POLAROGRAPHIC REDUCTION OF PYRIDINIUM ION IN PYRIDINE

TETRAETHYLAMMONIUM PERCHLORATE AS BACKGROUND ELECTROLYTE

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As part of the current interest in the use of nonaqueous solvents for analytical techniques, the utility of pyridine as a polarographic and voltammetric solvent is being systematically investigated. Although the dielectric constant of pyridine is quite low (12.3 at 25°), it is a good solvent for a large number of inorganic and organic substances; this solubility compensates for the low dielectric constant, for it is possible to dissolve sufficient "inert" electrolyte to lower the solution resistance to a convenient level and to suppress the effect of migration of the electroactive ions. Lithium salts are among the most soluble and perchlorates are among the most completely dissociated of salts in nonaqueous solvents; these have been extensively used as backgound electrolytes for polarography in organic solvents.

Lithium perchlorate (0.1 *M*) was used in the investigation of the polarographic reduction of pyridinium ion produced by the Lewis acid–base reaction of solvent pyridine with Brønsted acids of aqueous pK_a less than 9, Lewis acids such as alkyl halides, and alkylpyridinium salts, which allowed the direct analytical determination of such acids[1].

The investigation of another background electrolyte, specifically 0.1 *M* tetraethylammonium perchlorate, for the reduction of pyridinium ion was undertaken in hope of obtaining more information on possible ion-pair formation between the acid anion and the pyridinium ion, as well as in further improving the analytical procedure. The perchlorate anion is commonly used in background electrolytes because of its lack of surface activity and low tendency to ion-pairing. The tetraethylammonium ion is considerably larger in ionic radius than lithium or other alkali metal ions and thus is less prone to ion-pair formation; it is also less surface-active than the larger tetra-*n*-butylammonium ion and, in general, would have less effect on polarograms than similar ions of larger *n*-alkyl groups[2].

EXPERIMENTAL

Reagents

Merck reagent-grade pyridine was dried with Linde molecular sieves type 4A[3]. $LiClO_4$ (G. F. Smith, anhydrous), Et_4NClO_4 (Eastman white label), C_6H_5COOH (National Bureau of Standards Standard Sample No. 39g), $LiNO_3$ (Baker's Analyzed), C_6H_5COOEt (Matheson), C_6H_5COONa (Merck U.S.P.), CH_3COOH (DuPont reagent grade), LiOAc (Fisher Purified), and $C_6H_5COONEt_4$ (Southwestern Analytical Chem-

TABLE I

POLAROGRAPHIC REDUCTION OF PYRIDINIUM ION IN PYRIDINE SOLUTION AT 25° IN THE PRESENCE OF VARIOUS ADDED SUBSTANCES

Pyridinium ion precursor & (Concn., mM)	*Background electrolyte (0.1 M)*	*Compound added & (Concn., mM)*	*No. of runs*	$-E_{\frac{1}{2}}$ (V) *Prewave*	*Main wave*	*Notes*[b]
C_6H_5COOH (0.1–10)	Et_4NClO_4		40	None	1.62 ±0.01	$i_d/C = 3.25\ \mu A/mM$
C_6H_5COOH (1)	Et_4NClO_4	$LiClO_4$ (1–10)	13	None	1.62–1.41	$E_{\frac{1}{2}}/\log C = 106$
C_6H_5COOH (1)	$LiClO_4$	Et_4NClO_4 (0–8)	6	1.20–1.16	1.31–1.38	Waves merge: $E_{\frac{1}{2}}/\log C = -17$
C_6H_5COOH (1)	$LiClO_4$	Et_4NClO_4 (0–10)	22	1.09–1.12	1.30–1.33	No merging: $E_{\frac{1}{2}}/\log C = -13$
C_6H_5COOH (3)	Et_4NClO_4	ØCOONEt$_4$ (0–8)	18	None	1.67 ± 0.02	
C_6H_5COOH (2)	$LiClO_4$	ØCOONEt$_4$ (0–7)	21	1.09 ± 0.02	1.35 ± 0.01	
—	Et_4NClO_4	ØCOONEt$_4$ (0–8)	15	None	1.67 ± 0.02	$i_d/C = 0.73\ \mu A/mM$; see text
HOAc (32)	Et_4NClO_4	ØCOONEt$_4$ (0–6)	21	None	1.72 ± 0.02	
—	Et_4NClO_4	ØCOONa (0–5)	18	None	None	No waves; $E_{discharge} = -1.9$ V
C_6H_5COOH (3)	Et_4NClO_4	ØCOONa (0–5)	21	None	1.62 ± 0.01	i_d is constant
C_6H_5COOH (3)	Et_4NClO_4	ØCOOEt (0–4)	12	None	1.60 ± 0.08	i_d is constant
—	Et_4NClO_4	ØCOOEt (0–10)	6	None	None	No waves: $E_{discharge}$ does not shift
HOAc (3.2)	Et_4NClO_4	LiOAc (0–6.7)	21	None	1.72–1.58	i_d is constant; $E_{\frac{1}{2}}/\log C = 110$
$HpyrNO_3$ (2)	Et_4NClO_4	$LiNO_3$ (0–7.1)	18	1.07 ± 0.01	1.31 ± 0.01	i_d and $E_{\frac{1}{2}}$ are constant
C_6H_5COOH (4)[a]	Et_4NClO_4	ØCOONEt$_4$ (0–6.25)	13	None	1.65 ± 0.08	

[a] Temperature for this set of runs: 40°.

[b] C refers to the concentration in millimoles per liter of the compound added (Column 3); number is in mV per log millimolar concentration.

icals) were used without further purification. Pyridinium nitrate was prepared as described previously[1]. Argon (99.99% pure), used for deoxygenation of solutions, was first dried over Drierite and then equilibrated with pyridine at the temperature of use before being bubbled through the solution. The mercury used in the D.M.E. was triple-distilled.

Apparatus

Polarograms, obtained with a three-electrode configuration, were recorded with a Sargent Model XV Polarograph, equipped with a Sargent Model A IR Compensator. The D.M.E. was made from marine barometer tubing; $m^{2/3}t^{1/6}$ in 0.1 M Et_4NClO_4 at 0.00 V, 25° and h=68.6 cm was 1.462 (m=1.212 mg/sec, t=4.51 sec). The 1 M $AgNO_3$–Ag reference electrode, NAgE[3], and the counter electrode (platinum wire, 26 gauge by 8 in.) were inserted in separate compartments (containing background electrolyte) of a jacketed three-compartment cell, which permitted bubbling argon through the solution before the run and passing argon over the solution during the run; the third compartment, in which the D.M.E. was inserted, was filled with the test solution. Gels of methyl cellulose containing 0.1 M Et_4NClO_4 in pyridine and glass frits separated the compartments. The temperature was regulated to 25±0.2°, except where otherwise indicated.

Procedures

Stock solutions of the background electrolytes were prepared by dissolving weighed quantities and diluting to known volume. Stock solutions of other reagents were prepared by dissolving weighed quantities and diluting to known volume with stock background solution. Test solutions were prepared by pipetting appropriate amounts of reagent stock solutions into 10-ml volumetric flasks and diluting to volume with background solution. Argon was bubbled through each test solution for 15 min; the D.M.E. was then inserted, and the polarogram taken with argon passing over the solution. The starting potential and current sensitivity were adjusted in each case on the basis of the portion of the polarogram of particular interest.

Potentials reported are *vs.* the NAgE and are presumably corrected for potential drop due to solution resistance.

Potentiometric titration of the acidity of the tetraethylammonium benzoate was carried out in aqueous solution with a Leeds & Northrup Model 7401 pH meter with a glass indicating electrode and a saturated calomel reference electrode, using standard 0.1 N sodium hydroxide and magnetic stirring.

RESULTS AND DISCUSSION

Data for various solution compositions and experiments subsequently described are summarized in Table I. Representative polarograms are shown in Fig. 1.

Comparison of Et_4NClO_4 and $LiClO_4$ as background electrolytes

The properties of Et_4NClO_4 and of $LiClO_4$ as background electrolytes for reduction in pyridine are compared in Table II. Solutions of Et_4NClO_4 have an appreciably more negative decomposition potential, as well as a markedly lower resistance. A prewave, which is attributed to impurities in the pyridine, appeared at *ca.* −2.1 V in

Et_4NClO_4 solution; its height varied between 0.3 and 1.0 µA with an average of 0.7 µA. In addition, a wave of negligible magnitude (average, 0.13 µA) usually appeared at approximately −0.8 V; since this wave is at such a positive potential compared to that of the pyridinium ion reduction, it was not studied further. A similar wave appeared in 0.1 *M* $LiClO_4$ but at a slightly more positive potential. This minute wave is probably due to impurities in the solvent or a small amount of dissolved oxygen; the use of Et_4NClO_4, which had been recrystallized from acetonitrile and benzene, did not appreciably change the height.

Electrocapillary curves of 0.1 *M* Et_4NClO_4 solutions are rather flat on top, which may indicate some sort of adsorption phenomenon; the electrocapillary maximum is at about −0.55 V.

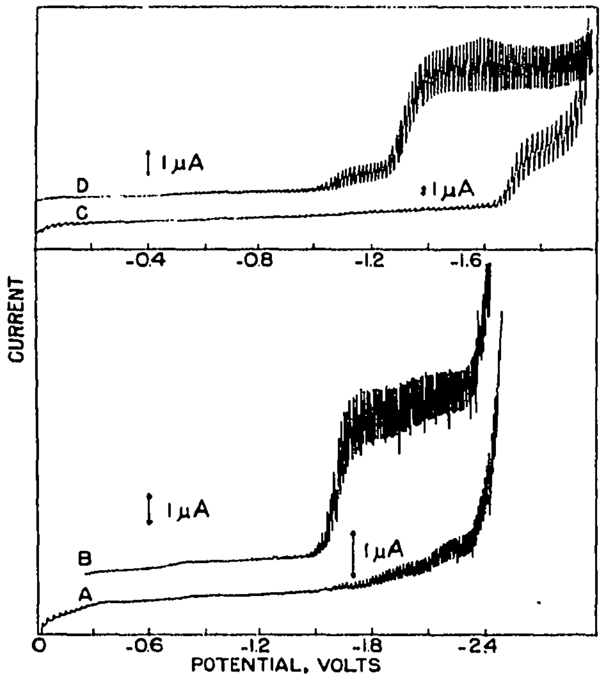

Fig. 1. Polarograms of background electrolytes and pyridinium reduction in pyridine. (A) 0.1 *M* Et_4NClO_4; (B) 2 m*M* benzoic acid in 0.1 *M* Et_4NClO_4; (C) 0.1 *M* $LiClO_4$; (D) 2 m*M* benzoic acid in 0.1 *M* $LiClO_4$.

TABLE II

COMPARISON OF $LiClO_4$ AND Et_4NClO_4 AS BACKGROUND ELECTROLYTES IN PYRIDINE SOLUTION AT 25°

Background	*No. of runs*	*Resistance (kohm)*	*Impurity wave*		*Prewave*		*Decomposition potential*[a] *(V)*
			$-E_{\frac{1}{2}}$ *(V)*	i_d *(µA)*	$-E_{\frac{1}{2}}$ *(V)*	i_d *(µA)*	
0.1 *M* $LiClO_4$	11	7	0.56 ± 0.04	0.21 ± 0.13	1.70 ± 0.02	0.42 ± 0.08	−1.98 ± 0.03
0.1 *M* Et_4NClO_4	16	4.2	0.77 ± 0.06	0.13 ± 0.05	2.09 ± 0.10	0.66 ± 0.21	−2.41 ± 0.10

[a] Potential corresponding to intersection of extrapolated residual current and decomposition current lines.

Pyridinium reduction wave

On addition of benzoic acid to a 0.1 *M* Et_4NClO_4 background solution, a wave ($E_{\frac{1}{2}} = -1.62 \pm 0.01$ V) was produced, whose height increased linearly with acid concentration and which presumably was due to reduction of pyridinium ion produced by reaction of pyridine with benzoic acid. Its $E_{\frac{1}{2}}$ differed appreciably from that reported for the reduction of the same species with 0.1 *M* $LiClO_4$ as background electrolyte ($E_{\frac{1}{2}} = -1.36 \pm 0.04$ V)[1]. In addition, no prewave appeared before the main reduction wave, as was observed when 0.1 *M* $LiClO_4$ was used. The diffusion current constant, I, in 0.1 *M* Et_4NClO_4 solution is 1.40 ± 0.22 compared to 2.23 ± 0.25 (sum of wave and prewave) in 0.1 *M* $LiClO_4$ solution.

A plot of log h *vs.* log i_d for the wave produced by benzoic acid in Et_4NClO_4 solution for 4 values of the height of the mercury column, h, between 55 and 70 cm was a straight line with a slope of 0.68. In spite of some erratic behavior at 40°, the temperature coefficient of the limiting current was about 2%/degree. Since a square-root dependence of i on h and a temperature coefficient between 1 and 2%/degree are usually indicative of diffusion control, the current-producing reaction would appear to be diffusion-controlled.

Because of the appreciable difference in $E_{\frac{1}{2}}$ for the reduction of pyridinium ion in the 2 background electrolytes and the presence of a prewave just preceding the main wave for this reduction only in 0.1 *M* $LiClO_4$, the effect of addition of one background electrolyte to the other was investigated. On addition of 1–10 m*M* $LiClO_4$ to 0.1 *M* Et_4NClO_4 solution containing 1 m*M* benzoic acid, the $E_{\frac{1}{2}}$ shifted toward that found in 0.1 *M* $LiClO_4$ alone. A plot of $E_{\frac{1}{2}}$ *vs.* log [$LiClO_4$] was a straight line with a slope of 0.106 V per ten-fold change in $LiClO_4$ concentration. No prewave to the pyridinium reduction wave appeared on addition of the $LiClO_4$.

On adding Et_4NClO_4 to a solution 1 m*M* in benzoic acid and 0.1 *M* in $LiClO_4$, the 2 waves corresponding to the pyridinium prewave and the main pyridinium reduction seemed to merge, *i.e.*, the prewave became less sharply defined; the total current did not change. $E_{\frac{1}{2}}$ for both main pyridinium wave and prewave shifted to slightly more negative potentials on the addition of Et_4NClO_4 (a plot of $E_{\frac{1}{2}}$ *vs.* log [Et_4NClO_4] was a straight line with a slope of −0.017 V).

When, however, a separate solution was prepared for each Et_4NClO_4 concentration (0–8 m*M*), prewave and main wave remained separate and well defined. Again, the $E_{\frac{1}{2}}$ values of both waves became more negative; a plot of $E_{\frac{1}{2}}$ *vs.* log [Et_4NClO_4] was a straight line whose slope was −0.013 V, which is quite close to the previous value of −0.017 V. Thus, although the merging of the waves is not consistent, the magnitude of the shift in $E_{\frac{1}{2}}$ is. This shift, however, is quite small and it may be concluded that Et_4NClO_4 in concentration up to 10 m*M* has very little effect on $E_{\frac{1}{2}}$ in 0.1 *M* $LiClO_4$.

Effect of anion addition

The effect of addition of an excess of the anion of the pyridinium salt present was investigated; if ion-pairing were an appreciable factor, the limiting current for the pyridinium wave would be expected to decrease with increasing anion concentration.

Addition of sodium benzoate (0–5 m*M*) in 0.1 *M* Et_4NClO_4 solution, which was 3 m*M* in benzoic acid, produced no change in diffusion current; the maximum change in i_d was about 0.5 μA in a current of 7.13 μA at 0.0 mM added benzoate; the average i_d for the 0–5 mM range was 7.18 μA. $E_{\frac{1}{2}}$ remained constant at −1.62 V, but maxima appeared on the pyridinium wave. No wave appeared at −1.6 V when the same salt was added in 1 mM concentration in the absence of benzoic acid, but both the impurity prewave and the discharge potential shifted by about 0.4 V to more positive potentials; this shift may be due to the presence of sodium. No shift in the electrocapillary maximum was observed from the current oscillations on the polarograms.

The results on addition of ethyl benzoate (0–4 mM), in both the absence and presence of benzoic acid, were similar to those for sodium benzoate with the exception that the discharge potential was not shifted, even at 10 mM ethyl benzoate.

Two other acid–salt systems were examined. On addition of lithium acetate (0–6.7 mM) to solutions of 3 mM acetic acid in 0.1 M Et_4NClO_4, i_d remained constant, but $E_{\frac{1}{2}}$ became more positive; a plot of $E_{\frac{1}{2}}$ *vs.* log [LiOAc] was a straight line of slope +0.110 V/ten-fold concentration change, which is quite comparable to the slope (+0.106) for the addition of $LiClO_4$ to a solution of benzoic acid in 0.1 M Et_4NClO_4. The change in $E_{\frac{1}{2}}$ is consequently due to the addition of lithium(I).

The waves in solutions of pyridinium nitrate in 0.1 M Et_4NClO_4 closely resemble those obtained when 0.1 M $LiClO_4$ is used as background electrolyte (Table III). When lithium nitrate (0–7.1 mM) was added to pyridinium nitrate in 0.1 M Et_4NClO_4, both $E_{\frac{1}{2}}$ and i_d remained essentially constant.

TABLE III

COMPARISON OF BEHAVIOR OF PYRIDINIUM ACETATE, PYRIDINIUM NITRATE AND PYRIDINIUM BENZOATE IN PYRIDINE

Pyridinium species	*Background*	$-E_{\frac{1}{2}}$ *(V) (prewave)*	$-E_{\frac{1}{2}}$ *(V) (main wave)*	I[a]
HOAc	0.1 M $LiClO_4$[b]	1.12 ± 0.04	1.36 ± 0.07	2.16 ± 0.10
	0.1 M Et_4NClO_4	(none)	1.72 ± 0.02	1.82 ± 0.39
$HpyrNO_3$	0.1 M $LiClO_4$[b]	1.13 ± 0.05	1.39 ± 0.03	2.01 ± 0.07
	0.1 M Et_4NClO_4	1.07 ± 0.010	1.31 ± 0.01	1.92 ± 0.07
Benzoic acid	0.1 M $LiClO_4$[c]	1.13 ± 0.05	1.39 ± 0.03	2.01 ± 0.07
	0.1 M Et_4NClO_4	(none)	1.62 ± 0.01	1.40 ± 0.22

[a] $I = i_d/Cm^{2/3}t^{1/6}$; I represents the sum of the main wave and prewave, where the latter appeared.
[b] Data taken from ref. 1.
[c] Corresponding values in ref. 1 are −1.10 ± 0.03 V, −1.36 ± 0.04 V and 2.23 ± 0.25 V.

Addition of tetraethylammonium benzoate (0–8 mM) to solutions containing 3 mM benzoic acid in 0.1 M Et_4NClO_4, resulted in a linear increase of i_d with concentration of the benzoate salt, equivalent to 0.93 μA/mmole; $E_{\frac{1}{2}}$ became slightly more negative, *i.e.*, from −1.65 V at 0 mM quaternary salt to −1.70 V at 8 mM. Potentiometric titration of the tetraethylammonium benzoate in aqueous solution with a standard sodium hydroxide solution produced a titration curve with a well-defined end-point, which indicated that the benzoate salt contained an acid impurity equivalent to 16.7% benzoic acid by weight. On a molar basis, 16.7% benzoic acid corresponds to 1 mole of acid impurity for each 2 moles of tetraethylammonium benzoate in the preparation. This is in agreement with the current–concentration ratios of 3.25 μA/mmole for benzoic acid and 0.93 μA/mmole for the benzoate.

CONCLUSIONS

Tetraethylammonium perchlorate is at least as good, if not better, than lithium perchlorate as a background electrolyte for the reduction of pyridinium ion in pyridine. Its decomposition potential in 0.1 M solution is much more negative than that of the corresponding lithium solution, which makes available a greater potential range. There is a slight problem in obtaining pure samples of Et_4NClO_4, but the reduction wave observed for the impurity in the sample used occurs at a potential far removed from that of pyridinium ion reduction. The fact that the prewave observed in $LiClO_4$ solutions does not always appear in Et_4NClO_4 solution adds to the ease of data interpretation, although the cause for the difference is not yet known.

The wave patterns produced by benzoic acid, pyridinium nitrate, and acetic acid in 0.1 M Et_4NClO_4 are not all similar; the variation in $E_{\frac{1}{2}}$ for reduction of the pyridinium ion produced by each of these acids (Table III) may have obvious analytical value if other electroactive species are present in the sample. A prewave appears only in solutions of pyridinium nitrate.

The addition of lithium(I) in the form of acetate or perchlorate to Et_4NClO_4 solutions shifts $E_{\frac{1}{2}}$ for the pyridinium wave to more positive potential at a rate of about 0.1 V per unit change in the log of the lithium(I) concentration. Lithium nitrate did not seem to have the same effect, which may indicate that $LiNO_3$ is more strongly ion-paired than the other 2 lithium(I) salts. Addition of sodium(I) as sodium benzoate shifts the prewave and discharge potentials of Et_4NClO_4 when this substance is used as the background electrolyte.

No change in i_d for the LiOAc–HOAc, pyridinium nitrate–$LiNO_3$, benzoic acid–sodium benzoate, and benzoic acid–ethyl benzoate systems was observed on adding the indicated salt containing the acid anion; furthermore, no shift in $E_{\frac{1}{2}}$ could be associated with the addition of the excess acid anion. The fact that excess anion has no noticeable effect on the polarographic reduction of the pyridinium ion, would indicate either a lack of ion association effects between anion and pyridinium ion, or formation of a stable ion-pair. In this regard, those species most difficult to reduce in 0.1 M Et_4NClO_4, as indicated by their more negative half-wave potentials (Table III), *i.e.*, those derived from acetic and benzoic acids, also have lower diffusion current-constant values. Such a phenomenon is compatible with a situation in which the ions involved are highly associated in solution and hence are both less easily reduced and less available for reduction.

The potential phenomena summarized in the previous paragraphs may be due to electrocapillary effects associated with the nature of the double layer in Et_4NClO_4 solution; in $LiClO_4$ solution, the presence of the large excess of lithium(I) would seem to "level" such potential phenomena. For example, the electrocapillary maximum (E.C.M.) occurs at −0.35 V in 0.1 M $LiClO_4$ and at −0.55 V in 0.1 M Et_4NClO_4. The shifts in $E_{\frac{1}{2}}$ for the main pyridinium reduction wave in going from $LiClO_4$ to Et_4NClO_4 solution (Table III) are -0.36 ± 0.08 V for pyridinium acetate, $+0.08 \pm 0.04$ V for pyridinium nitrate and -0.22 ± 0.04 V for pyridinium benzoate. These shifts parallel the E.C.M. shift in 2 of the 3 cases. The third case is that involving nitrate, whose solutions also show differences in other respects, as discussed.

In connection with the behavior encountered in the present study it is interesting to note that LARSON AND IWAMOTO[4] observed that $E_{\frac{1}{2}}$ for metal ion reductions in acetonitrile varied with $LiClO_4$ concentration, but not with Et_4NClO_4 concentration; this difference in behavior of the two background electrolytes was ascribed to a probable difference in nature of the "solvated" cations.

Conductance data for solutions of salts in pyridine, summarized by DRAGO AND PURCELL[5], indicate the extensive association of such electrolytes in pyridine, presumably because of its low dielectric constant. The equivalent conductances at infinite dilution, Λ_0, and association constants (in parentheses) of some salts of interest are pyridinium nitrate 102 (19,600), silver nitrate 87 (1070) and sodium nitrate 80. DRAGO AND PURCELL conclude that "anion solvation through specific interaction does not occur in pyridine but the cation Li^+ is co-ordinated and solvated more than Na^+ and K^+".

The data (polarographic and titrimetric) for tetraethylammonium benzoate indicate that the polarographic reduction of pyridinium ion can be used to determine the free acid in such ester preparations.

Because of the variation in $E_{\frac{1}{2}}$ for pyridinium ion reduction in Et_4NClO_4 solution with anion nature and in the presence of alkali metal ions, the use of $LiClO_4$ as background electrolyte would be advisable in determining total acid concentration of unknown samples[1].

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SUMMARY

Tetraethylammonium perchlorate, compared to lithium perchlorate as background electrolyte for the reduction of pyridinium ion in pyridine, is effective over a wider potential range, but is more difficult to obtain in a pure state; slight amounts of impurities do not, however, affect the pyridinium wave. The pyridinium wave produced in 0.1 M Et_4NClO_4 may occur at a more negative potential than the main pyridinium wave in 0.1 M $LiClO_4$, depending on the source of the pyridinium ion, but still appears to be due to a diffusion-controlled reduction, whose limiting current is linearly proportional to concentration; the prewave observed in $LiClO_4$ background generally does not appear in Et_4NClO_4 background. Specific differences in the effect of Li(I), Na(I) and Et_4N(I) background cation appear to be due to electrocapillary phenomena and perhaps to the extent of solvation of the ions. The constancy of current for solutions containing acetic acid with added acetate, pyridinium nitrate with added nitrate, and benzoic acid with added benzoate indicate that the pyridinium reduction is independent of anion concentration.

RÉSUMÉ

Les auteurs ont examiné la réduction de l'ion pyridinium dans la pyridine en comparant le perchlorate de tétraéthylammonium (Et_4NClO_4) au perchlorate de lithium. La vague du pyridinium obtenue avec Et_4NClO_4 0.1 M peut se produire à un potentiel plus négatif que celle obtenue avec $LiClO_4$ 0.1 M. La prévague observée avec $LiClO_4$ comme solution de base n'apparaît généralement pas avec Et_4NClO_4. Ces différences dans l'influence de Li, Na et Et_4N, comme cations de base, semblent être dues à des phénomènes d'électrocapillarité et probablement à la solvatation des ions. La réduction du pyridinium est indépendante de la concentration de l'anion.

ZUSAMMENFASSUNG

Es wird die polarographische Reduktion von Pyridinionen in Pyridin untersucht. Es zeigt sich, dass Tetraäthylammoniumperchlorat im Vergleich zu Lithiumperchlorat als Grundelektrolyt über einen grösseren Potentialbereich wirksam ist. Geringe Verunreinigungen beeinflussen die Pyridinstufe nicht. Die Pyridinstufe, welche in 0.1 *M* Et_4NClO_4 erzeugt wird, tritt bei negativeren Potentialen auf als die in 0.1 *M* $LiClO_4$. Die beim $LiClO_4$ allgemein beobachtete Vorstufe tritt beim Et_4NClO_4 nicht auf. Spezifische Unterschiede zwischen Li(I), Na(I) und Et_4N(I) können auf ein Elektrokapillarphänomen und vielleicht auf das Ausmass der Solvation der Ionen zurückzuführen sein. Die Reduktion des Pyridins ist unabhängig von der Anionenkonzentration.

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