PURIFICATION OF PYRIDINE FOR VOLTAMMETRIC STUDIES

EFFECT OF IMPURITIES

DAVID A HALL and PHILIP J ELVING

The University of Michigan, Ann Arbor, Mich (U S A)

(Received March 28th, 1967)

The importance of the degree of purity of a solvent used as a medium for voltammetric studies cannot be overemphasized Solvents commonly used in nonaqueous voltammetry such as acetonitrile, dimethylformamide, dimethylsulfoxide and pyridine are received from the manufacturer with questionable degrees of purity with respect both to their water content and to other contaminants specific to the particular solvent Some of these contaminants may have adverse effects on the electrolytic behaviour of the compounds studied in them, *e.g*, intermediates, such as free radicals, may be destroyed without detection, extra waves may appear, wave patterns may be distorted, and control of proton concentration, so important in the study of organic compounds, may be impossible

Various more or less effective means of purification have been reported for specific solvents, *e g*, ref 1 In some cases, impurities have been detected, their voltammetric characteristics described, and, because of lack of an adequate means of purification, the solvents have been prudently used, pyridine is an example[2-5].

A small prewave to the pyridinium ion reduction in pyridine has been related to a predischarge wave present in the absence of protons, the sum of the two wave-heights is constant[2] The magnitude of the prewave varies with the brand of pyridine and even with different lots of the same brand Contrary to what one might assume, presumably better quality spectral-grade samples of pyridine show, in some cases, a higher prewave than ordinary reagent-grade solvents

Since the detection of the prewave and the postulation of its origin in impurities, the authors' laboratory has embarked on a concerted effort to remove and, if possible, to identify the impurities Many means of purification, such as that mentioned[6] for the purification of pyridine for nonaqueous titrations, have been tried, these methods, although quite effective in removal of water and active proton-containing compounds, leave the prewave material untouched However, a successful means of purification has been developed, although the impurities have not yet been satisfactorily identified owing to their very low concentration in pyridine, *e g.*, o 2 m*M*

The method of purification, which can be described as zone fractional crystallization, is capable of reducing the concentration of prewave-producing material below the detection limits of polarography, *i.e*, o oi m*M* Water and other impurities are also removed Comparison of the electrocapillary curves observed in the presence and absence of oxygen in pyridine in various stages of purification containing two different background electrolytes has revealed important effects due to the

impurities Since the stability of the diphenylpicrylhydrazyl free radical was found to be dependent on the concentration of proton-releasing impurities present, this phenomenon can be used as an index of the purity of the pyridine

EXPERIMENTAL   .

Reagents

The pyridine used was a composite of Baker & Adamson reagent grade (Lot No Z144) and J T Baker analyzed reagent grade (Lot No 37529), the mixture contained a concentration of impurity which is the average of that found in many brands and lots The Baker & Adamson pyridine was rich in the prewave-producing material, the J. T. Baker pyridine, which was free of the impurity, was used as a diluent Lithium perchlorate (G Frederick Smith Chemical Co anhydrous grade) was dried at 110° for 2 h Tetraethylammonium perchlorate (Eastman) was vacuum-dried at room temperature Nitrogen, which had been passed through anhydrous calcium sulfate, was used to provide a dry inert atmosphere above the freezing solvent and the melting solid Argon was similarly dried.

Apparatus

The fractional crystallization apparatus consisted of a glass freezing tube (14-in long; 2-in diameter) provided with a polyethylene cap having a nitrogen inlet and an entrance for the stirrer blade, which was a one-turn screw type blade (o 75-in wide, 1-in long), driven by a 1200-rev./min motor

Polarograms were recorded by means of a Sargent Model XV Polarograph in conjunction with a Sargent Model A IR Compensator. The Sargent Model XV was used as a potential source for electrocapillary curve measurement

The D.M.E. capillary, made from marine barometer tubing, had an $m^{2/3}t^{1/6}$ product in o.1 M LiClO$_4$ in oxygen-free pyridine at open circuit of 1 467 ($t=4$ 18 sec, $m = 1$ 12 mg/sec). Two jacketed three-compartment cells were used One cell used only for pyridine solutions of Et$_4$NClO$_4$ had a platinum spiral counter electrode in one end compartment and a normal silver electrode (NAgE) in pyridine[7] in the other. Sintered glass disks and gel salt bridges (o.1 M Et$_4$NClO$_4$ in pyridine plus 7 5% by weight of methyl cellulose) separated the compartments, o 1 M Et$_4$NClO$_4$ was present in the reference and counter electrode compartments. The second cell, which was used only for pyridine solutions of LiClO$_4$, was the same as the first except that the gel salt bridges consisted of o.8 M LiClO$_4$ in pyridine plus 10% by weight of methyl cellulose and o.1 M LiClO$_4$ was present in the reference and counter electrode compartments.

All potentials reported are *versus* the NAgE at 25°.

Fractional crystallization procedure

The freezing tube containing 500 ml of reagent-grade pyridine was so mounted that the blade of the stirrer was at half the total depth of the pyridine. The polyethylene cap was placed in position and the dry nitrogen stream turned on to displace air from the tube. The stirring motor was then turned to its maximum speed and a Dry Ice–2-propanol bath at —75° was brought into position such that the lower 2 inches of the freezing tube were immersed in the bath. Sufficient time was allowed for crystal

formation at the bottom of the freezing tube; then, the bath was lowered and the crystals allowed to melt until only a few remained on the bottom of the tube; the depth of immersion of the tube in the bath was then increased ca 1.5 inches at a time, allowing crystal formation at each stage until the top of the bath was at a level about 1 inch above the stirrer blade The time necessary was ca 2 h, by which time about 50% of the pyridine was frozen The stirrer was then stopped, the bath lowered, the liquid fraction decanted, the tube was re-capped, and the solid fraction allowed to melt in a stream of dry nitrogen The zone fractional crystallization was then repeated on the liquified solid fraction

Polarograms were taken of 0 1 M LiClO$_4$ solutions in the pyridine fractions obtained in each stage of the purification process

Electrocapillary curve procedure

The electrocapillary curves were taken at $25° \pm 0$ 2°, drop-time was measured at 100-mV intervals between 0 0 V and the cathodic background electrolyte discharge. Solutions containing oxygen were air-saturated, those which did not contain oxygen, were deaerated by a 20-min purge with dried argon Curves were taken on the composite reagent-grade pyridine, the liquid fraction of the first fractionation, and the solid fraction of the second fractionation Polarograms of these samples, which contained a suitable electrolyte, were recorded before and after the electrocapillary data had been taken.

ZONE FRACTIONAL CRYSTALLIZATION

The results of purification of pyridine shown in Table I are based on several purification experiments and on a postulated concentration of predischarge wave-producing material of 0 02 g per liter of pyridine, which corresponds to a 0 2 mM concentration of a substance with a molecular weight of 100 The figure of 0 2 mM is based on the average of the prewaves for a large number of pyridine samples, as-

TABLE I

POLAROGRAPHIC EVALUATION OF THE PURIFICATION OF PYRIDINE BY ZONE FRACTIONAL CRYSTALLIZATION

Pyridine used	Volume (ml)	Predischarge wave[a]		Impurity[b]	
		$E_{1/2}$ (V)	i (μA)	mM	g
Composite Reagent Grade	1000	-1 72	0 78	0 200	0 020
First fractionation					
Liquid fractn	585	-1 72	1 27	0 323	0 019
Solid fractn.	415[c]	-1 71	0 09	0 024	0 001
Second fractionation.					
Liquid fractn	130	-1 72	0 23	0.059	0 0008
Solid fractn	225	Not detectable			

[a] In 0 1 M LiClO$_4$ solution
[b] Weight based on 0 02 g/1000 ml as discussed in text
[c] 60-ml sample removed for polarographic evaluation of predischarge wave

suming a 1-electron process[2] Polarograms of o 1 M LiClO$_4$ solutions of the starting material and two fractions are shown in Fig. 1.

A material balance for the predischarge wave material for the first fractionation, based on the measured currents, shows a total weight of 0.0199 g, compared to the hypothetical starting weight of o 0200 g The efficiency of the first fractionation was 88%, defined as follows:

$$\%E = \frac{(\text{wt}\ X/\text{ml original pyridine}) - (\text{wt}\ X/\text{ml 1st solid fraction})}{\text{wt}\ X/\text{ml original pyridine}}\ 100$$

The efficiency of the second fractionation was 78% The yield of purified pyridine, based on the original volume of pyridine, was 27%
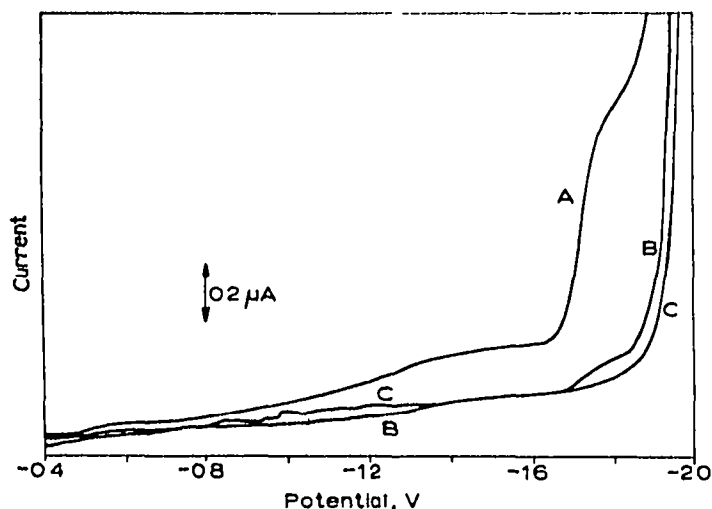

Fig 1 Effect of zone fractional crystallization on the magnitude of the predischarge wave in a o 1 M LiClO$_4$ in pyridine solution (A) Composite reagent-grade pyridine (B) First solid fraction obtained (C) Second solid fraction obtained

EFFECT OF PURIFICATION ON ELECTROCAPILLARY BEHAVIOR

Electrocapillary curves of o 1 M LiClO$_4$ and o 046 M Et$_4$NClO$_4$ solutions in pyridine obtained from different purification stages were measured in the absence and presence of oxygen In the subsequent discussion, "purified pyridine" refers to the second solid fraction obtained in the crystallization and "impure pyridine" to the first liquid fraction.

Lithium solutions

The electrocapillary maximum in o 1 M LiClO$_4$ in purified pyridine is at −o 40V.

The concentration of impurities significantly affects the electrocapillary curves in both the presence and absence of oxygen. Figures 2 and 3 show the relevant electrocapillary curves, the depth of the indentation at −0.40 V in the presence of oxygen, which is probably the most striking characteristic of the electrocapillary curves, markedly increases with increasing purity; this potential is located at the foot of the

first reduction wave of oxygen. Such a decrease in drop-time may be attributed to adsorption of oxygen on the surface of the mercury drop[8], since no such decrease in drop-time is seen at −0 40 V in the absence of oxygen

Associated with increase in impurity is a decrease in magnitude of the apparent maximum on the first oxygen reduction wave at −0 60 V and a shift of the second
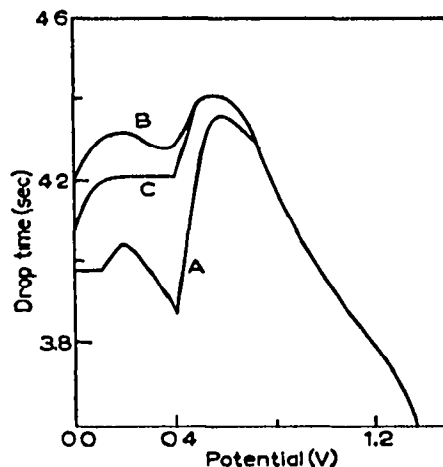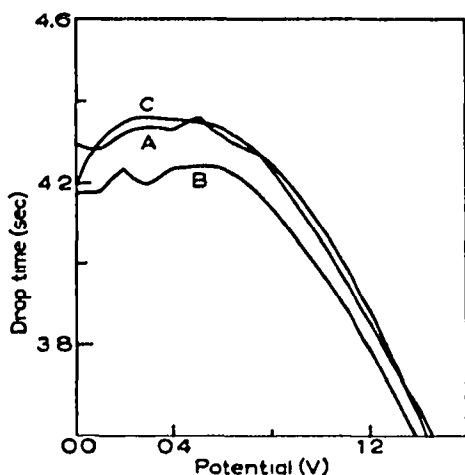

Fig 2 Electrocapillary curves of 0 1 M LiClO₄ solution in various grades of pyridine in the absence of oxygen (A) Pyridine from the second solid fraction of zone fractional crystallization (B) Composite reagent-grade pyridine (C) Pyridine from the first liquid fraction of zone fractional crystallization

Fig 3 Electrocapillary curves of air-saturated 0 1 M LiClO₄ solutions in various grades of pyridine A, B and C as in Fig 2
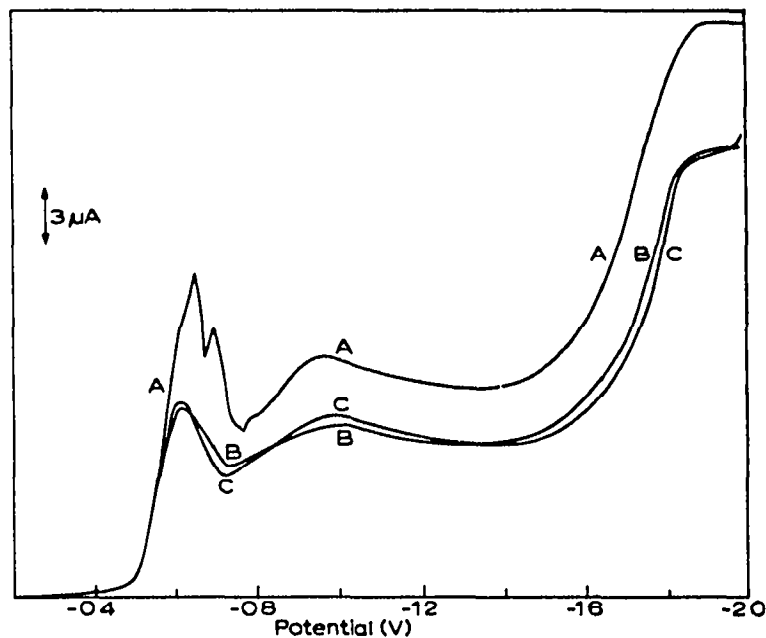

Fig 4 Polarograms of air-saturated 0 1 M LiClO₄ solutions in various grades of pyridine. A, B and C as in Fig 2

reduction wave half-wave potential to more positive values (Fig 4, Table II) The peaking is believed to be due to formation of a film by the product of the first oxygen reduction; the film acts as an insulator to further current passage. This assumption is supported by the fact that the current reaches its maximum value at about half of the drop growth and approaches a minimum as the mercury drop reaches its maximum size. The current reversal phenomenon occurs between −0.60 and −0 70 V and persists until a potential of ca −1 80 V is reached, when the film is reduced

TABLE II

EFFECT OF IMPURITIES ON THE POLAROGRAPHIC BEHAVIOR OF OXYGEN IN PYRIDINE

Pyridine	Wave	o 1 M LiClO$_4$ solution				o 046 M Et$_4$NClO$_4$ solution			
		$E_{1/2}$ (V)	i_1 (μA)	i_1/i_{111}	Slope[a] (mV)	$E_{1/2}$ (V)	i_1 (μA)	i_1/i_{111}	Slope[a] (mV)
Composite Reagent	I	−0 55	13 76	4 1	42	−0 94	9 45	1 2	69
Grade	II	−0 84	3 36		112	−1 61	8 04		126
	III	−1 75	21 40						
First fractionation	I	−0 55	13 68	3 5	44	−0 93	10 77	1 4	78
Liquid fractn	II	−0 83	3 90		96	−1 52	7 77		120
	III	−1 77	21 16						
Second fractionation	I	−0 57	18 26	4 3	50	−0 95	9 84	1 08	66
Solid fractn.	II	−0 86	4 28		78	−1 64	8 76		126
	III	−1 71	20 49						

[a] Slope defined by $(E_{1/4}-E_{3/4})$, where $(E_{1/4}-E_{1/4}) = 0\ 056/n$ at 25° for a reversible process, and 0 056/αn_a for an irreversible process

Consequently, the impurities must aid film formation, addition of water to the sample solution produces the same effect, i.e , a lowering of the entire wave pattern with respect to current

The maximum in the electrocapillary curve at −0 50 V and the subsequent depression between −0 80 and −1 2 V (Fig 3) can apparently be associated with the film formation

Tetraethylammonium solutions

The electrocapillary maximum in purified pyridine is at −0 38 V.

The effect of impurities on the electrocapillary curve is negligible in the absence of oxygen Curves taken in the presence of oxygen show some deviation from one another with changes in the solvent purity, but these are insufficient to permit any conclusions to be drawn.

More pronounced effects are observed for polarograms of Et$_4$NClO$_4$ solutions (Fig. 5; Table II) As the purity of the pyridine is increased, the height of the second reduction wave relative to that of the first wave increases and both half-wave potentials shift to more negative potential with the shift for the second wave being much more pronounced.

Addition of water had effects on the first and second oxygen reduction waves in air-saturated 0.1 M Et$_4$NClO$_4$ solution in purified pyridine similar to those observed as the purity of the pyridine used was decreased As the water content in-

creased, the ratio of the first to the second wave in the purified pyridine solution increased from an initial value of 1 08 to 3 55 in the presence of 0 62% water, at the same time, the half-wave potential of the first wave shifted from −0 95 to −0.91 V and that of the second wave from −1 62 to −1 40 V It seems reasonable to assume from these observations that water has a pronounced effect on the mechanism of the oxygen reduction in tetraethylammonium perchlorate solutions and that zone fractional crystallization of pyridine removes water from the solvent.
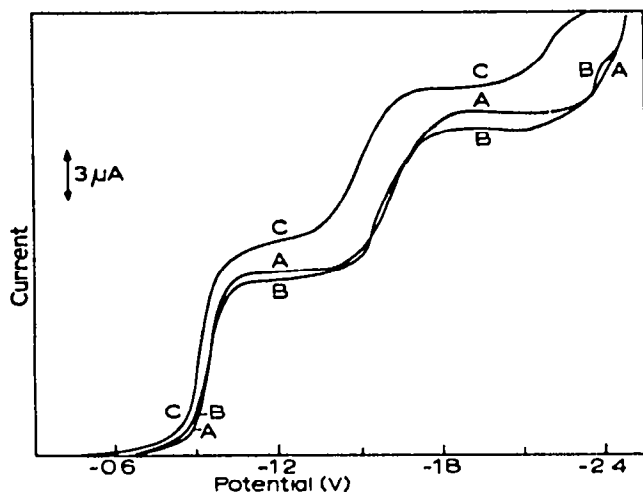

Fig 5 Polarograms of air-saturated 0 016 M Et₄NClO₄ solutions in various grades of pyridine A, B and C as in Fig 2

FREE RADICAL STABILITY

As a qualitative test of the effect of the impurity concentration on the stability of a free radical, 1–2 mg amounts of the free radical diphenylpicrylhydrazyl (DPPH) were dissolved in ca 50 ml of purified and of reagent-grade Baker & Adamson pyridine (Lot No Zo69), which were saturated with oxygen and stored in the dark (DPPH undergoes photolytic decomposition) The solution in reagent-grade pyridine changed from violet to yellowish-brown almost immediately indicating a loss of the hydrazyl, which is violet in color. After 7 h, the solution in purified pyridine still retained some violet color but was changing to yellowish-brown, after standing overnight, the degradation was complete A product of this reaction has been isolated and identified by means of its infrared spectrum as diphenylpicrylhydrazine, which is formed on reaction of DPPH with compounds containing an active hydrogen. This would indicate that the impurities include one or more active hydrogen compounds (the latter does not include water, since the addition of water to a solution of DPPH in pyridine has no apparent effect)

CONCLUSIONS

Voltammetric studies to be made in pyridine should include examination of

the effect of impurities in the solvent on the electrode reaction being studied, if these effects are found to be adverse, purification of the pyridine should be undertaken It would be desirable to require purification for all work in pyridine, e g , by a satisfactory method such as that described in the present paper Work is now in progress on the mechanism of oxygen reduction in purified pyridine.

SUMMARY

Purification of pyridine by zone fractional crystallization reduces the concentration of prewave-producing contaminant below polarographic detection limits, i e , o o1 mM. A qualitative test based on the stability of the free radical diphenylpicrylhydrazyl has shown the method to be capable of reducing the concentration of proton-releasing impurities Water is also removed Investigation of the effect of the contaminants in normal reagent-grade pyridine on the electrocapillary curves and polarograms of pyridine solutions containing lithium perchlorate and tetraethylammonium perchlorate as background electrolytes in the presence and absence of oxygen, has indicated that the impurities are capable of changing the mechanism for the electrochemical reduction of oxygen in pyridine

RÉSUMÉ

La purification de la pyridine par cristallisation fractionnée permet de réduire la concentration des contaminants en dessous des limites de détection polarographique (o o1 mM) On a examiné l'influence des contaminants de la pyridine sur les courbes électrocapillaires et sur les polarogrammes à l'aide de solutions pyridine contenant du perchlorate de lithium et du perchlorate de tétraéthylammonium comme électrolytes de base, en présence et en l'absence d'oxygène On constate que les impuretés peuvent changer le mécanisme de la réduction électrochimique de l'oxygène dans la pyridine

ZUSAMMENFASSUNG

Die Reinigung von Pyridin durch fraktionierte Zonenkristallisation verringert die Konzentration von Vorstufen erzeugenden Verunreinigungen unterhalb der polarographischen Nachweisgrenze von o o1 mM Ein qualitativer Test, der auf der Stabilität des freien Radikals Diphenylpicrylhydrazyl beruht, zeigte, dass diese Methode im Stande ist, die Konzentration von protonenlosenden Verunreinigungen zu verringern Wasser wird ebenfalls beseitigt Die Untersuchung des Einflusses der Verunreinigungen in normal reinem Pyridin auf die Elektrokapillaritätskurven und auf die Polarogramme von Pyridinlösungen, die Lithiumperchlorat und Tetraäthylammoniumperchlorat enthalten, in Gegenwart und Abwesenheit von Sauerstoff zeigten, dass die Verunreinigungen im Stande sind, den Mechanismus der elektrochemischen Reduktion von Sauerstoff in Pyridin zu ändern

REFERENCES

1 A WEISSBERGER, E S PROSKAUER, J A RIDDICK AND E E TOOPS, *Organic Solvents Physical Properties and Methods of Purification*, Interscience Publishers, New York, 1955
2 M S SPRITZER, J M COSTA AND P J ELVING, *Anal Chem*, 37 (1965) 211
3 W R TURNER AND P J ELVING, *Anal Chem*, 37 (1965) 467
4 J C HICKEY, M S SPRITZER AND P J ELVING, *Anal Chim Acta*, 35 (1966) 277
5 L FLOCH, M S SPRITZER AND P J ELVING, *Anal Chem*, 38 (1966) 1074
6 W M BANICK, *Anal Chem*, 34 (1962) 296
7 A CISAK AND P J ELVING, *J Electrochem Soc*, 110 (1963) 160
8 J VOLKE, *Talanta*, 12 (1965) 1097