Recycling of the Supporting Electrolyte Tetra\((n\)-butyl\)ammonium Hexafluorophosphate from Used Electrolyte Solutions

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Procedures are designed for the recycling of the supporting electrolyte tetra\((n\)-butyl\)ammonium hexafluorophosphate (TBAHFP) from electrolyte solutions used for electroanalytical or electrosynthetic purposes. The quality of the recycled product is assessed from cyclic voltammograms and is comparable to TBAHFP from the original synthesis.

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Experimental

General

Cyclic voltammetry was performed in a three-electrode cell equipped with a Pt working electrode tip (BAS, electroactive area \( A = 0.08 \text{ cm}^2 \)), a Pt wire counter electrode (fitted with a ground glass joint) and an Ag/Ag+ reference (0.01 M AgClO₄ in acetonitrile/0.1 M TBAHFP) connected to the cell by a classical or double-reference (7) Haber-Luggin capillary. All potentials are referred to an external \( f_{c}/f_{c}^{+} \) standard in the respective electrolyte. A BAS 100A electrochemical analyzer or a BAS 100B/W electrochemical workstation were used to generate the potential sweep and to record the current signal. In the latter case, data were collected on a personal computer. BAS 100A plots were digitized later. Plots were generated from all digital data with the X Window system-based program XEASI (8) on a UNIX workstation.

Purification of Solvents

\( \text{N,N-Dimethylformamide} \) was fractioned three times in vacuo (\( \text{P}_2\text{O}_5 \) was added before the first fractionation) and stored in the dark.

\( \text{Pyridine} \) was kept over KOH for several weeks and distilled just before use.

\( \text{Acetonitrile} \) was distilled from \( \text{P}_2\text{O}_5 \), NaH, and \( \text{P}_2\text{O}_5 \) again. The resulting solvent was passed through a column with \( \text{Al}_2\text{O}_3 \) (neutral, dried at 140°C, and stored under Ar).

\( \text{Dichloromethane} \) was distilled from \( \text{P}_2\text{O}_5 \) and then \( \text{K}_2\text{CO}_3 \) before it was passed through an \( \text{Al}_2\text{O}_3 \) column (activation as given above).

Preparation of Electrolyte Solutions

In most cases, the electrolyte was prepared from 1.94 g TBAHFP and placed in a Schlenk flask. Air was removed by evacuating and filling with Ar three times before 50 mL of the solvent (dried as described above) were added in an Ar counter current. The electrolyte was deoxygenated by three freeze-pump-thaw cycles.

Cell Assembly

The glass cell was usually dried at 140°C, equipped with the counter electrode, evacuated, and filled with Ar three times. A volume of 20 mL of electrolyte was added against an Ar flow. Then, the working and the reference electrode were introduced. After background currents were recorded, weighed samples of the substrates were added against an Ar flow.

Synthesis of Tetra(\( \text{n-butyl} \))ammonium Hexafluorophosphate

We synthesized TBAHFP based on a procedure cited by Fry (2,9) and improved and optimized by Salbeck (10). We synthesized TBAHFP based on a procedure cited by Fry (2,9) and improved and optimized by Salbeck (10), Fry (11), as well as in our laboratory.

A 100 g sample (0.31 mol) of \( \text{NBU}_4\text{Br} \) (Fluka, purum) was dissolved in 250 mL acetone (for synthesis) and then mixed with 50 g (0.4 mol) \( \text{NH}_4\text{PF}_6 \) (Fluka, purum) in 350 mL acetone. Colorless \( \text{NH}_4\text{Br} \) precipitated and was filtered off (glass funnel with folded filter or Büchner funnel). The clear solution was concentrated to a volume of approximately 200 mL with a rotary evaporator. The desired TBAHFP was then precipitated by the addition of 400 mL water or ethanol (12) forming a dark brown amorphous mass, which was collected, air-dried and recrystallized from 200 mL ethanol. The mother liquor was rejected. The crystalline product was recrystallized from ethanol until the mother liquor became colorless (usually 2 or 3 further recrystallizations; allow to cool down slowly; collect mother liquor, see below). Finally, three additional recrystallizations from ethanol yielded after 48 h of drying at 100°C in vacuo 35-40 g colorless crystals (50-60% of the SE contained in the electrolyte solution).

From the collected solutions, 5-10 g more of raw TBAHFP could be separated by evaporation of the solvent to a volume of 200 mL. This raw SE was usually purified together with the product of the next batch of electrolyte recycling. The evaporated ethanol may be reused in further recrystallizations.

From hexakis(dimethylamino)benzene solutions. The solution [= 1 L; mixture of \( \text{CH}_2\text{Cl}_2 \) and acetonitrile; concentration of TBAHFP: 0.1 M; contaminated with fc and with hexakis(dimethylamino)benzene and derivatives, as well as their oxidation products] was evaporated to dryness with a

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rotary evaporator. The solid residue was recrystallized from ethanol/water and the resulting crystals were washed with 150 mL water. Three further recrystallizations from ethanol/water yielded after drying for 48 h at 100°C and 3 x 10^{-2} mbar 32.3 g pure TBAHFP (85% of the amount in the starting solution).

Results and Discussion

TBAHFP can be recycled from used electrolyte solutions with good yields. The procedures described differ mainly in the removal of the electrolyte solvents and in the solvent applied for recrystallization. Distillation or evaporation of the solvent can be used successfully. Distillation may be advantageous if solvents with high boiling points are present (e.g., propylene carbonate in the first procedure).

TBAHFP is essentially insoluble in water. Therefore, the addition of water to the solvent during recrystallization increases the yield of the recycled SE. Any residual water can be easily removed during the final drying stage.

The recycling procedures used involve only a minor overhead compared to the original synthesis of TBAHFP. The main time-consuming manipulations, both in the synthesis and the recycling protocols, are the recrystallization steps. Fortunately, TBAHFP yields pure and good quality crystals upon slow cooling of the saturated ethanol or ethanol/water solutions.

The starting solutions were highly colored in both cases due to the contaminants [Co (salen), dication of hexakis(dimethylamino)benzene (13)]. Consequently, any remaining impurities could easily be detected by visual inspection.

Of course, the quality of the recycled TBAHFP for use in electrochemical experiments can finally be assessed by recording the cyclic voltammetric curves and comparing them with those from electrolyte solutions prepared with the original SE. Thus, both background voltammograms and voltammograms of substrate solutions were recorded for the SE from the original synthesis and the recycling procedure (F1 and F2).

The background curves in DMF and pyridine electrolytes prepared from recycled TBAHFP (F1, top) do not show any signals due to electroactive contaminants. Cyclic voltammograms of [Co(salen)]^+ consist of a simple, well-defined, quasi-reversible peak couple (F1, bottom left). These were identical to current/potential curves recorded in electrolytes prepared from original TBAHFP. The cation [Co(salen)]^+ is a Lewis acid (14), and it is extremely susceptible to reactions with bases. Presence of basic impurities, even in small concentrations, causes a splitting of the reduction peak (5). An example is shown in F1, bottom right, where DMF of a non-satisfactory purity was used. The voltammograms clearly indicate the absence of any basic impurities in the electrolytes prepared from the recycled SE.

In F2A, background cyclic voltammograms of electrolytes prepared with new and recycled TBAHFP in mixtures of CH_2Cl_2 and acetonitrile (1:1) are presented,
extending over the entire accessible potential window. In this case, again, the curves of the recycled SE do not indicate any remaining impurities.

Cyclic voltammograms of hexakis(dimethylamino)benzene in this solvent system (F2B; oxidation occurs in three stages up to a tetrakation (6)) also do not reveal significant differences between electrolytes prepared from new or recycled SE. The slight potential shifts of the peaks on the reverse scan are within the reproducibility observed with this system.

The recycling procedure described here is successful since TBAHFP crystallizes very well from ethanol. Addition of water decreases the solubility of this SE and increases the yield.

If other contaminants were present in the electrolyte solutions, the recycling procedure may not be as effective as in the cases discussed, particularly, if the solubility behavior of the contaminants were similar to that of TBAHFP. In such cases, one trial recycling run can easily show the quality of the recycled SE from cyclic voltammograms.

**Conclusion**

Good quality TBAHFP can be recycled from used solutions of this SE after electroanalytical or electrosynthetic experiments. Only minor overhead is involved as compared to the original synthesis of TBAHFP. Thus, the recycling procedure can be recommended to decrease the purchase and disposal costs of TBAHFP as well as the volume of liquid wastes produced.

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**References**

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9. The original procedure described by Fry (2) was referenced as: J.A. Ferguson, Interface 6(2), Aug. 10, 1970. Interface was a newsletter edited by graduate student Pete Kissinger (11).
12. In some cases, precipitation with water yielded a black, highly viscous oil, which could not be filtered. Then, ethanol proved to be a better solvent for the process. We recommend to test the use of water with a small sample of the electrolyte.