrium Constants for Principal Species Produced in Reaction of Amines with Acids in Acetonitrile

Base titrated	Acid titrant	K_{BHA}^d × 10 ^{5 a, b}	K_{AHA}^f × 10 ^{-2 b, c}
Butylamine ^d	2,6-Dihydroxybenzoic	147	Very small
Dibutylamine	2,6-Dihydroxybenzoic	47, 52	Very small
Tributylamine	2,6-Dihydroxybenzoic	53, 56	Very small
Dibutylamine	Salicylic	5.5, 4.3	9, 8
Tributylamine	Salicylic	4.3, 4.8	15, 10
Aniline ^e	Picric	85, 78	Very small

^a See eq. 6a. ^b Where two values are given, titrations were carried out at two different concentrations (generally near 4 and 15 mM). ^c See eq. 4. ^d Additional equilibrium involved: eq. 5, $K_{\text{BHB}}^f = 26$ (ref. 5). ^e Additional equilibrium involved: eq. 6, $K_{\text{BHA}}^f = 450$ and 470 for two titrations (see text). For all other systems in table, this reaction goes essentially to completion (not for benzoic acid titrations; see text).

c. Additional Equilibria. Three examples will be given of titrations in which additional equilibria must be considered. First, *n*-butylamine forms a homoconjugate complex, BHB^+ .⁵ However, this complex is not very stable ($K_{\text{BHB}}^f = 26$) and its influence is limited to the early stages of the titration. Second, in the titration of aniline with picric acid some reversion (molecular, rather than electrolytic, dissociation) of the ion pair BH^+A^- into the parent acid and base occurs, since aniline is a relatively weak base (reaction 6 is significantly incomplete). From eq. 2, 6, 6a, and 6d it follows that the difference in pK_a values of picric acid and anilinium ion is given by

$$\Delta pK_a = pK_{\text{HA}}^d - pK_{\text{BH}^+}^d = -\log(K_{\text{BHA}}^f K_{\text{BHA}}^d)$$

Substituting values from Table III, it is found that

$$\Delta pK_a = -\log(460 \times 82 \times 10^{-5}) = 0.42$$

This value is in exact agreement with that found by independent potentiometric measurements in this laboratory.^{8,10} Furthermore, French and Muggleton¹⁵ reported, on the basis of a precise conductivity study of anilinium picrate, values for K_{BHA}^d and K_{BHA}^f of 104×10^{-5} and 425, respectively, in satisfactory agreement with those listed in Table III.

Finally, *n*-butyl-, dibutyl-, and tributylamine were titrated with benzoic acid (Figure 6). We were unable to account satisfactorily for the observed titration curves (for details, see ref. 2). On the basis of the foregoing, one would predict that differences in the reaction of a given base with benzoic and salicylic or 2,6-dihydroxybenzoic acids will be characterized by smaller values of K_6 and K_{6a} and a larger value of K_4 in the case of benzoic acid. That this indeed is so can be seen qualitatively by comparing Figure 6 with Figures 2 and 3. However, satisfactory matching of calculated and experimental curves could not be obtained. It was evident that these systems represent complex, intermediate cases for which even small variations in K_6 , K_{6a} , and K_4 cause striking shifts in the titration curves over the entire concentration range. Nevertheless, the curves are consistent with the following values of the equilibrium constants: $K_{6a} \sim 2 \times 10^{-6}$ for *n*-butyl- and dibutylamine, 3×10^{-6} for tributylamine (evaluated for the early stages of the titrations); K_6 near 10^{+3} ; and $K_4 > 10^{+3}$. In order to refine the values of K_6 and K_4 it will be necessary to determine independently K_2 for benzoic acid (for the values of K_{6d} for the amines, see ref. 10) and also to evaluate K_4 independently (for example, by measuring the increase in solubility of sodium or silver benzoate on adding benzoic acid).

Conclusions

1. It was shown that the reaction of amines with substituted benzoic acids and picric acid is determined mainly by equilibria 6, 6a, and 6b.

2. The increased stability of 2,6-dihydroxybenzoate ion over that of salicylate ion, derived from intramolecular hydrogen bonding, results in a marked decrease in (a) the solvation of the simple anion (Table II); (b) the stability of its ion pair with ammonium ions (Table III) (likewise salicylate ion pairs are much less stable than those of benzoate; see text); (c) the stability of its homoconjugate complex with free acid (Table III) (likewise, picrate ion is strongly stabilized by intramolecular hydrogen bonding in acetonitrile as solvent and does not form homoconjugated complexes as unsubstituted phenol does).⁸

3. The ion pairs of substituted benzoic acids with incompletely substituted ammonium ions are markedly more stable than those with quaternary ammonium ions (compare Tables I and III). Evidently in the former case the ion pair is stabilized by hydrogen bonding with the acidic protons of the incompletely substituted ammonium ion.

4. Whereas perchlorate ion forms ion pairs of com-

(15) C. M. French and D. M. Muggleton, *J. Chem. Soc.*, 2131 (1957).

parable stability with incompletely and completely substituted ammonium ions (Table I), the more basic 2,6-dihydroxybenzoate and particularly salicylate ion form much more stable ion pairs with incompletely substituted ammonium ions (Table III) than with

quaternary ammonium ions (Table I). Again hydrogen bonding stabilizes the ion pairs in the former case.

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A Study of Double Layer Repulsion and van der Waals Attraction in Soap Films

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Measurements of equilibrium thicknesses of soap films over a range of ionic strengths are presented for mobile and rigid films of sodium lauryl sulfate in the presence of lithium chloride. The forces determining this thickness are discussed in terms of existing theories of van der Waals attractions and of electric double layer repulsion. Some of the problems involved in the experimental testing of these theories are brought out. While there is good qualitative agreement between theory and experiment, definite quantitative discrepancies appear also. It is suggested that some of these could stem from limitations of the double layer theory.

The principal long-range forces between large charged particles in solution are the double layer repulsion due to the interaction of their ionic atmospheres and the van der Waals attraction attributed¹ mainly to electromagnetic dispersion forces as postulated originally by London.² The theory of both effects has been elaborated in considerable detail and most of modern interpretation of the stability and flocculation of colloids is based upon both of them.^{3,4} These theories are derived from basic principles of physics, but the simplifying assumptions that are necessary to keep the mathematics tractable limit the region of strict applicability to low salt concentrations and low surface potentials. Their rigorous application to real systems is not always easy and the treatment of flocculation is particularly difficult because of the complex kinetics and the uncertain geometry of the region of interaction. Hence the value of these theories in this field has occasionally been questioned.⁵

The only early evidence bearing directly upon double layer repulsion was a study⁶ of iridescent (or Schiller) layers of ferric and tungstic oxides which yielded only qualitative agreement as would be expected in view of

the difficulties involved in these systems. Recent experiments involving the direct measurement of the force barrier between two crossed platinum wires,⁷ although much simpler in geometry and minimizing the kinetic factor, can determine only the maximum height of the repulsion barrier, but not its position. The results of these experiments could in general be explained by the theories^{3,4} but suggested the existence of some hitherto unknown, additional repulsive force.

The past decade has produced direct measurements of London interactions between macroscopic plates and lenses under vacuum⁸⁻¹⁰ which agree with the theoretically expected distance dependence as well as with the absolute value. However, the minimum distance accessible to these methods is about 1μ which is quite large compared with separations involved in colloidal phenomena and the techniques are not readily applicable to measurements in solutions because of the required vacuum.

In recent years it became clear¹¹⁻¹⁵ that a critical test of the theory can be provided in principle by the equilibrium thickness of a thin liquid film—a soap film. This equilibrium thickness varies, depending on the conditions, between some 50 and 1000 Å., which is just the order of distance between interacting colloidal particles. Qualitatively, when an ionic surfactant is used to stabilize the film, this thickness decreases upon addition of salt, in harmony with the reduced range of double layer repulsion according to the stability theory. Moreover, as the van der Waals forces between all the particles of the liquid film tend to compress the

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