

Laboratory Techniques in Electroanalytical Chemistry

Second Edition, Revised and Expanded

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Solvents and Supporting Electrolytes

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I. INTRODUCTION

Almost every electrochemical experiment is carried out in a medium consisting of a solvent and supporting electrolyte. Many such combinations have been used by electrochemical experimenters; as a glance at the Appendix will show, selection of a solvent and electrolyte has been the subject of much discussion in the literature. Yet the problem is not intrinsically complicated; a handful of solvent–electrolyte combinations would probably suffice for the majority of electrochemical applications. For this reason, a few particularly good solvent systems (the term “solvent system” is used here to describe the medium consisting of both solvent and supporting electrolyte) are recommended here, in lieu of an extended but uncritical listing of all such systems. The systems to be recommended have been chosen from among many that have been reported. However, because the novice will certainly want to develop a feel for what makes a “good” solvent system, the first part of the chapter discusses desirable criteria, as well as the ways in which electrochemical results may depend on the nature of the particular solvent–electrolyte combination employed. Because special situations frequently do require special solutions, Section III describes some less common solvents and electrolytes that have been found useful in special situations. Finally, the Appendix offers a guide to further readings of a more comprehensive nature.

A. Solvent Selection Criteria

There is no universal solvent, and even for a given application one rarely finds an ideal system. One must factor some informed guesswork into one’s choice of solvent and electrolyte. In order to optimize conditions for an electrode reaction, one must consider how its chemical and electrochemical features, for

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example, the chemical properties of expected intermediates, might be affected by the solvent or electrolyte. A solvent is chosen such that its merits outweigh its disadvantages in a particular situation. A good solvent system for one type of experiment may be wholly unsuitable for other applications. The most important properties that the ideal solvent system ought to possess are *electrochemical inertness* (stability over a wide range of potentials), *high electrical conductivity*, *good solvent power*, *chemical inertness*, *availability in pure form or ease of purification*, and *low cost*, although others must sometimes be considered. We now examine each of these in detail.

Electrochemical Inertness

The solvent system should not undergo any electrochemical reaction over a wide range of potentials from very positive (strongly oxidizing) to very negative (strongly reducing). The potential at which electrochemical reaction of the solvent system (either the supporting electrolyte or the solvent itself) commences is known variously as the *solvent breakdown potential*, *solvent decomposition potential*, or *solvent background limit*. Certain systems can be used over a very wide potential range; one of the best for this purpose is a solution of tetrabutylammonium hexafluorophosphate in acetonitrile, which exhibits anodic and cathodic breakdown limits of +3.4 and -2.9 V (vs. SCE), respectively [1]. In practice, however, one rarely needs both extended positive and negative ranges in a single set of experiments; solvents are frequently used that exhibit either a very negative or very positive decomposition potential, but not both. Thus, both nitrobenzene [2] and methylene chloride [3] have been used for studies of oxidation processes because they are hard to oxidize, notwithstanding the fact that they are quite easily reduced. Conversely, liquid ammonia and methylamine are good solvents for electrochemical reductions, although poor for oxidations [4]. It is reported that potentials as positive as +4.5 V (vs. SCE) can be reached in liquid SO₂ [5].

The potential limit is frequently set by the electrochemical behavior of the supporting electrolyte, not the solvent. For example, dipolar aprotic solvents such as acetonitrile (AN), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) are very difficult to reduce; the reduction of alkali metal ions to the corresponding metals (ca. -2 V vs. SCE) is the potential-limiting process in such solvents, and by use of the more difficult-to-reduce tetraalkylammonium salts one can reach considerably more negative potentials. The decomposition potentials of tetraalkylammonium ions at mercury themselves become more negative as the alkyl groups become larger (Me₄N⁺: -2.65 V; Bu₄N⁺: -2.88 V) [6]. One can frequently extend the accessible cathodic range by using a large tetraalkylammonium ion, but double-layer and adsorption effects can negate this generalization [6,7]. DMF and DMSO are not suitable as solvents for anodic studies because they are fairly easily oxidized, but as noted earlier, AN is very difficult to oxidize, and in this solvent the decomposition potential of the sup-

porting electrolyte is usually the limiting process. At very positive potentials, oxidation of the anion of the supporting electrolyte is often the limiting process. Not only should easily oxidized ions such as bromide and iodide not be used for anodic studies, but even nitrate and perchlorate salts should be avoided when one wishes to operate at very positive potentials; at these potentials tetrafluoroborate and hexafluoroborate salts are preferred because of their stability to oxidizing conditions [1].

Electrochemical reaction of the solvent or supporting electrolyte need not be undesirable. Sometimes one can take advantage of such behavior by using the product of such a reaction as a chemical reagent. For example, one can generate bromine by anodic oxidation of bromide ion or lithium by cathodic reduction of lithium ion. There can be real advantages to electrochemical generation of reagents this way instead of using the bulk reagent, for example, avoiding the need to handle dangerous substances and being able to add the reagent in regulated amounts by careful control of the electrolysis current [8].

Electrical Conductivity

In order to support passage of an electric current, the solvent system should have low electrical resistance. This implies that the solvent should have a moderately high dielectric constant (≥ 10); the prevalence of ion pairing and even multiple ionic association in less polar solvents results in relatively low ionic mobility and conductance. The fact that nonpolar solvents tend not to be very good solvents for salts in the first place makes it even harder to contemplate using them. A number of the most common solvents for organic electrochemistry have satisfactory dielectric constants (DMF: 36.7; AN: 37.5; DMSO: 46.7), and their electrolytic solutions have acceptably high conductances [9–11]. Solvents of substantially lower polarity than these, however, have been used successfully despite their high electrical resistance (e.g., tetrahydrofuran, THF [12], and methylene chloride [3], whose dielectric constants are 7.3 and 8.9, respectively [13]). Lower conductivity can be tolerated more readily in low-current applications such as voltammetry than in preparative electrolyses. Although voltammograms can be badly distorted by uncompensated resistance under conditions of high electrical resistance, the distortion can be largely corrected by using high electrolyte concentrations (not always possible in resistive solvents, which tend to be poor solvents for salts) and by computational correction of the voltammogram [11]. A new element has entered the scene in recent years with the development of small-diameter (diameter $\leq 10 \mu\text{m}$) microelectrodes [14]. These can be used in highly resistive media [11,15–19], including the absence of supporting electrolyte [20], and in fact even in the gas phase [21].

Good Solvent Power

An electrochemical solvent must be able to dissolve a wide range of substances at acceptable concentrations. In general, this means that electrolytes must be

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