

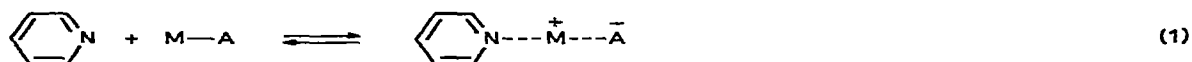
SOLUTE-SOLVENT INTERACTION IN PYRIDINE*

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Electrochemical techniques, primarily those related to polarography but including potentiometry and conductometry, as well as spectrophotometry and calorimetry, are being used to study solute-solvent interaction in pyridine by means of investigation of the nature and behavior of the adduct or solvate species produced when a compound MA is dissolved in pyridine where M is a Lewis acid such as a proton, a metal ion, a quaternary (R_4N) ion or an alkyl moiety, *i.e.*



The phenomena involved are readily illustrated by considering the well-defined diffusion-controlled polarographic waves produced by solutions of such acids in pyridine (Fig. 1), whose wave heights correspond to a one-electron reduction per acid group in the original MA species and are due to a one-electron reduction of the pyridine ring in the solvate species¹.

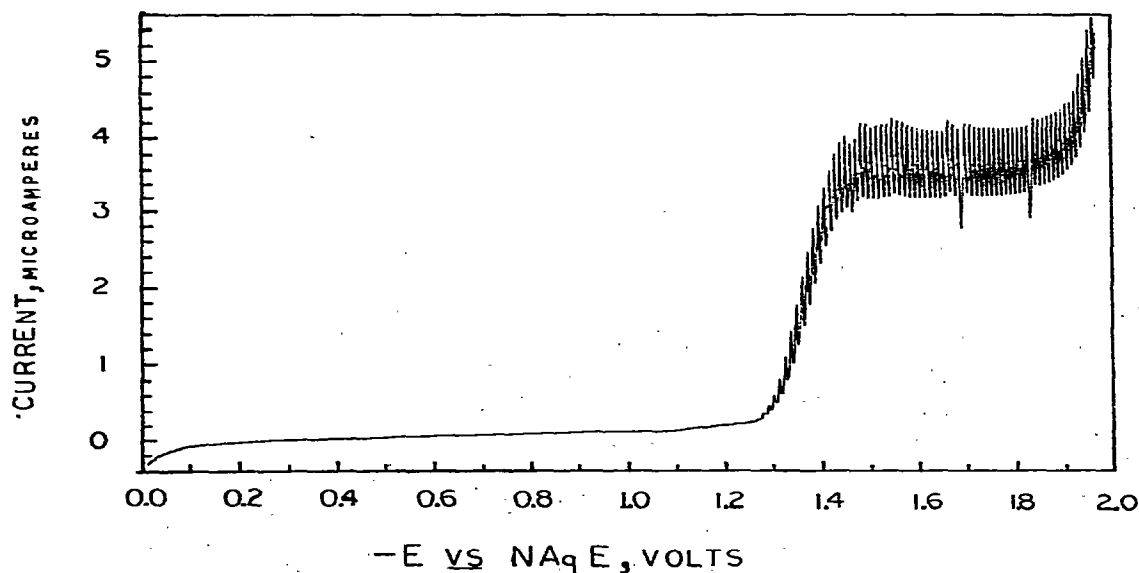


Fig. 1. Polarogram of a pyridine soln., which is 1.01 mM in benzoic acid and 0.1 M in lithium perchlorate.

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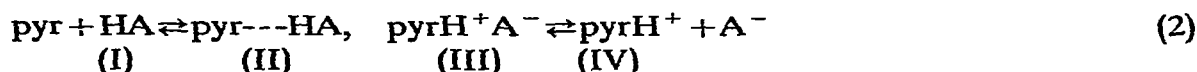
Nature of the polarographic wave

The pyridine in a pyridinium species dissolved in pyridine is apparently sufficiently polarized as a result of coordination with the Lewis acid that it is effectively easier to introduce an electron into the aromatic ring than into the originally positive Lewis acid. (The data available indicate that the Lewis acids which are most effective in causing ring reduction are those which normally show a high activation overpotential for reduction at a mercury electrode, *e.g.*, H(I), Li(I), Mg(II) and Al(III)²⁻⁴.)

The essential electrolytic step is a 1e attack on the pyridinium species, probably at the carbon-nitrogen bond system in the ring, to produce a free radical (stabilized in an acid-base adduct?), although the site of electron addition is not necessarily connected with the site of subsequent free radical dimerization or ring fission, since the latter reactions may follow electron rearrangement subsequent to electron addition. Shift in electron density in the pyridinium species may possibly favor electron attack at the 4-position of the pyridine ring. The complex initially produced between the Lewis acid and the free radical anion may preserve the ring structure, which could be converted on exposure to water and/or oxygen to a lactam structure, whose opening would lead to polymerization; dimerization may occur during the reaction with water with possible stabilization of the Lewis acid as the hydroxide or derived species. Dimerization immediately following electron transfer would lead to more or less stable bipyridyls (probably 2,2' or 4,4')^{2,4}.

FUNDAMENTAL EQUILIBRIA

The basic equilibrium in the case of a Brønsted acid is the following:



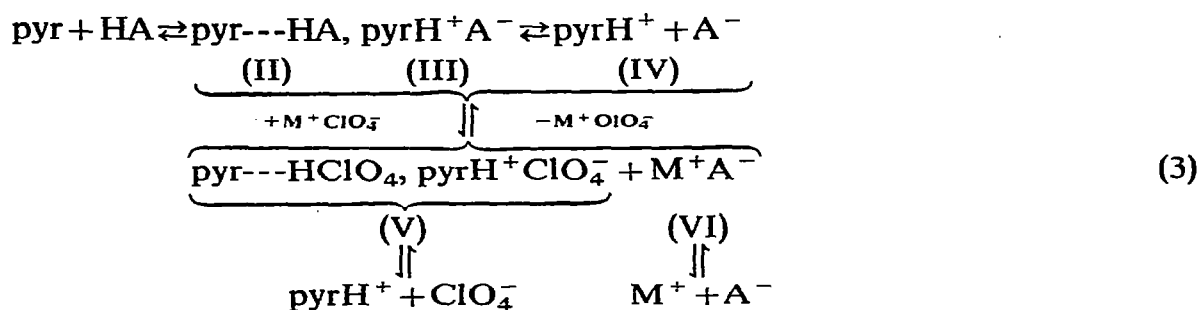
where pyr represents pyridine, HA a monobasic uncharged Brønsted acid, II the hydrogen-bonded nonionic solvate adduct, III the corresponding ionized but undissociated ion pair, and IV the dissociated pyridinium ion; species II and III represent the two extremes of the state of the associated species (the HA species—or MA in the general case—also participates in a similar ion-pair dissociation equilibrium)⁵.

The reaction of eqn. (2) is obviously the counterpart of that for HA dissolved in water. However, in pyridine, the electrochemical reducibility of the product solvate provides a mean for evaluating the reaction.

The strong Lewis-base character of pyridine promotes solubility of Lewis acid-containing compounds, but the low dielectric constant (12.3) causes ion-pairing and association to be pronounced. (The normal value of Trouton's constant (21.7) for pyridine indicates a relative lack of association of the pyridine molecules in the liquid state.)

Equilibria under polarographic conditions

Under polarographic conditions, *i.e.* in the presence of a large (generally, hundredfold) excess of a background electrolyte (MB) such as a perchlorate, the following equilibria are operative⁶:



In the equilibria involving species V (analogous to II and III in nature) and its ions, dissociation would be favored because of the large size of the symmetrical perchlorate ion as well as that of the pyridinium ion. The extent of dissociation of VI (associated ion-pair) would depend on the sizes and symmetry of the ions involved, especially that of the cation.

BRØNSTED ACIDS AS SOLUTE SPECIES

For convenience in subsequent discussion, dissociation constants of Brønsted acids in water are indicated as pK_a^{aq} , and in pyridine as pK_a^{pyr} .

*Et*₄*N*(I) as background cation

In solutions where M of the background electrolyte is a large symmetrical ion, *e.g.* *Et*₄*N*(I), species VI in eqn. (3) tends to be largely dissociated and the overall equilibrium of eqn. (3) is controlled by that between species II, III and IV, which would depend on the mutual interaction in the species $\text{RN} \cdots \text{H}^+ \cdots \text{A}^-$ where the associative attraction between H^+ and A^- might be expected to be generally proportional to pK_a^{aq} , on the basis that pK_a^{aq} is a measure of the mutual interaction in the system $\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{A}^-$. Experimentally, the half-wave potential of the polarographic wave is dependent on the chemical nature of the anion A of the original Brønsted acid, and separate but parallel linear correlations are found for each type of acid anion, *e.g.*, carboxylic, phenolic and nitrogen heterocyclic, between $E_{\frac{1}{2}}$ and pK_a^{aq} with a levelling effect for acids of pK_a^{aq} less than *ca.* 3 (Fig. 2)⁵.

The data in Fig. 2 include those for 29 acids (1 inorganic, 9 monocarboxylic, 8 dicarboxylic, 1 carboxylic phenol, 4 phenols and 6 purines), which produce 39 diffusion controlled steps. The pK_a^{aq} values vary from -1.13 to 12.1. The straight line portions of the plots are expressed by the following equations⁵:

$$\text{Carboxylic acids: } E_{\frac{1}{2}}/V = -1.10 - 0.124 pK_a^{\text{aq}} \quad (4a)$$

$$\text{Phenols: } E_{\frac{1}{2}}/V = -0.79 - 0.124 pK_a^{\text{aq}} \quad (4b)$$

$$\text{Purines: } E_{\frac{1}{2}}/V = -0.62 - 0.124 pK_a^{\text{aq}} \quad (4c)$$

There are four items which need to be explained in connection with the data of Fig. 2: (1) the variation in $E_{\frac{1}{2}}$ with pK_a^{aq} ; (2) the effect of acid type on the relationship observed; (3) the deviations of some acids from the curves of Fig. 2, in particular the fact that the first waves of some diprotic acids are below the curve, indicating the compounds to be apparently stronger acids than indicated by the $E_{\frac{1}{2}}-pK_a^{\text{aq}}$ relation-

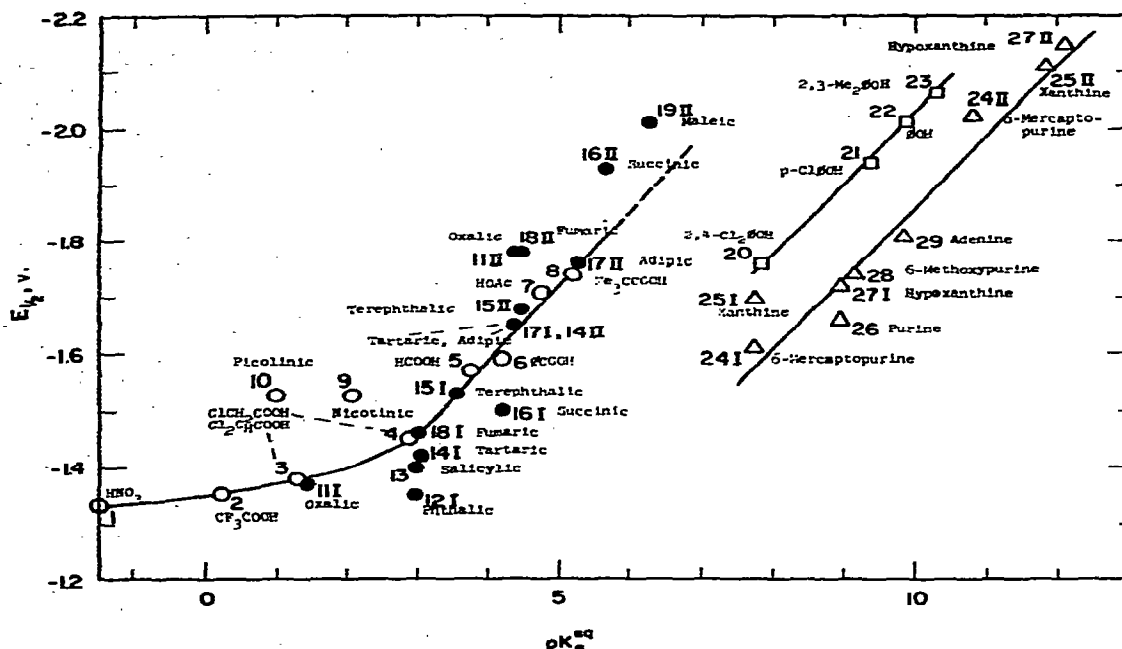


Fig. 2. Relation between $E_{1/2}$ of waves given by Brønsted acids in pyridine (0.1 M in Et_4NClO_4) and the aq. $\text{p}K_a$ values of the acids. In the case of diprotic acids, I refers to the first reduction wave seen and $\text{p}K_1$, and II to the second wave and $\text{p}K_2$.

ship, and that the second waves of the same acids have an $E_{1/2}$ above the line, indicating the second acid function to be weaker than indicated by the $E_{1/2}$ - $\text{p}K_a$ function; and (4) the difference in behavior when the background cation is $\text{Et}_4\text{N}(\text{I})$ and when it is $\text{Li}(\text{I})$ (cf. subsequent discussion).

1. *Variation of $E_{1/2}$ with $\text{p}K_a^{\text{aq}}$.* A suggestive lead in respect to the variation of $E_{1/2}$ with $\text{p}K_a^{\text{aq}}$ in Et_4ClO_4 solution is given by the studies of Streuli and coworkers⁷⁻⁹ who potentiometrically titrated carboxylic acids and phenols in pyridine. They obtained two linear, more or less parallel relationships when the half-neutralization potential measured at the glass electrode (E_{hnp}) was plotted against $\text{p}K_a^{\text{aq}}$, and concluded that the E_{hnp} is a measure of the $\text{p}K_a$ in pyridine ($\text{p}K_a^{\text{pyr}}$). There was no explanation given of why separate curves were obtained for the carboxylic acids and the phenols.

It is apparent that, if linear relationships are obtained between E_{hnp} vs. $\text{p}K_a^{\text{aq}}$ and $E_{1/2}$ vs. $\text{p}K_a^{\text{aq}}$, there should be a linear relation or relationships between E_{hnp} and $E_{1/2}$. A plot of the latter two values against one another for the carboxylic acids and phenols common to both studies (Fig. 3) gives a straight line⁵. (It is possible that the phenols fall on a separate line, slightly displaced from that for the carboxylic acids, but the number of phenol points are too few for a definitive statement to be made.) The agreement strongly suggests that $E_{1/2}$ for the pyridinium species reduction in pyridine is a measure of $\text{p}K_a^{\text{pyr}}$ and reflects the extent of ionic character in the coordinated solvent-acid system.

Similar, but generally less consistent relations between E_{hnp} and $\text{p}K_a^{\text{aq}}$ have been reported for acids and bases in a considerable number of other solvents⁹⁻¹².

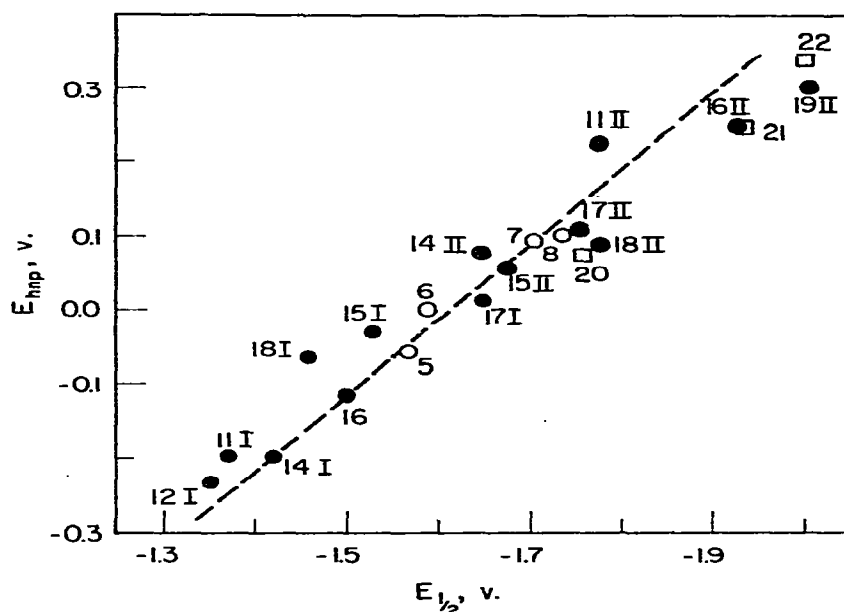


Fig. 3. Correlation between titrimetric half-neutralization potentials (E_{hnp}) (refs. 7-9) and polarographic half-wave potentials ($E_{\frac{1}{2}}$) (ref. 5) of acids in pyridine. Dashed line represents a 1:1 relation. (○) Monocarboxylic acids, (●) dicarboxylic acids, (□) phenols. Numerals refer to the acids as listed in Fig. 2.

Recently, Morales¹³ obtained two parallel linear relationships when he plotted E_{hnp} for benzoic acids and phenols in DMSO *vs.* their pK_a^{aq} values, and a narrow band when E_{hnp} in DMSO was plotted *vs.* E_{hnp} in pyridine.

2. *Dependence of $E_{\frac{1}{2}}$ on pK_a^{pyr} .* The dependence of $E_{\frac{1}{2}}$ in pyridine on pK_a^{pyr} can be qualitatively seen by considering pK_a as a measure of the binding between the proton and the anion in the solvated acid:



The ease of electron attack on a carbon-nitrogen bond in the ring would be proportional to the electron density at the nitrogen site. The latter, in turn, would depend on the strength of the binding between the proton and the anion in the above species. The weaker the binding between the proton and the anion, *i.e.* the smaller the pK_a , the greater would be the withdrawal of electrons from the nitrogen towards the proton and the easier would be the attack at the nitrogen site by electrons from the electrode.

The argument can be placed on a quantitative basis by considering the basic equilibria involved in the dissociation of the pyrHA species⁵:



where K_a is virtually the acid dissociation constant, K_a , in pyridine, and in the essential steps in the electrode reaction,



where $k_{f,h}^0$ is the forward heterogeneous rate constant for the reaction of eqn. (7), whose irreversibility may be due to instantaneous electron rearrangement within the molecule after electron transfer, or to the rapid conversion of pyrH^0 . In any event, reactions 6 and 8 are rapid compared to the rate-determining reaction 7. By an argument analogous to that used for the situation involving fast preprotonation preceding electron transfer¹⁴, $E_{\frac{1}{2}}$ for reaction 7 can be expressed, on the basis of reaction 6, as

$$E_{\frac{1}{2}}/V = \text{const.} + (0.059/\alpha n_a)(\log K_d - \log [A^-]) \quad (9)$$

Equation (9) indicates that an increase in K_d (pK_a^{pyr}) makes $E_{\frac{1}{2}}$ more positive, as observed and previously discussed. The shift in $E_{\frac{1}{2}}$ for a benzoic acid solution on addition of tetraethylammonium benzoate gave a reasonable value of 0.66 for α ^{5,15}.

Involvement of an undissociated species in the electrode process is supported by the fact that protonation of the ketyl radical, produced on polarographic reduction of benzophenone in pyridine in the presence of 2,4-dimethylphenol as proton source, involves the undissociated acid¹⁶, as well as by the following argument.

Dissociation constants of Brønsted acids in pyridine are smaller than in water, as expected on the basis of dielectric constants. pK_a values of HClO_4 , HNO_3 , and HI in pyridine have been conductometrically determined¹⁷ to be 3.12, 4.30, and 3.23, respectively; pK_a values in pyridine, relative to that of HNO_3 , were potentiometrically determined¹⁸ to be: for HCl , +1.60; for HBr , +0.30; for HI , -0.60; for HClO_4 , -0.78. Consequently, since many of the Brønsted acids studied in pyridine have pK_a^{aq} values exceeding 3.4, pK_a^{pyr} values for these acids would exceed 7.7⁵.

Furthermore, for acids of $pK_a^{\text{aq}} \geq 3.4$, the concentration of associated species II and III in pyridine nearly equals the analytical concentration of the acid. It is these weaker acids that produce waves whose $E_{\frac{1}{2}}$ are dependent on pK_a^{aq} (Fig. 2; eqns. 4a-c).

Because the polarographic waves produced by the acids in pyridine are diffusion-controlled and proportional to their analytical concentration, it is reasonable to attribute the diffusing species for acids in the category just discussed, to the associated species II and III. The additivity of the wave for polyprotic acids and for mixtures of acids^{1,5,6,15} also supports the conclusions that the diffusing species is II or III, rather than IV. Although the equilibrium of the reaction of eqn. (6) may be largely to the left, it is sufficiently rapid that the limiting current is controlled by diffusion.

3. Dependence on acid type. The magnitude of the solvent effect on acid type, if $E_{\frac{1}{2}}$ in pyridine (0.1 M in Et_4NClO_4) does reflect pK_a^{pyr} , is seen in the hypothetical example that three acids—one each being carboxylic, phenolic and purine in nature—of identical pK_a in water, would have the following relative pK_a values in pyridine: carboxylic acid, pK'_a ; phenol, ($pK'_a - 2.5$); purine, ($pK'_a - 3.9$). These differences correspond to free energy contributions of 3.4 and 5.3 kcal mol⁻¹ for the phenols and purines, respectively, compared to the carboxylic acids.

Electrostatic effects depending solely on the dielectric constants of the solvents can be eliminated as the principal cause, because these should be essentially comparable. Similarly, differences in change of activity with the three types of acids on solvent

change are not likely to be so great, *i.e.* acid concentrations in the present study were *ca.* 10^{-3} M and background electrolyte concentration was 0.1 M.

An interpretation based on the electron-acceptor properties of the acids, assuming charge-transfer complex formation with pyridine, can also be rejected⁵. The cause of the systematic difference between the three groups of acids, therefore, must be sought in the effect of the non-electrostatic type of solvent-solute interaction on the process of ionic dissociation of the acid-pyridine complexes.

The results obtained are entirely consistent with their being due to the contribution of the dispersion effect to the medium effect on free energy in connection with specific solute-solvent interaction, which Grunwald and Price¹⁹ have related to the interaction of delocalized oscillators in the anion with dispersion centers in nearby solvent molecules. The magnitudes of the free energy changes are consistent with Grunwald's prediction, as well as with the fact that the negative charge on a carboxylate anion is fairly well localized on the COO^- group, but the negative charge on a phenolate ion and—even more so—on a purine-derived anion must be comparatively spread out over the molecules.

Consequently, it follows from the preceding discussion that the dissociation of an acid in pyridine can be considered on a formal basis to involve, first, formation of the acid-solvent adduct, then, formation of the equilibrium associated species (solvated acid molecule through solvated proton-anion ion-pair), and, finally, dissociation to the pyridinium ion and the anion, where the latter is surrounded by a solvent sheath.

The variations in dissociation constant can also be related to varying degree of solvation ("solvation number") of the anions in water and in pyridine^{5,20}.

4. *Deviations from $E_{\frac{1}{2}}-pK_a^{\text{aq}}$ plots.* Deviations from the regular $E_{\frac{1}{2}}-pK_a^{\text{aq}}$ relationships of Fig. 2 can be interpreted on the basis of the changes in dielectric constant and solvent basicity between pyridine and water, *e.g.* the absence of competing protons in pyridine, and solvent coordination (solvation)⁵. Thus, acids which exist as zwitterions in water (Nos. 9 and 10), are weakened in pyridine compared to other carboxylic acids since the very large excess of pyridine, whose nitrogen is comparable in basicity to those in Nos. 9 and 10, does not allow the latter acids to be protonated.

In the case of dicarboxylic acids, where internal chelation in the monoanion is sterically possible in aqueous solution, the acid for the first dissociation stage (marked I on Fig. 2) is relatively stronger in pyridine than in water, because the cyclic form of the monoanion is more stable in pyridine due to the inability of pyridine to act as a hydrogen donor in hydrogen bonding with the monoanion to stabilize the open form of the latter; the reverse effect is then obviously seen in the case of the second dissociation stage (marked as II).

Where the geometric structure is unfavorable for intramolecularly hydrogen-bonded monoanion formation, the data for both dissociation stages fall on the line, *e.g.* Nos. 15 and 17.

Li(I) as background cation

When the background electrolyte cation is a small ion, which can function as a strong Lewis acid, *e.g.* Li(I), a pronounced levelling effect is seen for the polarographic reduction wave in pyridine. Thus, all Brønsted acids of pK_a^{aq} less than *ca.* 9, as well as such Lewis acids as *n*-butyl bromide, which forms butylpyridinium bromide in pyridine, and ethylpyridinium bromide, produce an identical $E_{\frac{1}{2}}$ of -1.36 ± 0.03 V,

which is the same as that observed for acids of aqueous pK_a less than *ca.* 0 in Et_4NClO_4 background solution (Fig. 2)^{1,6}. (The diffusion current constant in LiClO_4 solution for nitric acid, 3 carboxylic acids, 1 phenol and 2 alkyl bromides is 1.93 ± 0.05 ; sulfuric and phthalic acids show only one wave of similar $E_{1/2}$ with a diffusion current constant which is somewhat less than twice that observed for the monofunctional acids; coulometry at controlled electrode potential of mono- and difunctional acids shows that the reduction involves one electron per acid function in the parent molecule.)

The levelling effect is due to the displacement of the equilibria of eqn. (3)—as a result of the stability of ion-paired species VI—so as to convert a significant portion of the pyridinium species produced by dissolution of any Brønsted acid to pyridinium and perchlorate ions, resulting in a common $E_{1/2}$ value for the pyridinium reduction. This aspect of the model of eqn. (3) is supported by the fact that Et_4NClO_4 solutions of Brønsted acids of pK_a^{aq} less than *ca.* 3, for which the tendency to form associated species II and III would be small and the pyridinium species would exist as the dissociated ion IV, show a levelling off in $E_{1/2}$, which potential, as mentioned, is identical with the common $E_{1/2}$ observed for Brønsted acids in LiClO_4 solution.

Effectively, the coordination system representing SHA (the monosolvated acid) and MB shifts to produce MA and the common reducible species, SHB, where HB (*e.g.* HClO_4) is generally a much stronger aqueous acid than HA, and SHB is generally largely dissociated in pyridine:



This ion-exchange equilibrium in the bulk solution, involving competition between the Lewis acids H(I) and Li(I) to form predominantly slightly dissociated LiA, has been evaluated from potential shifts, conductivity and spectra, and is related to the stability of Li(I) coordination with anions. The detailed derivations of the equations used to evaluate the exchange equilibria of eqn. (10) are given in ref. 6.

Ion-exchange reactions of this and similar types probably play important roles in the polarography of ionic or charged reducible species in solvents of low dielectric constant. The analytical implications of these equilibria have been discussed elsewhere^{1,5,6}.

Thus, phthalic acid produces one polarographic wave in pyridine (Et_4NClO_4 background) corresponding to a $1e$ process, which indicates that the monoanion in pyridine is sufficiently stable to resist further removal of an acid proton to form a second pyridinium species. The addition of small amounts of Li(I) to the previous solution produces a second wave, which can be attributed to the formation of strongly associated dilithium phthalate and additional pyridinium perchlorate, accompanied by disruption of the hydrogen bonding in the cyclic hydrogen phthalate ion (Fig. 4).

The lithium phthalate wave corresponds to the passage of two electrons per phthalate molecule.

Peover and Davies²¹ report the effects of association of Li(I) with the semiquinone and dinegative ion of anthraquinone on the polarographic behavior of the latter compound in DMF (0.1 M Et_4NClO_4).

1. Potentiometry. Potentiometric measurements on solutions of acids in pyridine are explicable on the basis that the glass electrode potential in pyridine reflects the proton, *i.e.* pyrH^+ , availability⁶. The order of potentials for a group of acids (HNO_3 , carboxylic, phenolic) in pure pyridine (Fig. 5) is generally similar to that of the

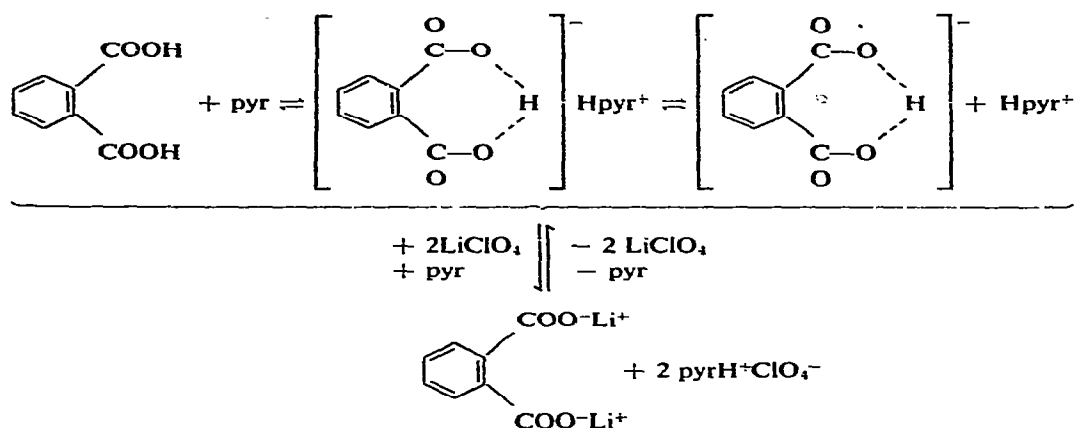


Fig. 4. Equilibria involving phthalic acid in pyridine soln. in the presence and absence of Li(I).

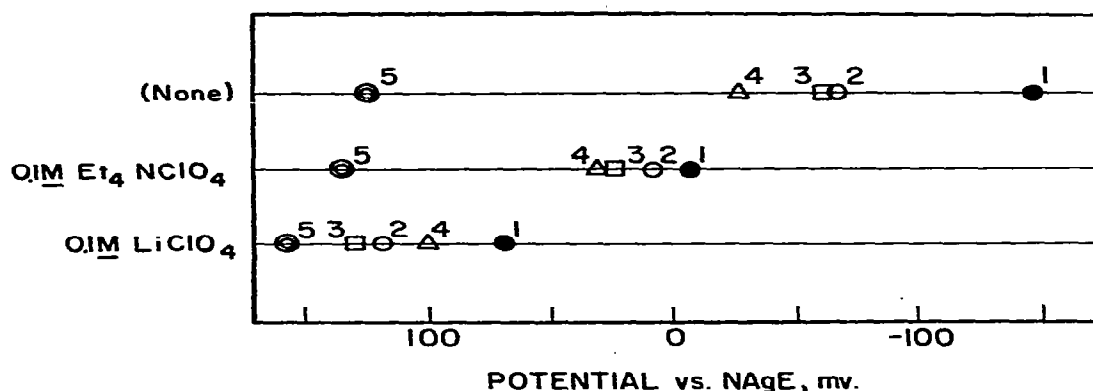


Fig. 5. Potential of a glass electrode in pyridine containing $9.9 \times 10^{-3} M$ acid in the presence or absence of $0.1 M$ perchlorate. Acids: (1) phenol, (2) HOAc, (3) benzoic acid, (4) *p*-nitrophenol, (5) HNO_3 .

pK_a^{aq} values except that the phenol appears as a stronger acid, *i.e.* its behavior parallels that of phenols on titration and on polarography in pyridine compared to that of carboxylic acids.

In Et_4NClO_4 solution, the potentials shift in a more acidic direction with an unchanged order; in LiClO_4 solution, there is a still greater shift with a more pronounced levelling effect.

Calculations involving the potentiometric measurements, including estimation of equilibrium constants, are given in ref. 6.

An interesting problem is the fact that the dissociation constant for LiClO_4 has been reported in an apparently competent study²² to be about $\frac{1}{13}$ of that for pyr-HClO_4 , whereas our conductivity measurements and Fuoss plots indicate the dissociation constant for LiClO_4 to be larger than—or, at least, equal to—that of pyr-HClO_4 ^{6,23}. Our data are in good agreement with those of Davies¹⁷.

2. *Spectrophotometry.* Spectrophotometric measurements on pyridine solutions of appropriate Brønsted acids as the Et_4NClO_4 content is replaced by LiClO_4 allow evaluation of the shift from the "acid" form (pyridinium salt: pyrHA) to the "anion" form (free anion plus ion-paired LiA); an isobestic point is seen⁶ (Fig. 6).

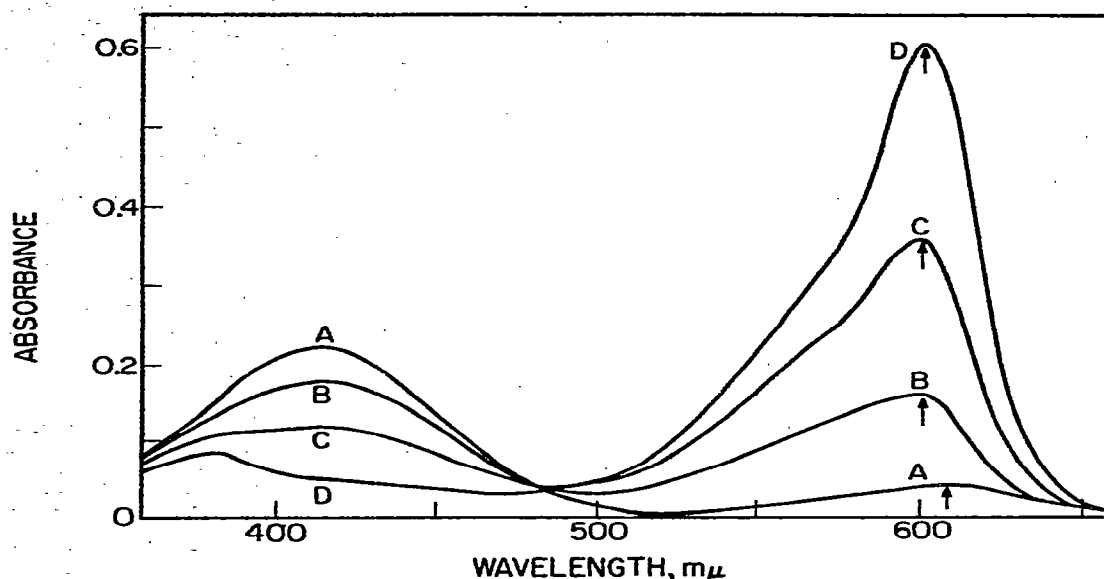


Fig. 6. Spectra of $1 \times 10^{-5} M$ bromocresol purple in Et_4NClO_4 , LiClO_4 and their mixtures (total salt concn. = $0.1 M$). LiClO_4 concn.: (A) 0, (B) 16.7, (C) 47.4, (D) 100.0 mM. Arrows indicate maxima.

The equilibrium constant found for the reaction of eqn. (10), where HA was originally $7.7 \times 10^{-5} M$ *p*-nitrophenol (PNP) and MB was $0-0.327 M$ LiClO_4 , is $(3.80 \pm 0.51) \times 10^{-5}$. Equations for the calculation of the equilibrium of eqn. (10) from spectrophotometric data are given in ref. 6.

Addition of salts to solutions of *p*-nitrophenol (PNP) in pyridine produces a new absorption peak which is due to the formation of the anionic form of PNP and the exact position of whose λ_{max} depends on the cation of the added salt⁶. Acetates and benzoates have a particularly strong tendency to form the anion form of PNP as indicated by the large absorbance. For the salts of stronger aqueous acids, the tendency to produce the anion form decreases in the order: lithium salts > sodium salts > tetraalkylammonium salts. This order is probably related to the increasing radii of the cations and the consequently increasing dissociation constants of the *p*-nitrophenolates.

EFFECT OF SOLVENT COMPOSITION

The influence of the nature of the solvent on the electrochemical reduction mechanism is exemplified by the variations in plots of $E_{\frac{1}{2}}\epsilon$ (ϵ = dielectric constant) and $I\eta^{\frac{1}{2}}$ (I = diffusion current constant; η = solution viscosity) vs. solvent composition as pyridine is replaced by water (Figs. 7 and 8)²⁴. The results of such progressive water addition to pyridine solution support the pyridine ring reduction mechanism. (The product $\epsilon E_{\frac{1}{2}}$ is used since $E_{\frac{1}{2}}$ of an ion varies as ϵ^{-1} of the solution on the Bockris model; the use of $I\eta^{\frac{1}{2}}$ is a similar correction for the effect of the viscosity of the medium on the diffusion coefficient.)

In the case of a 1 mM benzoic acid solution ($0.1 M$ in LiClO_4), only the pyridine ring is reduced up to 8% water by volume, when there begins to be also proton reduction via the familiar catalytic hydrogen evolution mechanism. The latter becomes

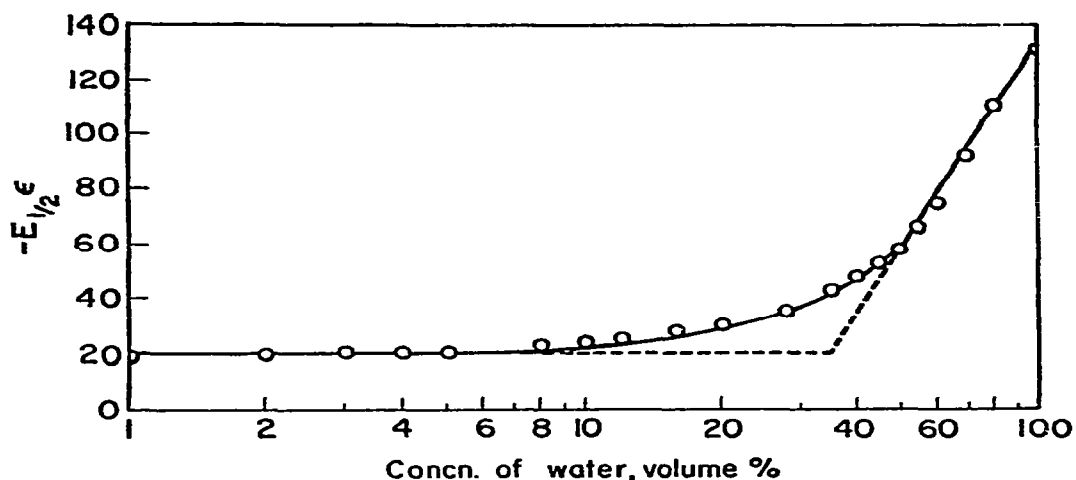


Fig. 7. Variation with water content of the product, $E_{1/2} \times \epsilon$, for reduction of pyridinium ion in pyridine-water solns.

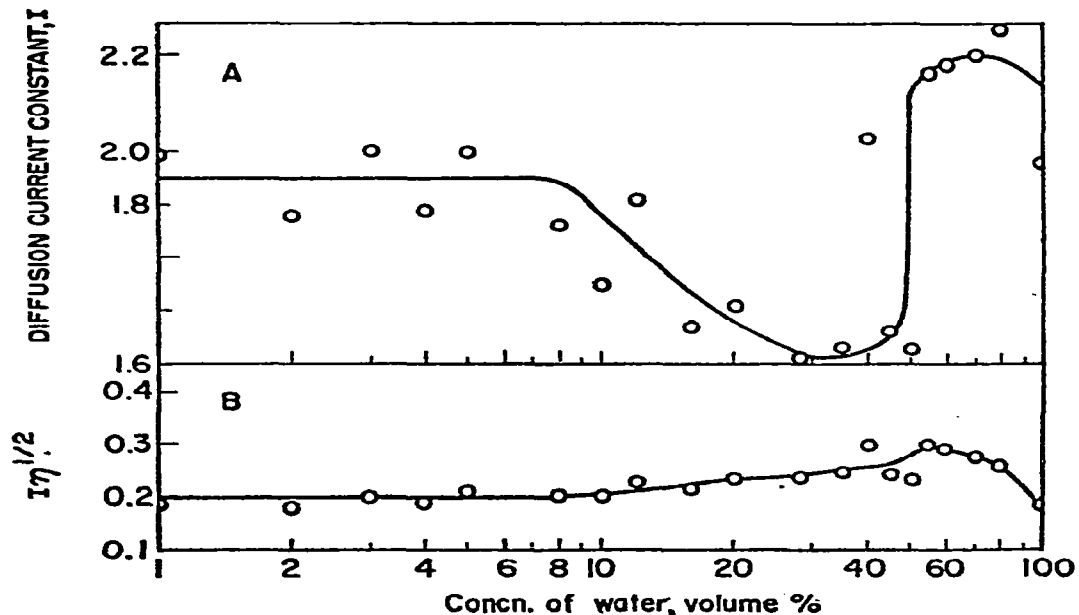


Fig. 8. Effect of water on polarographic current for reduction of pyridinium ion in pyridine-water solns. (A) Diffusion current constant, $I = i_d / C m^3 t^k$, (B) $I \eta^k$.

the only process operative when the water exceeds 50%; the shift in predominant mechanism occurs at *ca.* 35% H_2O .

The relative effects of complexation of metal ions by solvent pyridine and background anion are evident from the differences in half-wave potential data in water and in pyridine, when referred to a common reference electrode²⁵ (Table 1).

Even though unknown liquid junction potentials introduce uncertainties, it is apparent that the $E_{1/2}$ values are less different where complexation involving the background anion is not involved, *e.g.* in nitrate media. Similarly, although all of the diffusion current constants are less in pyridine than in water, the relative decrease is greater where complexation is more pronounced.

TABLE I

Cation	Anion present	$E_{\frac{1}{2}}$ vs. SCE/V		
		pyr	H ₂ O	Difference
Tl(I)	NO ₃ ⁻	-0.39	-0.46	+0.07
	Cl ⁻	-0.39	-0.46	+0.07
Zn(II)	Cl ⁻	-1.52	-1.00	-0.52
Pb(II)	NO ₃ ⁻	-0.52	-0.39	-0.13
	Cl ⁻	-0.87	-0.42	-0.45

ALKALI METAL IONS AS SOLUTE SPECIES

Na(I), K(I), Rb(I) and Cs(I) are reversible reduced electrochemically in pyridine (Et₄NClO₄ background); the lack of concentration-dependence of $E_{\frac{1}{2}}$ suggests that ion-pair formation is not a controlling factor²⁶.

Polarographic reduction of Li(I) shows some irreversibility. On controlled electrode potential electrolysis, one electron is consumed per lithium atom in the test solution but lithium is absent in the mercury pool electrode. This, plus other evidence, points to the reduction of one solvent molecule per metal atom in the primary solvation sheath rather than direct reduction of the metal atom. Cyclic voltammograms of Li(I) have a double reduction peak; the first peak may involve reduction of a pyridine molecule in the Li(I) solvation sheath; the second peak may involve reduction of pyridine in a (pyr→H₂O)_nLi(I) species.

An attempted calculation of p in the overall reaction



from the shift in solution discharge potential for a 0.1 M LiClO₄ solution in pyridine as the pyridine is displaced by water gave a value of 5.9, compared to the generally expected²⁴ coordination number of six for Li(I). The data indicate that Li(I) is present only as the pyridine complex at less than 12% water and almost entirely as the *aquo* complex in solutions containing more than 50% water.

The diffusion current constants of the alkali metal ions in pyridine are considerably smaller than those in water (viscosities at 25°: pyridine 0.88 cP; water 0.89 cP*) and can be correlated with the ionic conductance of alkali metal salts in pyridine, indicating strong solvation of the ions by pyridine with the resulting ion-solvent complexes being more bulky than those in water²⁶.

ALUMINUM(III) AS SOLUTE SPECIES

A solution of a strong Lewis acid such as Al(III) gives a polarographic reduction wave in Et₄NClO₄ and LiClO₄ solutions, whose $E_{\frac{1}{2}}$ is comparable to those observed for strong Brønsted acids and whose current corresponds to the passage of two electrons per Al(III) ion^{2,4,25}. On controlled potential electrolysis, where a coulometric end-point corresponding to $n=2$ is obtained, the Al(III) is recovered unchanged and a reactive species is formed which produces a polymer on exposure to air and water; one electron is transferred per pyridine molecule reduced^{2,4}.

* 1 cP = 10³ kg m⁻¹ s⁻¹

In this case, as in that of the Brønsted acids, it can be postulated that pyridine molecules solvating or complexing Al(III) are opened by $1e$ attacks on a bond adjacent to the nitrogen atom in the pyridine ring; this electroreduction is facilitated by the electron-withdrawing effect of Al(III) on the nitrogen and the resulting free radical anions are stabilized by coordination with the Al(III). A similar process may well occur with Li(I) with formation of a strongly associated free radical anion-lithium(I) complex, analogous to the metal ketyls frequently postulated in nonaqueous electrochemistry.

EXPERIMENTAL

The details of the experimental studies involving polarography and related electrochemical techniques, conductometry, potentiometry and spectrophotometry have been described^{1,2,5,6,16,25,26}.

Polarographic measurements were made using (a) three-electrode configurations in properly isolated three-compartment cells and (b) operational amplifier-based equipment which adequately corrected for the resistance in the solution systems. The reference electrode was silver immersed in a 1 M AgNO₃ solution in pyridine, which electrode has a potential of 0.03–0.09 V *vs.* the aqueous saturated calomel electrode (liquid junction potential included), depending on the nature of the bridge between the pyridine and aqueous solutions^{25,26}.

The pyridine used was generally purified by zone fractional crystallization²⁷, which produced a product containing (a) less than 0.005% H₂O as determined by Karl Fischer titration and mass spectrometric measurements, and (b) less than 10^{-5} M concentration of polarographically active impurities as determined from electrochemical measurements, *e.g.* drop time curves. The water content during an experiment was generally below 0.10% as determined by operational tests involving water-sensitive phenomena.

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SUMMARY

The nature of the interaction between MA and solvent pyridine to form the pyridinium species, pyrMA, is being investigated on the basis of the electrochemical reduction of the pyridinium moiety; M is a Lewis acid, *e.g.*, a proton, a metal ion, a tetraalkylammonium ion or an alkyl group. The anion A influences the various equilibria involving the pyridinium species through (a) its chemical type, *e.g.*, whether derived from a carboxylic acid, a phenol or a heterocyclic ring, (b) the contribution of the dispersion effect to the medium effect on free energy in connection with specific solute-solvent interaction, (c) the association of M and A in the MA species, *e.g.*, as measured in pyridine, water and other solvents, and (d) interactions involving other ions present such as those of the background electrolyte in polarography. Ion

association and ion exchange involving competitive Lewis acids are important and can be evaluated by spectrophotometric, potentiometric and conductometric measurements, as well as by polarography. The overall influence of the solvent on the pyridinium equilibria is illustrated by the effect of the addition of water.

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