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Electrochemistry in Media of Exceptionally Low Polarity: Voltammetry with a Fluorous Solvent

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Abstract

This work demonstrates the first cyclic voltammetry in a perfluorocarbon solvent without use of a cosolvent. The novel electrolyte tetrabutylammonium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate (NBu₄BArF₁₀₄; 80 mM) allows for voltammetry of ferrocene in perfluoro(methylcyclohexane) by lowering the specific resistance to $\Omega 268 \text{ k cm}$ at 20.8 °C. Despite significant solution resistance, the resulting voltammograms can be fitted quantitatively without difficulty. The thus determined standard electron transfer rate constant, k° , for the oxidation of ferrocene in perfluoro(methylcyclohexane) is somewhat smaller than for many solvents commonly used in electrochemistry, but can be explained readily as the result of the viscosity and size of the solvent using Marcus theory. Dielectric dispersion spectroscopy verifies that addition of NBu₄BArF₁₀₄ does not significantly raise the overall polarity of the solution over that of neat perfluoro(methylcyclohexane).

Keywords

fluorous phase; voltammetry; electrolyte; dielectric spectroscopy; ferrocene

1. Introduction

Organic solvents have found extensive application as solvents for electrochemistry [1]. Their wide-ranging solvent environments provide electroactive species with distinctive solubility, stability, and reactivity characteristics [1,2]. In particular, through the development of electrochemically stable lipophilic electrolytes [3], electrochemistry was demonstrated with low polarity solvents such as cyclohexane [4], heptane [5], and super-critical CO₂ [6]. While many of these solvents have no permanent dipole moment, they still exhibit a significant degree of polarizability. Fluorous solvents, on the other hand, have a very low polarizability, resulting in very weak van der Waals forces between their molecules and making them the most nonpolar solvents known [7]. For example, on the π^* scale of solvent polarity/polarizability [8], where dimethylsulfoxide is defined as 1 and cyclohexane 0, perfluorooctane can be found at -0.41 .

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In fact, octane and perfluorooctane do not mix at room temperature precisely because octane is too polarizable [9].

This extremely low polarity makes fluoruous phases very useful for probing the electrochemical behavior of species at near gas-phase conditions [10]. Advantages also arise from the exceptional level of chemical inertness of perfluorocarbons and—in view of spectroelectrochemistry [11,12]—their optical transparency down to 160 nm and the low absorbance in a wide range of the IR spectrum [11]. Since fluoruous phases have become important tools in catalytic synthesis [7,13] and separation techniques [14], electrochemistry in these media could allow online monitoring of reaction progress and separation efficiency. Other possible applications lie in battery technology and the study of fluoruous monolayers on macroscopic surfaces [7,15] and nanoparticles [7,16]

Despite the many possible uses of electrochemistry with fluoruous solvents, voltammetry in a perfluorocarbon solvent has not been reported yet. Even the most lipophilic salts known are only sparingly soluble in a fluoruous solvent, and any salt that does dissolve is heavily ion-paired [17,18]. Geiger and LeSuer demonstrated voltammetry with perfluoro(methylcyclohexane) (1) and an electrolyte consisting of the tetrakis(3,5-trifluoromethyl)phenyl borate anion and an imidazolium cation with a fluoruous ponytail, but they had to use the comparatively polar benzotrifluoride with a dielectric constant of 9.2 as cosolvent in a 1:1 ratio to perfluoro(methylcyclohexane) [19].

We demonstrated previously the first potentiometric sensors based on fluoruous membranes using perfluoro(perhydrophenanthrene) as the membrane matrix and the sodium salt of tetrakis[3,5-bis(perfluorohexyl)phenyl]borate to provide for ionic sites [17,18]. The receptor-free and receptor-doped [20] sensors displayed excellent selectivities and show promise to reduce biofouling. However, the low solubility of this salt (1 mM) and strong ion pairing resulted in bulk resistances too large for any electrochemical technique requiring significant current. Using the novel fluorophilic electrolyte prepared from this tetrakis[3,5-bis(perfluorohexyl)phenyl]borate and the tetrabutylammonium cation ($\text{NBu}_4\text{BArF}_{104}$) (2), we report in this work the first demonstration of voltammetry in an undiluted perfluorocarbon solvent, specifically perfluoro(methylcyclohexane). This compound is an excellent representative of fluoruous solvents as its π^* value (-0.48) and dielectric constant (1.86) are very low even among fluoruous phases [21]. With its boiling point of 76°C at 1.00 atm (partial pressure 0.139 atm [22] at 25°C), perfluoro(methylcyclohexane) is much more convenient to work with than the more volatile perfluorohexane or perfluorocyclohexane. Moreover, unlike the commercially available perfluoro(dimethylcyclohexane) and perfluoro(perhydrophenanthrene), perfluoro(methylcyclohexane) is not a mixture of isomers.

2. Experimental

2.1 Chemicals

All reagents were of the highest commercially available purity. Perfluoro(methylcyclohexane) and tetrabutylammonium chloride were used as received from Alfa Aesar (Ward Hill, MA, USA) and Fluka (Milwaukee, WI, USA), respectively. Sodium tetrakis[3,5-bis(perfluorohexyl)phenyl] borate tetrahydrate was prepared according to a previously described procedure [17].

$\text{NBu}_4\text{BArF}_{104}$ was synthesized by metathesis from tetrabutylammonium chloride and sodium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate. 10.0 g of sodium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate tetrahydrate and 1.03 g of tetrabutylammonium chloride were added to a separatory funnel containing 300 mL water and 300 mL FC-72 (perfluorohexanes). The mixture was shaken until all of the salt dissolved. The FC-72 layer was collected, washed

three times with 300 mL water, dried with MgSO_4 and filtered. The solvent was removed by rotary evaporation and further drying under vacuum at 75 °C for 48 hours, yielding $\text{NBu}_4\text{BARF}_{104}$ as a colorless, wax-like material in quantitative yield. ^1H NMR (500 MHz, FC-72 , δ): 0.507 (t, $J_{\text{HH}} = 7.2$ Hz, $-\text{CH}_3$, 12H), 0.75–0.90 (m, $-\text{CH}_2\text{CH}_3$, 8H), 1.04–1.19 (m, NCH_2CH_2- , 8H), 2.42–2.58 (m, NCH_2- , 8H), 7.31 (s, $p\text{-ArH}$, 4H), 7.51 (s, $o\text{-ArH}$, 8H). The corresponding tetraethyl- and tetrahexylammonium salts were prepared analogously. Differential scanning calorimetry (DSC, see Supplementary Material for details) revealed a glass-transition temperature of -21 °C, showing that **2** is a highly viscous ionic liquid at room temperature.

2.2 Resistance Measurements

The specific resistance of the 80 mM $\text{NBu}_4\text{BARF}_{104}$ /perfluoro(methylcyclohexane) solution was measured by impedance spectroscopy using a homemade cell. A Solartron SI 1287 electrochemical interface was used in combination with a Solartron 1255B frequency response analyzer (Solartron Analytical, Farnborough, Hampshire, England) at an AC amplitude of 100 mV, swept over a frequency range from 100,000 Hz to 10 Hz, using a DC offset equal to that of the open circuit potential. Solution resistance was determined by a fit of the resulting complex impedance plot to a model circuit consisting of a resistor in series with a parallel resistor/capacitor. The cell was made of two polished stainless steel disks separated by a Teflon ring (0.2 cm thick, 0.7 cm inner diameter). In each measurement, the fluorosol solution was injected into the cell, the cell was placed in a Teflon pocket, and the pocket was suspended in a water bath thermostated at 20.8 °C. All samples were placed in the bath for at least 20 minutes prior to measurement. The cell constant was determined by a KCl conductivity standard purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.3 Voltammetry

Voltammetry was performed with a CHI600C Potentiostat in combination with a CHI200B Picoamp Booster and Faraday Cage (CH Instruments, Austin, TX, USA). A 10 μm diameter Pt microelectrode from Bioanalytical Systems (BAS; West Lafayette, IN, USA) was used as the working electrode, a Au disk electrode (BAS) as the auxiliary electrode, and a silver wire (>99%, Alfa Aesar) as a quasi-reference electrode. Cyclic voltammograms (CVs) of ferrocene were performed at concentrations of 5.43, 2.72, 1.36, and 0.68 mM. Each concentration was scanned at 10, 50, 100, and 1000 mV/s. The resultant CV curves were then fitted using the DigiElch software package (ElchSoft, Kleinromstedt, Germany). All voltammograms are resistance corrected using the method outlined in the Supplementary Material before fitting.

Polishing equipment was purchased from Buehler (Lake Bluff, IL, USA). Prior to each experiment, the working electrode was polished on Microcloth polishing pads, first with 5.0 μm Micropolish II deagglomerated alumina, then with 1.0 μm and 0.25 μm MetaDi Supreme polycrystalline diamond suspension, and lastly with 0.05 μm Micropolish II deagglomerated alumina. The polished electrode was then ultrasonicated in a Triton X-100 detergent solution for 3 minutes, rinsed, and dried. Water used for the detergent solution and for rinsing the electrode was deionized and charcoal-treated (≥ 18.2 M Ω cm specific resistance) with a Milli-Q PLUS reagent-grade water system (Millipore, Bedford, MA, USA). Typically, samples were not purged of oxygen in order to minimize loss of solvent (purging did not have a significant effect on the shape of the CV in the potential range necessary to observe ferrocene), except in the case of the measurement of the electrochemical window (Figures 2 and 3), in which case the samples were purged with solvent-saturated argon for 30 min prior to measurement.

2.4 DOSY ^{19}F NMR

DOSY ^{19}F NMR was performed on a Varian INOVA 300 spectrometer equipped with a 4-nucleus probe capable of pulsed field gradients operating at 282.12 MHz. A bipolar pulse pair

stimulated echo (BPP-STE) sequence, as described in ref. ²³, was used to determine the diffusion coefficients of tetrakis[3,5-bis(perfluorohexyl)phenyl]borate and the solvent in a solution of 80 mM NBu₄BArF₁₀₄ in perfluoro(methylcyclohexane). The field gradient was calibrated using the self-diffusion coefficient of $6.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for perfluoro(methylcyclohexane) at 20 °C. This value was calculated using equation 1 from the self diffusion coefficient for 25 °C, as reported in ref. ²⁴.

2.5 Dielectric Dispersion Spectroscopy

Dielectric dispersion spectroscopy was performed with an HP8720 network analyzer and an open-ended coaxial [25] HP85070B probe (both Hewlett-Packard). In addition, a TE01-mode cylindrical dielectric resonator similar to the ones described in ref. 26 was used to measure the complex permittivity at 2.45 GHz. The value of 1.95 measured with the latter probe for the reference heptane agrees well with the literature value of 1.97 [27]. For perfluoro(methylcyclohexane), the fluoruous electrolyte solution, and heptane as reference, a consistent discrepancy of 0.30 was noted for the measurements with the two probes. Reasons for the discrepancy may be power reflection from the extremities of the specimen back to the probe face, or an air gap between the open-ended coaxial probe and the liquid sample [28,29], caused by surface roughness and the poor wettability of the Ni-coated probe with liquids of low polarity. The resulting shift in the dielectric constant (capacitive in nature in case of the latter explanation) was estimated from the TE01-mode cylindrical dielectric resonator measurements of heptane, and applied as a frequency independent correction for all measurements performed with the open-ended coaxial-line probe.

3. Results and Discussion

3.1 Electrolyte Characteristics

NBu₄BArF₁₀₄ was found to have a high solubility (greater than 80 mM) in perfluoro(methylcyclohexane), perfluorohexanes, perfluoroheptanes, perfluorodecalin, and perfluoro(perhydrophenanthrene), and a solubility of 8 mM in *n*-perfluorohexane. An 80 mM solution of NBu₄BArF₁₀₄ in perfluoro(methylcyclohexane) was measured to have a specific resistance of 268 kΩ cm at 20.8 °C. To explore how the alkyl substituents on the tetraalkylammonium cation affect the properties of BArF₁₀₄[−] salts, tetraethylammonium (NEt₄⁺) and tetrahexylammonium (NHx₄⁺) salts of BArF₁₀₄[−] were also prepared. NEt₄BArF₁₀₄ was found to have a high solubility in **1**, but an 80 mM solution of NEt₄BArF₁₀₄ in **1** exhibited a solution resistance approximately five times greater than solutions with **2** as the supporting electrolyte. This is indicative of stronger ion pairing for NEt₄BArF₁₀₄ than for the tetrabutylammonium salt **2**. On the other hand, NHx₄BArF₁₀₄ was shown to have a high solubility in **1** (greater than 80 mM) but a somewhat lower solubility than **2** in *n*-perfluorohexane and perfluorodecalin. It follows that among the three tested electrolytes, NBu₄BArF₁₀₄ is the most advantageous one since its cation is large enough to weaken ion pairing but not too large to compromise the solubility in fluoruous solvents.

3.2 Electrochemical Window

The electrochemical window provided by an electrolyte solution of 80 mM NBu₄BArF₁₀₄ in perfluoro(methylcyclohexane) spans 4.2 V, from +1.9 to −2.3 V vs. the ferrocenium/ferrocene couple (Fc⁺/Fc, Fig. 2). While the reduction limit is similar to that reported by Geiger and LeSuer for the 1:1 perfluoro(methylcyclohexane)/benzotrifluoride mixed solvent system [19], the oxidation limit of the perfluoro(methylcyclohexane) solution is 0.6 V greater than that of the solvent mixture.

To determine the cause of the reduction limit (i.e., to determine whether it is caused by the solvent or by the electrolyte salt), the reduction potentials of perfluoro(methylcyclohexane)

and the electrolyte were determined individually in a Na-distilled THF solution containing 0.1 M NBu_4ClO_4 . Each solution was purged for 30 min with Ar before measurements were taken. Addition of 20 mM $\text{NBu}_4\text{BArF}_{104}$ showed no significant change in the cyclic voltammogram. However, addition of perfluoro(methylcyclohexane) yielded an ill-defined reduction peak at -2.9 V vs. Fc^+/Fc (Figure 3), which is identical to a previously reported value for reduction of this compound in THF solution [30]. This shows that the reduction limit for our fluororous electrolyte solutions is given by the fluororous solvent. Since it has been shown that branched perfluorocarbons are more readily reduced than unbranched ones [30,31], it appears likely that use of a monocyclic or straight-chain perfluorocarbon as fluororous solvent would further extend the electrochemical window.

To explore the source of the oxidation limit, a solution of 0.1 M NBu_4PF_6 in anhydrous acetonitrile was used as the electrochemical solvent medium, which exhibited an electrochemical window from $+2.9$ V to -2.6 V vs. Fc^+/Fc . Samples were again purged with argon prior to voltammetric measurements. Upon addition of 25 mM $\text{NBu}_4\text{BArF}_{104}$ or 25 mM perfluoro(methylcyclohexane), no new oxidation peak could be observed, showing that the oxidation of both $\text{NBu}_4\text{BArF}_{104}$ and perfluoro(methylcyclohexane) in acetonitrile must occur at positive potentials that are outside the electrochemical window of acetonitrile. This indicates that the oxidation limit in the electrochemical window of the 80 mM $\text{NBu}_4\text{BArF}_{104}$ /perfluoro(methylcyclohexane) solution is not caused by the electrolyte or the solvent. Interestingly, upon taking a voltammogram of the $\text{NBu}_4\text{BArF}_{104}$ /perfluoro(methylcyclohexane) solution from -2.30 to $+7.45$ V vs Fc^+/Fc , a peak of relatively low intensity was observed with a half-wave potential of $+1.9$ V vs Fc^+/Fc (see Supplementary Material), suggesting that the oxidative limit of the electrochemical window is caused by a species of comparatively low concentration. Since this peak was observed even when perfluoro(methylcyclohexane) was purified by slow filtering through silica gel and storage over KOH, the impurities of perfluoro(methylcyclohexane) that are responsible for the oxidation limit of the electrochemical window do not appear to be polar in character. Moreover, since ^1H NMR spectra of commercial perfluoro(methylcyclohexane) show the presence of hydrogen-containing impurities in the mM range (in comparison, the solvent has a self concentration of 4.96 M), it may be that a low concentration of imperfectly perfluorinated solvent molecules with one (or more) hydrogens is responsible for the oxidative limit.

3.3 Voltammetric Measurements

Figure 4 shows CVs of 5.43 mM ferrocene in 80 mM $\text{NBu}_4\text{BArF}_{104}$ at various scan rates. The CV measured with a scan rate of 10 mV/s exhibits, in both the forward and backward scan, the typical shape expected for hemispherical diffusion at a microelectrode, i.e., the current reaches a plateau. At scan rates of 100 and 1000 mV/s, the forward scan still has the characteristics of hemispherical diffusion, while the reverse scan exhibits a peak maximum indicative of planar diffusion to the electrode. This suggests that the diffusion coefficient of Fc, which is oxidized in the forward scan, is significantly larger than the diffusion coefficient of Fc^+ , which is reduced in the backward scan. Indeed, upon fitting of the voltammograms, the diffusion coefficient for Fc was determined to be $(2.05 \pm 0.01) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ while that of Fc^+ was determined to be $(2.85 \pm 0.01) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. This disparity in diffusion coefficients is not surprising since in a fluororous solvent the cation Fc^+ is expected to form very stable ion pairs (and possibly even higher aggregates) with the electrolyte ions. Stability constants for ion pair formation in these solvents ($\log K_{\text{ip}}$ values from 14 to 16) [17,18,20] are among the strongest ones reported for any condensed phase, which is explained by the extremely low polarity/polarizability of fluororous media.

The accuracy of the diffusion coefficient of Fc^+ as determined by fitting of the CVs is supported by the observation that it is within 5.0% of the diffusion coefficient of the fluorophilic borate

in 80 mM NBu₄BArF₁₀₄ [$(3.0 \pm 1.5) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$], as determined by ¹⁹F Diffusion-Ordered NMR Spectroscopy (DOSY). This result is anticipated when considering that the ion pairs of the fluorophilic borate with tetrabutylammonium likely have very similar geometrical dimensions as the ion pairs of the fluorophilic borate with Fc⁺. The DOSY ¹⁹F NMR data along with the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi r \eta} \quad (1)$$

also permit a comparison of the effective radii of the BArF₁₀₄[−] anion, r_{anion} , and perfluoro (methylcyclohexane), r_{solvent} . Using equation 5, it follows that $r_{\text{anion}}/r_{\text{solvent}} = D_{\text{anion}}/D_{\text{solvent}}$ for a solution of the anion. Since the solution viscosity, η , is the same for both species, it does not affect $r_{\text{anion}}/r_{\text{solvent}}$. With the experimental values of D_{anion} and D_{solvent} (3.0×10^{-7} and $4.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively), $r_{\text{anion}}/r_{\text{solvent}}$ is calculated to be 14. This value is larger than what would be expected for an ion pair of BArF₁₀₄[−] and NBu₄⁺, confirming that not only ion pairs but also larger ionic aggregates are formed.

Figure 5 shows CVs of ferrocene in the concentration range from 0.68 to 5.43 mM. As anticipated, the CVs overlap very well upon normalization (see Supplementary Material), and the limiting oxidation current is directly proportional to the ferrocene concentration (see inset, Fig. 4). The CVs are indicative of a quasi-reversible electron transfer, as suggested by the asymmetry of the oxidation wave and supported by the fits that give a heterogeneous rate constant (k°) of $(7.13 \pm 0.04) \times 10^{-4} \text{ cm s}^{-1}$. The transfer coefficient determined through fitting was found to be 0.611 ± 0.002 . This value falls well within the range of 0.45 to 0.74 that has been published for Fc⁺/Fc in a variety of solvents from dichloromethane to methanol [32]. As shown in Figure 6, the predicted voltammetric curves overlap well with the experimental ones.

3.4 Heterogeneous Rate Constant

The k° of $(7.13 \pm 0.04) \times 10^{-4} \text{ cm s}^{-1}$ as determined by the above described fitting is somewhat smaller than the 0.03 to 8.4 cm/s for ferrocene oxidation at a Pt electrode in solvents ranging from chloroform to acetonitrile, as previously reported [32]. Two possible reasons for this observation appeared to be specific adsorption of the electrolyte onto the electrode surface [33,34], thereby inhibiting the electron transfer, or a slow rearrangement of the solvent and electrolyte, as described by the Marcus theory of electron transfer [35,36,37,40].

To test for the formation of an adsorbed electrolyte layer, a voltammogram of 80 mM NBu₄BArF₁₀₄/perfluoro(methylcyclohexane) was measured at 10 V/s in the range of −1.1 to 0.9 V vs. Fc⁺/Fc (see Supplementary Material). The results do not confirm the formation of an adsorbed layer since peaks indicative of adsorption or desorption events were not observed. However, the formation of such a layer cannot be excluded entirely since a particularly strongly adsorbed layer might not be desorbed in the potential range accessible.

An interpretation of k° based on the Marcus theory is more straightforward. The effect of solvent dynamics on k° has been studied with great detail and has been experimentally confirmed for solvents with a permanent dipole [35,36]. Modeling of the relationship between k° and the solvent dynamics involves the equation [35,37]:

$$k^\circ = K_p K_{EL} \tau_L^{-1} \left(\frac{\Delta G_{OS}^*}{4\pi RT} \right)^{1/2} \exp \left(\frac{-\Delta G^*}{RT} \right) \quad (2)$$

where K_p is the precursor formation constant, κ_{EL} is the adiabicity parameter, τ_L is the solvent longitudinal relaxation time, ΔG_{OS}^* is the free energy of activation for outer sphere reorganization, and ΔG^* is the sum of the inner and outer sphere reorganization free energies of activation. The longitudinal relaxation time is related to the Debye relaxation time (τ_D) by [38]

$$\tau_L = \left(\frac{\epsilon_\infty}{\epsilon_s} \right) \tau_D \quad (3)$$

where ϵ_∞ is the dielectric constant in the infinite frequency limit and ϵ_s is the static dielectric constant. For perfluoro(methylcyclohexane) at 20 °C, ϵ_∞ and ϵ_s are 1.859 and 1.85, respectively [39]. In cases where it is not known, τ_D can be estimated using the relation [38]

$$\tau_D = \frac{4\pi\alpha^3\eta}{k_B T} \quad (4)$$

where α is the radius of the solvent molecule and η is the solution viscosity. The combination of equations 1 to 3 gives:

$$k^o = K_p \kappa_{EL} \frac{\epsilon_s k_B T}{\epsilon_\infty 4\pi\alpha^3\eta} \left(\frac{\Delta G_{OS}^*}{4\pi RT} \right)^{1/2} \exp \left(\frac{-\Delta G^*}{RT} \right) \quad (5)$$

It has been reported previously that for ferrocene as the redox-active analyte and a variety of solvents ranging from chloroform to acetonitrile [32,41] (see also Figure 7) a plot of $\log k^o$ versus $\log \tau_L$ shows the expected linear relationship. This shows that for ferrocene the term $K_p \kappa_{EL} (\Delta G_{OS}^*)^{1/2} (4\pi RT)^{-1/2} \exp(-\Delta G^*/RT)$ has only a small dependence on the solvent.

In order to apply equation 5 to the fluorous electrolyte solutions, it had to be determined to what extent the addition of electrolyte affects the viscosity of perfluoro(methylcyclohexane). Upon addition of 80 mM NBu₄BArF₁₀₄ to perfluoro(methylcyclohexane), the diffusion coefficient of the solvent, as determined by DOSY ¹⁹F NMR, decreased only 33% from $6.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [24] to $(4.19 \pm 0.50) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which suggests that the addition of electrolyte only moderately increases the viscosity of the solution. Because the k^o determined in this work is 42 and 1.2×10^4 times smaller than for chloroform and acetonitrile, respectively, any effect of the electrolyte on the viscosity of perfluoro(methylcyclohexane) is comparatively small. Therefore, the published value for η of perfluoro(methylcyclohexane) of 1.56 cP [24] was used for all further calculations.

Using literature values for the viscosity and self-diffusion coefficient ($6.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) of perfluoro(methylcyclohexane) along with equation 1, a radius of 2.26 Å is obtained for perfluoro(methylcyclohexane). This radius along with equations 3 and 4 gives τ_L as 56 ps at 20 °C and permits the comparison of the relationship of k^o and τ_L from this work with corresponding data for non-fluorous solvents. Figure 7 illustrates that the experimentally determined k^o for the oxidation of ferrocene in the fluorous electrolyte solution falls on the same line as k^o values for non-fluorous solvents from the literature. This shows that while k^o for the oxidation of ferrocene in the fluorous electrolyte solution is smaller than for solvents commonly used in electrochemistry, its value can be readily explained as the result of the large viscosity and molecular size of the solvent perfluoro(methylcyclohexane).

3.5 Dielectric Spectroscopy

While this is the first report on voltammetry with a cosolvent-free perfluorocarbon, the question arises whether these experiments were in fact performed with the least polar organic phase to date. Or does the addition of the $\text{NBu}_4\text{BArF}_{104}$ electrolyte increase the polarity of the perfluoro (methylcyclohexane) phase to an extent that the electrolyte solution has a much more polar character than the fluoruous solvent alone? This question may be addressed through dielectrometry, which provides the dielectric constant as a measure of the molecular dipole moments and polarizability of a sample. Because of the inherent ionic conductivity of electrolyte solutions, the dielectric properties of the fluoruous media discussed here cannot be determined in the frequency range around 100 kHz, which is typically used for conventional dielectrometry. Instead, dielectric spectroscopy in the GHz range [42] was used in this study to assess the polarity of the electrolyte solution. Since relevant dynamic processes occur in the ps and ns range, the static dielectric constant can be determined by extrapolation of the real component, $\varepsilon'(\nu)$, of the frequency-dependent complex dielectric permittivity, $\varepsilon(\nu)$, from the GHz range to zero frequency. $\varepsilon(\nu)$ is given by [42]

$$\tilde{\varepsilon}(\nu) = \varepsilon'(\nu) - \sqrt{-1}\varepsilon''(\nu) \quad (6)$$

where $\varepsilon'(\nu)$ stands for dielectric dispersion, and the imaginary component $\varepsilon''(\nu)$ is the dielectric absorption. Because $\varepsilon''(\nu)$ is related to $\varepsilon'(\nu)$, it does not carry independent information and will not be discussed here.

As Figure 8 shows, $\varepsilon'(\nu)$ of solutions of the electrolyte salt $\text{NBu}_4\text{BArF}_{104}$ in perfluoro (methylcyclohexane) in the frequency range 0.2 to 20 GHz exceeded $\varepsilon'(\nu)$ of the pure perfluorocarbon by no more than 6.5%. The linear extrapolation of $\varepsilon'(\nu)$ in the range from 0.2 to 5.0 GHz suggests a static dielectric constant of the electrolyte solution of 1.96 and of pure perfluoro(methylcyclohexane) of 1.89. The latter value is in good agreement with the literature value of 1.86 [21].

4. Conclusions

Using the novel fluoruous electrolyte salt $\text{NBu}_4\text{BArF}_{104}$, we demonstrated that voltammetry can be performed with a perfluorocarbon solvent without the use of a cosolvent. Even though fluoruous phases are the least polar of all condensed phases, the observed CVs can be quantitatively fitted. The thus obtained k° is 1.6 orders of magnitude smaller than the smallest k° for oxidation of ferrocene in a set of common non-fluoruous solvents, for which k° values cover a range of 2.4 orders of magnitude. However, using Marcus theory, the small k° can be readily explained as the result of the large radius and the high viscosity of perfluoro (methylcyclohexane). While ion pair formation in these fluoruous phases is extremely strong and the formation of local pockets of higher polarity at the submolecular level is possible, dielectric spectroscopy confirms that the addition of electrolyte has only a minimal effect on the overall polarity of the fluoruous electrolyte solutions.

The unique solvent environment of fluoruous phases should provide an interesting medium for further experimentation. We are currently investigating the use of fluoruous media as new matrixes [43,44] for voltammetric and amperometric sensors as they are expected to exhibit selectivity patterns differing significantly from those of conventional hydrophobic phases [14,17,45] and have the potential to reduce chemical and biological fouling. Also, in view of a further extension of the already large solvent window, we are exploring the electrochemistry of different perfluorinated and partially fluorinated solvents.

5. Supplementary Material

Details of the differential scanning calorimetry, resistance correction, determination of the oxidation potential of the electrochemical window, and a voltammogram showing the absence of a desorptive peak are described in the Supplementary Material.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Izutsu, K. Nonaqueous Solutions. Wiley-VCH; Weinheim: 2002. Electrochemistry.
2. Ohrenberg C, Geiger WE. Inorg Chem 2000;39:2948–2950. [PubMed: 11232836]
3. Hill MG, Lamanna WM, Mann KR. Inorg Chem 1991;30:4687–4690.
4. Abbott AP, Claxton TA, Fawcett J, Harper JC. J Chem Soc Faraday Trans 1996;92:1747–1749.
5. Geng L, Ewing AG, Jernigan JC, Murray RW. Anal Chem 1986;58:852–860.
6. Abbott AP, Harper JC. J Chem Soc, Faraday Trans 1996;92:3895–3898.
7. Gladysz, JA.; Curran, DP.; Horváth, IT. Handbook of Fluorous Chemistry. Wiley & Sons; New York: 2005.
8. Brady JE, Carr PW. Anal Chem 1982;54:1751–1757.
9. Lo Nostro P, Scalise L, Baglioni P. J Chem Eng Data 2005;50:1148–1152.
10. Robinson EA, Schreiber HD, Spencer JN. J Phys Chem 1971;75:2219–2222. Ci X, Myers AB. J Chem Phys 1992;96:6433–6442.
11. Oberg KA, Palleros DR. J Chem Educ 1995;72:857–859. Lephart JO. Appl Spectrosc 1980;34:702–704.
12. Heineman WR. Anal Chem 1978;50:390A–402A.
13. Horváth IT, Rábai J. Science 1994;266:72–75. [PubMed: 17814001]
14. O’Neal KL, Geib S, Weber SG. Anal Chem 2007;79:3117–3125. [PubMed: 17375900]
15. Krafft MP, Goldman M. Curr Opin Colloid Interface Sci 2003;8:243–250.
16. Dass A, Guo R, Tracy JB, Balasubramanian R, Douglas AD, Murray RW. Langmuir 2008;24:310–315. [PubMed: 18052299]
17. Boswell PG, Bühlmann P. J Am Chem Soc 2005;127:8958–8959. [PubMed: 15969566]
18. Boswell PG, Lugert EC, Rábai J, Amin E, Bühlmann P. J Am Chem Soc 2005;127:16976–16984. [PubMed: 16316244]
19. LeSuer RJ, Geiger WE. J Electroanal Chem 2006;594:20–26.
20. Boswell PG, Szíjjártó C, Jurisch M, Gladysz JA, Rábai J, Bühlmann P. Anal Chem 2008;80:2084–90. [PubMed: 18290670]
21. Laurence C, Nicolet P, Dalati MT. J Phys Chem 1994;98:5807–5816.
22. Good WD, Dublin DR, Scott DW, George A, Lacina JL, Dawson JP, Waddington G. J Phys Chem 1959;63:1133–1138.
23. Wu D, Chen A, Johnson CS. J Magn Reson, Ser A 1995;115:123–126.
24. Xu S, Ballard L, Kim YJ, Jonas J. J Phys Chem 1995;99:5787–5792.
25. Baker-Jarvis J, Janezic MD, Jones CA. IEEE Trans Instrum Meas 1998;47:338–344. Gregory AP, Clarke RN. IEEE Trans Dielectr Electr Insul 2006;13:727–743.

26. Krupka, J.; Derzakowski, K.; Janezic, MD.; Baker-Jarvis, J. —TE₀₁₈ dielectric resonator technique for precise measurements of the complex permittivity of lossy liquids at frequencies below 1 GHz. 2004 Conference on Precision Electromagnetic Measurements Digest; London. 27 June–2 July, 2004; p. 469–470.
27. von Hippel, AR. Dielectric Materials and Applications. The M.I.T. Press; Cambridge, MA: 1954.
28. Arai M, Binner JGP, Cross TE. Electron Lett 1995;31:115–117.
29. Clarke, RN.; Gregory, AP.; Cannell, D.; Patrick, M.; Wylie, S.; Youngs, I.; Hill, G. A Guide to the Characterisation of Dielectric Materials at RF and Microwave Frequencies. The Institute of Measurement and Control, National Physical Laboratory; London: 2003.
30. Marsella JA, Gilicinski AG, Coughlin AM, Pez GP. J Org Chem 1992;57:2856–2860.
31. Pud AA, Shapoval GS, Kukhar VP, Mikulina OE, Gervits LL. Electrochim Acta 1995;40:1157–1164.
32. Baranski AS, Winkler K, Fawcett WR. J Electroanal Chem 1991;313:367–375. Pournaghi-Azar MH, Ojani R. Electrochim Acta 1994;39:953–955. Sun P, Mirkin MV. Anal Chem 2006;78:6526–6534. [PubMed: 16970330]
33. Fawcett WR. Can J Chem 1981;59:1844–1853.
34. Breiter M, Kleinerman M, Delahay P. J Am Chem Soc 1958;80:5111–5117.
35. Pyati R, Murray RW. J Am Chem Soc 1996;118:1743–1749.
36. Fawcett WR, Opallo M. Angew Chem Int Ed Engl 1994;33:2131–2143.
37. Marcus RA. Annu Rev Phys Chem 1964;84:155–196.
38. Frolich, H. Theory of Dielectrics. Oxford University Press; 1949.
39. Lifanova NV, Usacheva TM, Zhuravlev VI. Zh Fiz Khim 1992;66:237–240.
40. Fawcett WR, Foss CA. J Electroanal Chem 1989;270:103–118.
41. Clegg AD, Rees NV, Klymenko OV, Coles BA, Compton RG. J Electroanal Chem 2005;580:78–86.
42. Buchner R, Hefter GT, May PM. J Phys Chem A 1999;103:1–9. Wakai C, Oleinikova A, Weingaertner H. J Phys Chem B 2006;110:5824. Kaatz U. J Solution Chem 1997;26:1049–1112. Weingärtner H. Z Phys Chem 2006;220:1395–1405.
43. Lugert EC, Lodge TP, Bühlmann P. J Polym Sci, Part B: Polym Phys 2008;46:516–525.
44. Lai CZ, Koseoglu S, Lugert EC, Boswell PG, Rabai J, Lodge TP, Bühlmann P. J Am Chem Soc 2009;131:1598–1606. [PubMed: 19133768]
45. Vincent JM. J Fluorine Chem 2008;129:903–909.

Figure 1.
Structures of perfluoro(methylcyclohexane) (**1**) and NBu₄BARf₁₀₄ (**2**).

Figure 2. Cyclic voltammogram (CV) of perfluoro(methylcyclohexane) containing 80 mM $\text{NBu}_4\text{BArF}_{104}$, scan rate = 100 mV/s, showing the electrochemical background. Data is corrected for solution resistance.

Figure 3. CVs of a 0.1 M $\text{NBu}_4\text{ClO}_4/\text{THF}$ solution containing 0, 25, 50, or 75 mM perfluoro(methylcyclohexane): scan rate = 10 mV/s, $T = 21^\circ\text{C}$.

Figure 4.

CVs of 5.43 mM ferrocene and 80 mM $\text{NBu}_4\text{BArF}_{104}$ in perfluoro(methylcyclohexane) with various scan rates. Data is corrected for solution resistance.

Figure 5.

CVs of varied concentrations of ferrocene in 80 mM $\text{NBu}_4\text{BArF}_{104}$ /perfluoro (methylcyclohexane): scan rate = 10 mV/s, $T = 21^\circ\text{C}$. The inset shows the linear relationship between the limiting current and the ferrocene concentration.

Figure 6.

CV of 1.36 mM ferrocene normalized to the diffusion-limited current (solid) along with a fit based on $\alpha = 0.61$, $k^o = 7.13 \times 10^{-4} \text{ cm/s}$, $D(\text{Fc}) = 2.05 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D(\text{Fc}^+) = 2.85 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (dots).

Figure 7. Log-log plot of k° versus τ_L along with a linear fit for the literature data (open circles, [32,40, 41]) only. The fit is extrapolated to the τ_L for perfluoro(methylcyclohexane) (filled circle).

Figure 8. Dielectric dispersion spectrum of perfluoro(methylcyclohexane) with and without 80 mM $\text{NBu}_4\text{BArF}_{104}$.