Electrochemistry in Media of Low Dielectric Constant

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1 Introduction

The title of this article may appear to be a contradiction in terms, but electrochemical investigations in some media of low dielectric constant have several advantages over conventional solvents, as will be described. With the applications of electrochemistry becoming more diverse, novel media in which to study and carry out electrochemical reactions are receiving increased attention. Although the role of the solvent in an electrochemical process is frequently ignored it can significantly affect the course and kinetics of a reaction.

The general properties of the 'ideal' solvent for electrochemical experiments would be:

(i) Sufficient solubility of an electroactive species.
(ii) High conductivity with the incorporation of a suitable electrolyte.
(iii) High chemical and electrochemical stability.
(iv) Low melting point and a large liquid range.
(v) Easy to handle.
(vi) The correct viscosity to allow the desired transport.
(vii) Cheap.
(viii) Non-toxic and environmentally acceptable.

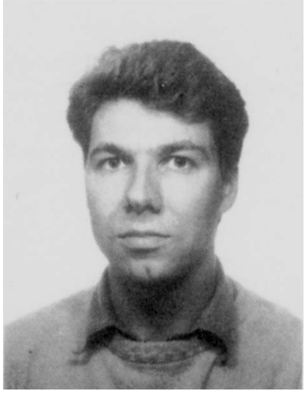
No solvent can meet all of these criteria and so a compromise must be sought. Water is clearly the most widely used solvent but it has the serious drawbacks that it is highly chemically and electrochemically active and factors such as pH frequently govern the reaction pathway. The 'window' of potentials over which water is electrochemically stable is about 1.5 ± 0.5 V, depending on the electrolyte and electrode used. It also has only sparing solubility for most organic solutes. Other inorganic solvents such as liquid ammonia and sulphur dioxide are of limited use because of their short liquid ranges and narrow potential windows. Their use is generally restricted to temperature-sensitive species.

Polar organic solvents such as dimethylformamide, acetonitrile, dimethylsulfoxide, and propylene carbonate are used extensively for organic electrosynthesis because of their wide potential windows (usually 3 to 4 V) and high solubility of organic species. They have also been used for the electrodeposition of alkali metals such as lithium and sodium for the battery industry. Most solvents have a convenient liquid range, are easily handled, and reasonably versatile. The use of these solvents does, however, present problems associated with dryness, purity, chemical interaction, and thermal instability.

Non-polar organic solvents have been largely ignored until recently. This review will highlight the unusual properties and electrochemical applications of a group of aromatic and polyaromatic solvents with a bulk dielectric constant less than 5. This includes naphthalene, benzene, phenanthrene, anisole, toluene, xylene, biphenyl, and terphenyl.

The major advantage of such media is that they are extremely inert. They have potential windows in the order of 4 V and in many cases it is the stability of the base electrolyte which prevents this from being wider. It has been shown that the stability of polyaromatic hydrocarbons (PAH) is related to the large energy difference between the HOMO and LUMO of the molecules. The oxidative and reductive stability limits are the formation of the respective ions which then usually dimerize or fragment.

In addition to their high electrochemical stability PAHs show high thermal stability and large liquid ranges (*o*- and *m*-terphenyl have liquid ranges of almost 300 K). Another factor which makes these solvents interesting is that they are non-coordinating, *i.e.* they will not interact with transition metal ions and thus affect their redox potentials. This has lead to their use as solvents for electroplating and electrowinning of metals as will be discussed later.



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2 Conductivity

Clearly, to be able to carry out electrochemical experiments the solvent needs to be made conducting by the dissolution of electrolytes. It was found that simple electrolytes such as KBr and quaternary ammonium salts such as tetramethyl- and tetraethylammonium bromide were sparingly soluble in solvents such as naphthalene.[1] Table 1 lists the solubilities of various quaternary ammonium electrolytes in a range of low dielectric constant solvents. It was concluded that the high solubility of tetrapropylammonium bromide was because the lattice energy was considerably smaller than the other electrolytes and thus the solvent–solute interactions become larger than the solute–solute interactions.

Table 1 The solubility (in mol dm^{-3}) of various quaternary ammonium electrolytes in different polyaromatic solvents at 150 °C. Data from reference 1.

Solvent	ϵ	TMABr	TEABr	TPABr
Naphthalene	2.54	5.7×10^{-5}	2.8×10^{-3}	1.91
1-Methylnaphthalene	2.92	7.1×10^{-5}	3.5×10^{-3}	0.13
1-Chloronaphthalene	5.04	1.6×10^{-4}	6.3×10^{-3}	0.89
Biphenyl	2.51	3.7×10^{-5}	9.9×10^{-4}	0.01
Fluorene		4.3×10^{-5}	4.2×10^{-3}	0.05

Several types of electrolytes have been found to dissolve in low dielectric constant solvents to give solutions which are conducting enough to carry out electrochemical investigations. Hurley and Wier[2] used ethyl pyridinium chloride in benzene to study aluminium electrodeposition. This solution forms a 'chlathrate', which is a two-phase system where the lower phase is a saturated solution of the electrolyte and the upper phase is almost pure solvent. This is typical of most of the alkyl-substituted monoaromatic solvent–electrolyte systems. Pickett[3] studied the tetrabutylammonium tetrafluoroborate (TBABF$_4$): toluene system and found that the lower, saturated level of the chlathrate was a mobile, transparent solution of molar composition 1 3 The specific conductance of this phase was similar to the room temperature molten salts based on alkylpyridinium tetrachloroaluminates, but less than that of 0 2 M $TBABF_4$ in acetonitrile solution

Gileadi *et al*,[4] also studied aluminium deposition in toluene from a $KAlBr_4$ electrolyte It was found that the maximum specific conductivity was reached when the ratio of KBr $AlBr_3$ was 1 2 and the charge was assumed to be transported by the species $[K_2(Al_2Br_7)]^+$ and $[K(Al_2Br_7)_2]$ Conduction was proposed to occur by a process of ion hopping between charged and neutral aggregates, *i e*

$$A^+ + B^-(A^+B^-)_nA^+ \rightarrow A^+ \cdots B(A^+B^-)_n \cdots A^+ \rightarrow A^+B^-(A^+B^-)_n + A^+ \qquad (1)$$

Specific conductivity for different salts was found to be in the order, KBr > NaBr > LiBr > RbBr and for the solvents, benzene > toluene > xylene

Campbell *et al* [5] showed that conductivity could be achieved in naphthalene by the dissolution of quaternary ammonium salts, and these ideas were expanded upon by Potter,[6] Geblewicz,[1] and Abbott [7]

Clearly, in a solution of such low dielectric constant any ionic species will be highly associated The theory of Bjerrum[8] predicts that the distance, *q*, at which two ions can be assumed to be associated with each other is given by

$$q = |z_1 z_2|e^2/2\epsilon kT \qquad (2)$$

where z is the charge of the ions, e is the protonic charge, ϵ is the bulk dielectric constant of the solvent, k is Boltzmann's constant, and T is the absolute temperature This critical capture distance for a PAH solvent is in the order of 140 Å, whereas the average inter-ionic distance for a 0 1 mol dm^{-3} electrolyte solution is about 25 Å Thus, almost all ions in solution will be close enough to another to become associated Figure 1 shows the equivalent conductivity of $TBABF_4$ in a 1 5 mol% phenanthrene in anisole solution at 25 °C as a function of the square root of the electrolyte concentration There are three distinct regions of this plot

(i) At very dilute concentrations (less than 1 mM) there is a decrease of equivalent conductance, Λ, with increasing electrolyte concentration This can be ascribed to the formation of ion pairs in solution

(ii) An increase in Λ up to 0 7 M, which is characteristic of the formation of triple ions

(iii) The subsequent decrease in Λ with concentration, which could be due to the formation of larger, uncharged aggregates such as quadrupoles, but is more likely to result from viscosity effects in such concentrated solutions

Classical theory[8] predicts that the equivalent conductance of a solution increases with the size of the ions Surprisingly, this is not the case for most quaternary ammonium salts in media of low dielectric constant Increasing the chain length on the quaternary ammonium cation from C_3 to C_{10} (an increase in the hard sphere radius of 50%) has almost no effect on the equivalent conductance as can be seen in Figure 1b Similarly, increasing the size of the anion from bromide to *p*-toluenesulfonate has little or no effect on the equivalent conductance

The ionic radius should have a marked effect upon the ion pair formation constant, which in turn will control the ionic strength and hence the conductivity Table 2 shows the interionic distance, *a*, of a series of quaternary ammonium salts in a solution of 1 5 mol% phenanthrene in anisole, calculated using a Bjerrum theory [7 8] As can be seen, *a* remains roughly constant and always less than the sum of the hard sphere ionic radii It must therefore, be assumed that the anion penetrates into the void space between the alkyl chains of the cation as shown in Figure 2 Experiments using a bulky tetraphenylborate anion which could not interpenetrate the cation chains showed an increase in the equivalent conductance as expected Subsequent investigations on similar electrolytes using NMR[9] and photochemical techniques[10] have confirmed that these interpenetrating ion pairs do exist in media of low dielectric constant NMR spectroscopy of $TBABH_4$ in $CDCl_3$ (ϵ = 4 8) has shown that three of the protons on the BH_4^- ion are in contact with the α-CH_2 protons on the quaternary ammonium cation and the fourth proton is associated with one β-CH_2 proton An interionic distance of 3 Å was calculated which agrees with the conductivity data when the size difference between the hydrogen and fluorine atoms is accounted for

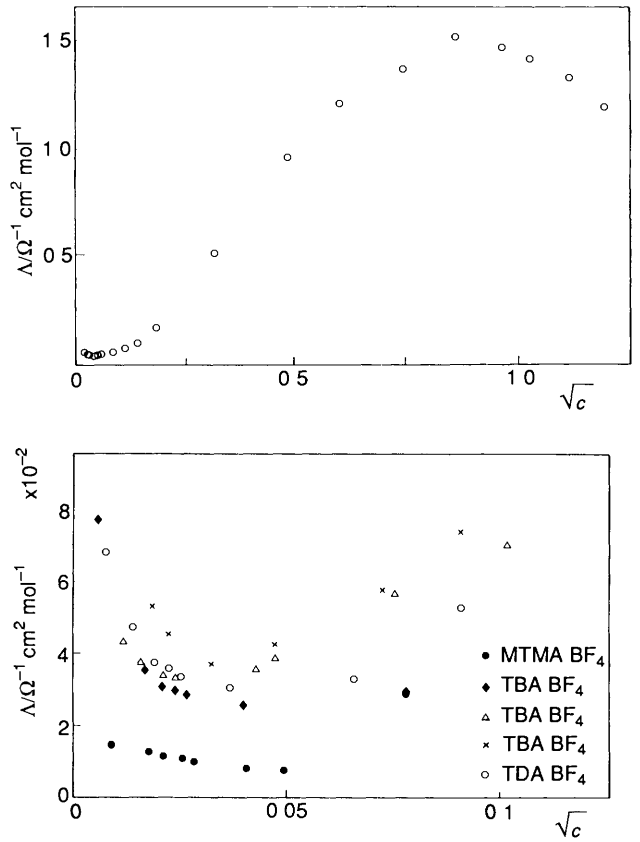

Figure 1 (a) The equivalent conductance of $TBABF_4$ in a 15 mol% phenanthrene in anisole solution at 25 °C (b) The influence of cation size on the equivalent conductance of various BF_4 salts
(Redrawn from reference 7)

Varying the type of aromatic solvent had little effect on the equivalent conductance of $TBABF_4$ in the dielectric constant range 2 5 to 4 5 [7] Thus, if the conductance can not be significantly increased by changing the size of the ions or the type of the polyaromatic solvent then the only way to achieve a higher conductivity is with a higher solubility of the electrolyte

Table 2 The measured, *a*, and theoretical, a_t interionic distances of a series of quaternary ammonium ions in a medium of dielectric constant 4 33 (Data from reference 7)

Salt	*a*/Å	a_t/Å
$C_{16}N(CH_3)_3BF_4$	4 96	4 85
$(C_3H_7)_4NBF_4$	5 47	5 83
$(C_4H_9)_4NBF_4$	5 51	6 17
$(C_6H_{13})_4NBF_4$	5 61	6 72
$(C_{10}H_{21})_4NBF_4$	5 41	7 55
$(C_4H_9)_4N$*p*-$CH_3C_6H_4SO_4$	4 99	7 75
$(C_4H_9)_4NBF_4$	5 51	6 71
$(C_4H_9)_4NBr$	5 23	6 11
$(C_4H_9)_4N(C_6H_5)_4B$	6 91	8 52

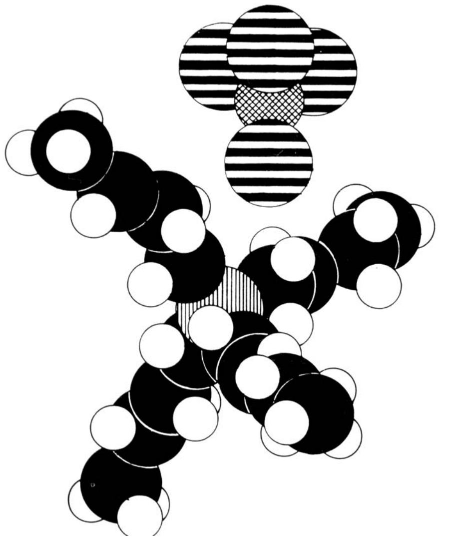

Figure 2 The interpenetration of the BF_4^- ion into the void spaces between the alkyl chains of the TBA^+ cation
(From reference 7.)

3 Solvent Characterization

Despite the fact that all of these solvents have similar dielectric constants they exhibit strikingly different solvent properties, particularly in their solubility of quaternary ammonium salts. Work by Geblewicz[1] showed that the solubility of tetrapropylammonium bromide, TPABr was 200 times larger in naphthalene ($\epsilon = 2.61$) than biphenyl ($\epsilon = 2.51$) at 150 °C (see Table 1). The solubility did not conform to a simple model of electrostatic association. The solvent–solvent interactions are small and relatively constant for such solvents and thus the cavity formation and solvent reorganization terms can be neglected from the classical solvation model. It was found that the electrolyte solubility was governed by short range solvent–solute interactions which could be directly correlated to the electronic polarizability, π^*, of the solvent molecules. Values of π^* were obtained by measuring the UV absorption spectra of indicator solutes in a range of solvents and comparing these to standard solvents. This so called solvatochromic shift method is the basis for several semi-empirical solvent polarity scales. The one proposed by Taft *et al*.[11] was found to be the most applicable for these systems. The values of π^* are calculated from

$$\pi^* = (\nu_0 - \nu_{max})/s \qquad (3)$$

where ν_0 and ν_{max} are the wave numbers of the absorption maxima of the indicator solute in cyclohexane and the test solvent respectively, and s is a constant specific to the indicator. The values for s and ν_0 have been tabulated for a range of indicator solutes.[11] This polarity scale is such that a non-polarizable solvent such as cyclohexane has a π^* value of 0 and polarizable DMSO has a value of 1.

Mixing PAHs with simple monoaromatic solvents such as benzene or anisole, to give solutions which could be handled at ambient temperatures, produced enhanced solvent properties[12,13] *i.e.* they produced solutions with π^* values greater than either of the components. Figure 3 shows a plot of π^* against the mol% of PAH added to an anisole solution. As can be seen the π^* value reaches a maximum after a small addition of PAH. This is attributed to the solvation sheath around the solute being saturated with the more polarizable PAH molecules. The smaller monoaromatic species are thought to fill the 'voids' between the poorly packing PAH molecules, producing an environment around the solute which has a higher total polarizability and thus enhanced solvent properties. An example of this enhancement was that a solution containing 15 mol% phenanthrene in benzene could dissolve 0.7 mol dm^{-3} of $TBABF_4$ at room temperature, which was about five orders of magnitude larger than pure benzene.

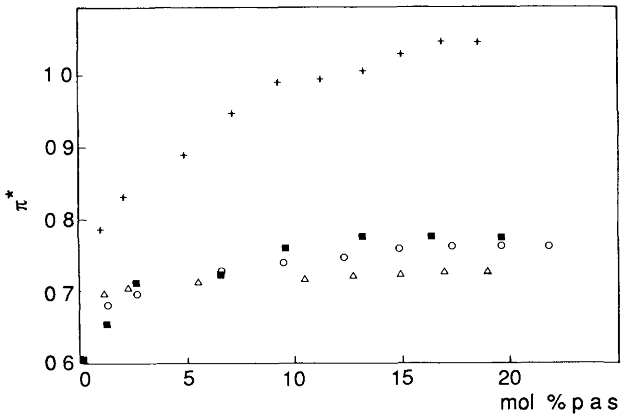

Figure 3 Dependence of π^* on the concentration of phenanthrene (+), Naphthalene (○), fluorene (□) and biphenyl (△)
(Redrawn from reference 13.)

Figure 4 shows a plot of the Gibb's Energy of solution, ΔG_s, for TPABr in various phenanthrene–benzene mixtures as a function of the electronic polarizability. This shows that the solubility of a solute in a solvent is directly proportional to the electronic polarizability of the solvent molecules. The solvatochromic shift method can therefore be used to predict the solubility of solutes in these media.

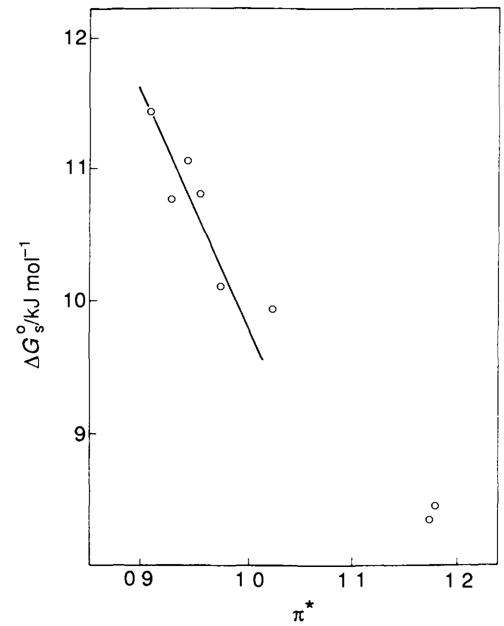

Figure 4 Gibbs energy of solution of TPABr in various phenanthrene/benzene solutions as a function of π^*
(Redrawn from reference 13.)

4 Solute Incorporation

Clearly now that the factors which produce the optimum potential window, electrolyte solubility, and conductivity have been quantified, the one remaining question is that of solute incorporation. Aromatic and polyaromatic solvents have the significant advantage that they are good at dissolving non-polar solutes. One of the first uses of naphthalene and its analogues, as an electrochemical solvent, was for the study of metal phthalocyanine redox chemistry.[5] It was found that these notoriously insoluble compounds were considerably more soluble in solvents of low dielectric constant than the previously used polar organic solvents.

Species with high ionic character must first be made hydrophobic before they can dissolve in non-polar solvents. A variety of methods exist for this which generally involve bulky ionophores. Honda *et al.*[14] used crown ethers to complex with sodium tetraphenylborate (NaTPB) forming a conducting solution in benzene. A conductivity of $2.3 \times 10^{-4}\ \Omega^{-1}\mathrm{cm}^{-1}$ was obtained with 0.1 M NaTPB in a 2:7 mole ratio of 15-crown-5 and benzene. These solvent media were used to investigate the behaviour of zinc, silver, and copper electrodes under positive polarization. The zinc and copper electrodes behave quite differently in benzene than in polar solvents, *i.e.* they do not oxidatively corrode as the ions would be too polar to dissolve, whereas the silver electrode did oxidize because the crown ether could solvate the Ag^+ ions in solution.

A wide range of complexes have been used to incorporate transition metal ions into aromatic solvents. By far the most work has been carried out on ligands with nitrogen moieties which donate electrons to the metal ion. Examples of the ligands used include, primary and secondary amines, nitriles, aniline, pyridine, picolines, diamines, and 1,10-phenanthrolene.[6,15–18]

Some metal salts which show covalent character, such as titanium tetrachloride and aluminium trichloride, form highly coloured charge-transfer complexes which dissolve very readily in aromatic solvents. The delocalized electrons of the solvent molecules can be partially donated to the metal in a weak 'ball to plane' type complex. Similar complexes also exist with aromatic ethers, but in this case bonding occurs partially through the oxygen.

5 Electron Transfer

As mentioned previously, aromatic solvents have the advantage that they allow electrochemical studies of non-polar solutes to be made. Lines and Parker[19] carried out investigations into the stability of aromatic anions of perylene and anthracene in benzene and chlorobenzene using mercury-coated platinum microelectrodes of effective diameter 60 μm. It was found that anions, dianions, and even trianions could be formed stably in solution because they were ion paired with the quaternary ammonium cations used for the base electrolyte. The results were, however, distorted by ohmic iR drop.

Wightman *et al.*[20] also used microelectrodes in non-polar media to study the oxidation of anthracene and 9,10-diphenylanthracene. The use of 6.5 μm electrodes reduced the ohmic distortions observed by Lines and Parker but even at relatively slow sweep rates (> 100 mVs^{-1}) iR artifacts were observed in benzene and other low dielectric constant solvents. Bond and Mann[21] extended these studies to electrodes with a radius of less than 1 μm and showed how the concentrations of the electrolyte and electroactive species together with the electrode size could affect the theoretical slope of a plot of E *versus* $\log (i_l - i)/i$. It was found that with electroactive solute concentrations of 10^{-5} mol dm^{-3} and electrolyte concentrations of 0.1 to 0.5 mol dm^{-3}, distortion-free cyclic voltammograms could be obtained on a 0.15 μm radius ultramicroelectrode with sweep rates up to 500 mVs^{-1}. The effect of the concentration of electroactive species on voltammogram shape is shown in Figure 5 for ferrocene oxidation in benzene containing 0.1 mol dm^{-3} tetrahexylammonium perchlorate, $THAClO_4$ at a 5 μm radius platinum electrode.

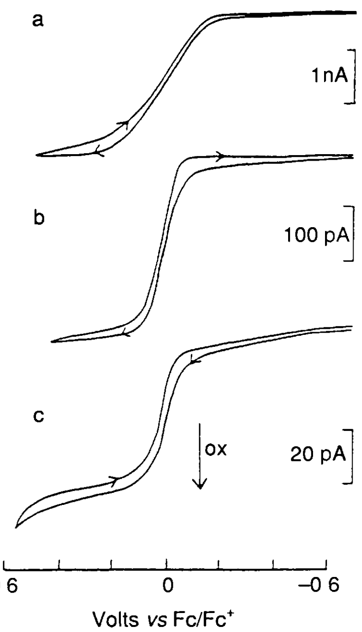

Figure 5 Cyclic voltammograms for the oxidation of ferrocene ($a = 10^{-3}$M, $b = 10^{-4}$M, and $c = 1.6 \times 10^{-5}$M) in benzene containing 0.1 M $THAClO_4$ at a 5 μm radius Pt electrode. Scan rate = 50 mVs^{-1}.
(Reproduced with permission from reference 21.)

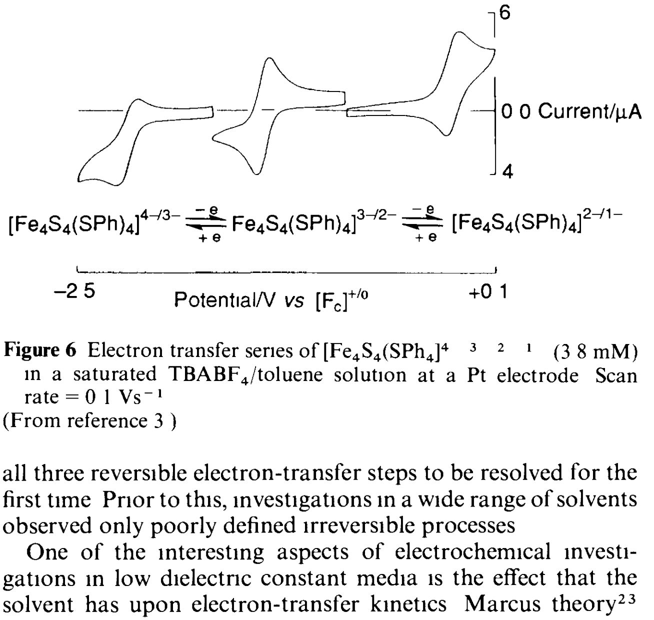

Figure 6 Electron transfer series of $[Fe_4S_4(SPh_4]^{4-/3-/2-/1-}$ (3.8 mM) in a saturated $TBABF_4$/toluene solution at a Pt electrode. Scan rate = 0.1 Vs^{-1}.
(From reference 3.)

Murray *et al.*[22] used media with lower dielectric constants than benzene in which to study electron-transfer processes. Heptane, which has a dielectric constant of 1.92 was made conducting with a mixture of dinonylnaphthalenesulfonic acid and trioctylphosphine oxide. This medium was used to investigate the redox properties of ferrocene, although the solution had the disadvantage of having only a 0.9 V potential window. The work also compared the electrochemical properties of a series of metal porphyrin compounds in toluene and methylene chloride and found that the two solvents had a marked effect on the redox behaviour.

Pickett[3] studied the electron transfer of $[Fe_4S_4(SPh)_4]^{n-}$ (where n is 1, 2, 3 or 4) in the toluene $TBABF_4$ chlathrate described above. Figure 6 shows that this solvent system allows all three reversible electron-transfer steps to be resolved for the first time. Prior to this, investigations in a wide range of solvents observed only poorly defined irreversible processes.

One of the interesting aspects of electrochemical investigations in low dielectric constant media is the effect that the solvent has upon electron-transfer kinetics. Marcus theory[23] predicts that the solvent reorganization energy, λ, is given by

$$\lambda = e^2(1/r - 1/d)(1/\epsilon_0 - 1/\epsilon) \qquad (4)$$

where e is a constant, r is the radius of the electroactive species, d is the electron transfer distance and ϵ_0 is the optical dielectric constant. In media such as those discussed here, the difference between the two dielectric constant terms becomes small, and in heptane the solvent reorganization energy is practically zero. Since the activation free energy of a process, $\Delta G^{\ddagger}$, is related to λ by

$$\Delta G^{\ddagger} = (\Delta G^0 + \lambda)^2/4\lambda \qquad (5)$$

where ΔG^0 is the standard free energy for converting the precursor into the successor state, then it follows that the progress of a reaction should be controlled by the value of ΔG^0. When $\Delta G^0 = 0$ then $\Delta G^{\ddagger} \approx 0$ and when $\Delta G^0 \gg \lambda$ then $\Delta G^{\ddagger} \rightarrow \infty$

Assuming that all other factors are constant, changing the medium for an electron-transfer process from water to heptane can cause a change in λ of over three orders of magnitude This, therefore, has obvious implications on the kinetics of the reaction, since the rate constant, k', is given by

$$k = K_p \kappa_{el} \nu_n \exp(-\Delta G^{\ddagger}/RT) \qquad (6)$$

where K_p is the precursor equilibrium constant, κ_{el} is the electronic transmission coefficient and ν_n is the nuclear collision frequency factor This is an area which is currently under investigation

One problem that does arise in low dielectric constant solvents is the choice of a suitable reference electrode The relatively high resistivities of these media means that an electrode with a low impedance is required Since chloride salts are relatively insoluble in such media, and generally highly hydrated, the Ag/AgCl couple is not generally suitable Several alternatives have been used, including a silver wire pseudo-reference electrode[16 22] and $Ag/AgNO_3$ or $Ag/AgClO_4$ in acetonitrile [19 20] These are rather unsatisfactory because they do not give a true reference potential and may cause problems due to solvent mixing More commonly used is the ferrocene/ferrocinium internal couple [3 5 21] Work by Wiles[24] and Abbott[18] found that couples such as silver/silver tetraphenyl borate and $Ag/AgBF_4$ were suitable for producing stable and reproducible reference potentials These reference electrodes have the advantage that they can be used and prepared directly in solvents of low dielectric constant and have a low impedance

6 Metal Deposition

By far the greatest electrochemical application of low dielectric constant media has been for the electrodeposition of metals Electroplating and electrowinning of metals is one of the largest industrial applications of electrochemistry Water as a solvent has obvious drawbacks because of the evolution of hydrogen at negative potentials This leads to poor surface finish, low current efficiency, and hydrogen embrittlement of many metal coatings Because of this, less than half of the metals known can be plated from aqueous media Alkali metals such as sodium and potassium are routinely plated from solvents such as DMSO and propylene carbonate Such solvents, however, can not be used for the deposition of transition metals since they form strong complexes causing a negative shift in the reduction potentials, usually into the region where solvent decomposition occurs Reviews on many of the unsuccessful attempts have been published elsewhere [6 25] Refractory metals such as titanium and tungsten are currently deposited from molten salt baths which operate at temperatures of 500 to 1000 °C This makes their use limited, difficult, and expensive One of the few options is to use non-polar solvents

Aromatic solvents have been used since the 1930s for the electrodeposition of aluminium The initial studies were made by Plotnikov in the Soviet Union and these ideas were expanded upon by Peled and Gileadi [4 26] Most of the work concentrated on a complex of $AlBr_3$ and KBr in toluene, xylene, or mesitylene This type of bath was found to be unsuitable for technical applications because of the low bath life-time, the corrosive reaction products, and the insufficient conductivity of the electrolyte Semi-production scale baths were achieved using diethylether and tetrahydrofuran as solvents and $LiAlH_4$ as an electrolyte

Although commercial application of this kind of process may seem unsuitable to scale up, a company in Germany, Schempp and Decker, built an industrial process based on triethylaluminium, alkali metal halides, and toluene High purity, bright, adhesive aluminium deposits were obtained from a bath of 15000 litres of toluene at 100 °C The deposition rate was 12 μm/h on a surface area up to 32 m² with a current efficiency of 90 to 100% [27] Aluminium alloys containing titanium and magnesium were also obtained by this method More comprehensive reviews of the properties of AlX_3/MX/toluene solutions and the aluminium plating process are published elsewhere [27 28] One disadvantage of this process is that the aluminium complex and electrolyte used are extremely water-sensitive

Work by Geblewicz, Potter, and Abbott[6 16 18 25] was successful in electrodepositing many of the transition metals from PAHs and their mixtures with monoaromatic solvents The metal ions were dissolved as long chain alkyl and aryl amine complexes and sufficient conductivity was achieved using tetrabutylammonium salts By this method zinc, cadmium, tin, mercury, lead, silver, cobalt, nickel, and iron were deposited as thick bright adherent layers up to 60 μm thick Later work[15 25] was also successful in depositing non-metals such as tellurium and silicon Figure 7 shows the cyclic voltammetry for the deposition of copper from a 15 mol% phenanthrene in anisole solution containing 51 mM CuCl (n-pentylamine) complex on a 10 μm gold microelectrode at 25 °C A characteristic nucleation loop can be seen which is indicative of a rapid nucleation process followed by the onset of diffusionally controlled deposition [18] It is typical of many of the complexes of transition metal ions studied in that it is an irreversible process This is because there are no ligands in solution to re-solvate the metal ions and the solvent is not sufficiently polar to stabilize the uncomplexed ion as would be the case for water or acetonitrile This has the disadvantage that soluble anodes can not be used, as is frequently done in commercial electroplating processes

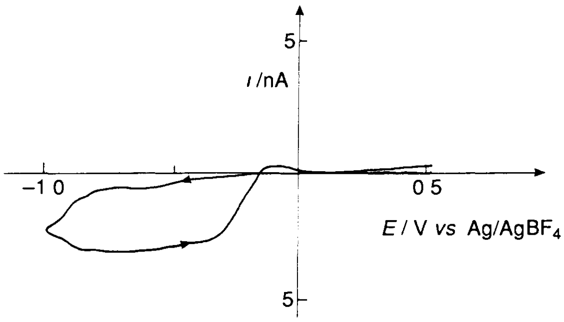

Figure 7 Cyclic voltammogram of a 51 mM CuCl n pentylamine complex in a 15 mol% phenanthrene in anisole solution on a 10 μm gold electrode at 25 °C
(Redrawn with permission from reference 18)

The electrodeposition of metals such as titanium, chromium, and aluminium proved to be slightly more difficult Although electrochemical investigations suggested the metal ions were being reduced to their respective M^0 states, no significant deposits were obtained following long term electrolysis [29] This was thought to result from the metals being deposited as small reactive nuclei which became re-oxidized upon reaction with some solution species It was discovered that 'wetting' the electrode surface with small islands of a fast nucleating metal such as silver or copper allowed metals such as titanium to be deposited

This section shows that low dielectric constant solvents can be used to electrodedeposit metals such as aluminium and titanium from media other than molten salts under ambient conditions

7 Conclusions

Clearly, solvents of low dielectric constant are practical and interesting media in which to carry out electrochemical investigations There are some problems associated with low dielectric constant media, most noticeably low solubility for ionic species and low conductivity However, methods of circumventing many of these problems have been highlighted in this review Probably their most useful property is the low degree of interaction with the solute which means that electron-transfer processes can be investigated without having to account for anomalous solvent effects The high chemical and electrochemical stability of these solvents allows a wide range of reactions to be investigated which are difficult or impossible to carry out in other media

Research in this subject is growing and some of the topics which are currently under investigation in media of low dielectric constant include double layer capacitance measurements, analysis of adsorption processes, electron transfer studies at water/anisole interfaces, and electrocrystallization reactions

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