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The effect of solvent on the Seebeck coefficient and thermocell performance of cobalt bipyridyl and iron ferri/ferrocyanide redox couples

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The conversion of thermal energy to electricity using thermoelectrochemical cells (thermocells) is seen as a developing approach to harvesting waste heat. The performance of a thermocell is highly dependent on the solvent used in the electrolyte, but the interplay of the various solvent effects is not yet well understood. Here, using the redox couples $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ and $(\text{Et}_4\text{N})_3/(\text{NH}_4)_4\text{Fe}(\text{CN})_6$, which have been designed to allow dissolution in different solvent systems (aqueous, non-aqueous and mixed solvent), the effect of solvent on the Seebeck coefficient (S_e) and cell performance was studied. The highest S_e for a cobalt-based redox couple measured thus far is reported. Different trends in the Seebeck coefficients of the two redox couples as a function of the ratio of organic solvent to water were observed. The cobalt redox couple produced a more positive S_e in organic solvent than in water, while addition of water to organic solvent resulted in a more negative S_e for the $\text{Fe}(\text{CN})_6^{3-/4-}$. UV-Vis and IR investigations of the redox couples indicate that S_e is affected by changes in solvent-ligand interactions in the different solvent systems.

Introduction

The direct conversion of thermal energy to electrical energy, without any carbon dioxide emissions, is an environmentally friendly method of sustainable energy production. Thermal energy can be converted to electricity using thermoelectrochemical cells (thermocells). These devices, which contain a redox active electrolyte and two electrodes working at different temperatures, have attracted increasing interest in recent years as a potentially lower cost alternative to the semiconductor-based devices, particularly for harvesting low grade waste heat.^[1]

Thermocells harvest thermal energy and produce electricity based on the Seebeck effect, whereby a potential difference is produced between two electrodes as a result of the existence of a temperature gradient. This temperature gradient (ΔT) across the cell affects the reversible potential of a redox couple, via the reaction entropy (S) of the process.^[2] The entropy change (ΔS) of the redox couple at different temperatures can be related to the Seebeck coefficient (S_e) of the redox couple by:

$$S_e = \frac{\Delta S}{nF}$$

The interaction between the solvent and the redox complex affects the entropy of the redox reaction through rearrangement of the solvation shell surrounding the redox ions upon electron transfer. However, the influence of different solvents, and the detail of how this affects the S_e of different redox couples, is not yet well understood. For transition metal-based cationic redox couples with different ligands, in aqueous and various organic solvents, it has been suggested that the reaction entropy is inversely dependent on the acceptor number of the solvent.^[3]

The use of ionic liquids is of increasing interest in thermocell technologies because of their high thermal stability, non-volatility, non-flammability and thermal stability.^[4] In these solvents, the charges of the redox ions and the charge density of the IL ions are both reported to be determinants of size and sign of the Seebeck coefficient.^[4c, 5] ILs with higher charge density ions have been concluded to produce stronger electrostatic interactions with charged redox ions, which leads to an increase in the entropy change of the reaction. The value of Seebeck coefficient has therefore been shown to have a linear dependence with $(Z_{\text{ox}}^2 - Z_{\text{red}}^2)/r$, where Z_{ox} , Z_{red} and r , are the charge of the

oxidised and reduced species and their effective radius, respectively.^[4c, 5-6] The sign of the reaction entropy and S_e is related to the absolute charges of the oxidised and reduced species. A positive S_e is produced when the oxidised species has a larger absolute charge than the reduced, and vice versa.^[4c] In terms of thermocell development, for individual cells it is the absolute magnitude of S_e that is important, rather than the sign; the sign simply dictates which electrode is the cathode and which is the anode. However, the development and study of both positive and negative S_e couples is important for thermocells in a series connected alternating p- and n- (positive and negative S_e) type arrangement.^[7]

The large positive Seebeck coefficient of the cobalt bipyridyl redox couple in organic solvents makes it a good candidate for use in thermocells. This high Seebeck coefficient has been attributed to the change in the spin state of the central metal ion ($\text{Co}^{2+/3+}$), which adds an additional contribution to the total entropy change, ΔS .^[4a] In prior work that measured the S_e of $\text{Co}(\text{bpy})_3^{2+/3+}$ in three different solvent systems (organic solvents, ILs and mixed IL/molecular solvents) it was found that the highest S_e is produced in pure organic solvents.^[4b] A slight decrease in S_e was measured after addition of ILs to organic solvents; this was attributed to the change in entropy of the redox reaction arising from the changes in the solvation shell surrounding the redox ions.

Recently, it has been reported that a large Seebeck coefficient (-2.9 mV/K) for the potassium ferri/ferrocyanide redox couple can be achieved through addition of organic solvents such as methanol or dimethyl sulfoxide (DMSO) to the aqueous solution.^[8] By studying the interaction of solvent and redox ions through FTIR and UV-Vis spectroscopy, the authors attributed this large Seebeck coefficient to the entropy change of the redox couple primarily as a result of rearrangement in the solvation shell which surrounds the $\text{Fe}(\text{CN})_6^{4-}$ ion. Using FTIR to study the $\text{C}\equiv\text{N}$ stretching modes of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$, it was found that while addition of organic solvent broadens the characteristic peak of $\text{Fe}(\text{CN})_6^{4-}$, it does not significantly affect the $\text{C}\equiv\text{N}$ stretching mode of $\text{Fe}(\text{CN})_6^{3-}$. This indicates the preferential solvation of $\text{Fe}(\text{CN})_6^{3-}$ ions by water molecules rather than organic solvent molecules, but a range of solvation states of the $\text{Fe}(\text{CN})_6^{4-}$ in a mixed solvent system, suggesting that it is this difference that leads to an increase in S_e . In addition, a high Seebeck coefficient of 4.2 mV K^{-1} for the $\text{K}_{3/4}\text{Fe}(\text{CN})_6$ redox couple in water has recently been achieved by introducing strong chaotropic cations,^[9] such as guanidinium, combined with urea.^[10] The authors proposed that while urea tends to bond with $[\text{Fe}(\text{CN})_6]^{3-}$, guanidinium has a stronger affinity for $[\text{Fe}(\text{CN})_6]^{4-}$, creating differences in interactions that synergistically increasing the entropy difference between the two halves and thus the Seebeck coefficient.

The importance of S_e in determining the performance of a thermocell, and the drive to develop new redox electrolytes for these devices, makes it crucial to fully understand the factors affecting the sign and magnitude of S_e . Here, the effect of solvent on S_e was studied using cationic (cobalt) and anionic (iron) based redox couples. The $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ redox couple was chosen and synthesised specifically with these counter-ions to enable solubility in both water and organic solvents, thereby allowing study of the same redox couple across different types of solvent. This complex was used for preparation of 0.01 M $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ in DMSO, 3-methoxypropionitrile (MPN), water and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{mim}][\text{NTf}_2]$), to investigate the effect of solvent on the electrochemical behaviour, Seebeck coefficient and cell performance. For further study of the effect of solvent on the Seebeck coefficient, the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple was investigated. The commonly used $\text{K}_{3/4}\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple is very poorly soluble in organic solvents, which makes studies of S_e difficult. To overcome this, $(\text{Et}_4\text{N})_3/(\text{NH}_4)_4\text{Fe}(\text{CN})_6$, which has a higher solubility in organic solvents,^[7] was synthesised and used to prepare mixed solvent systems with a higher ratio of organic solvents; this allowed us to gain further insight into the effect of solvents on the S_e in aqueous systems.

Results and discussion

Electrochemical behaviour, ion diffusivity and Seebeck coefficient of $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ in different solvent systems

Study of the electrochemical behaviour of $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ showed that it has a stable and quasi-reversible electrochemical behaviour in the different solvent systems (Figure 1a). Using water as the solvent resulted in a more reversible CV and higher current density, while the

lowest current was observed using IL as the solvent. The IL also gave a smaller diffusion coefficient for the cobalt redox ions, compared to those in DMSO or water (Table 1). This is consistent with the higher viscosity of the IL compared to the other solvents, which also results in smaller current densities.

Table 1 Diffusion coefficient of redox species in 0.01 M $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ in different solvents at 25 °C

Solvent	Viscosity (mPa.s) at 25 °C	Diffusion coefficient $\times 10^6 \text{ cm}^2 \text{ s}^{-1}$	
		$[\text{Co}(\text{bpy})_3]^{2+}$	$[\text{Co}(\text{bpy})_3]^{3+}$
Water	0.8 ^[11]	6.58 ± 0.22	10.62 ± 1.12
DMSO	2.0 ^[12]	0.67 ± 0.13	1.62 ± 0.26
MPN	1.1 ^[12]	0.48 ± 0.06	0.96 ± 0.07
$[\text{C}_2\text{mim}][\text{NTf}_2]$	27.5 ^[13]	0.17 ± 0.01	0.17 ± 0.02

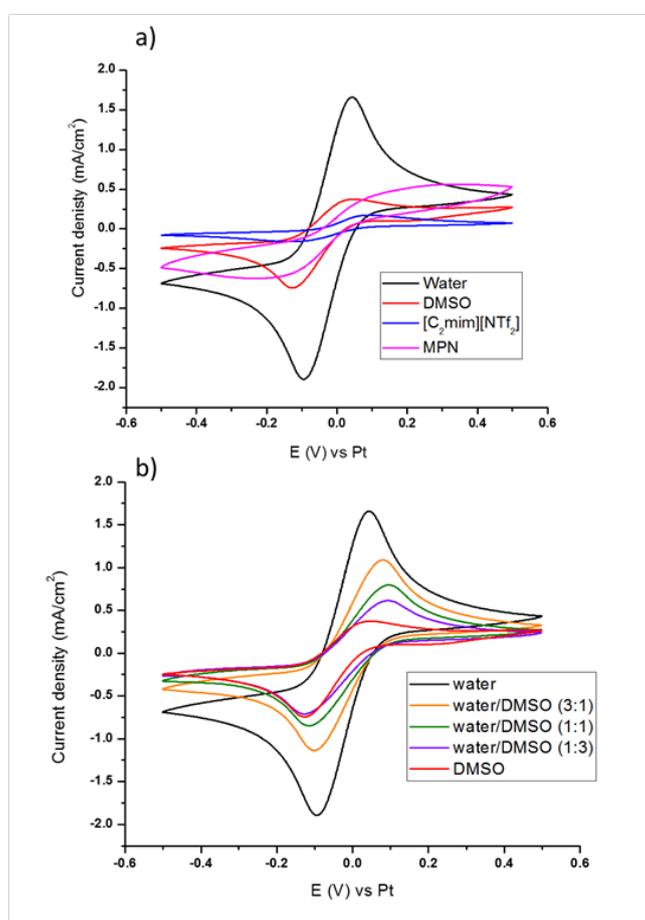


Figure 1 The electrochemical behaviour of 0.01 M $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$: a) in different solvent systems: water (—), DMSO (—), ionic liquid ($[\text{C}_2\text{mim}][\text{NTf}_2]$) (—) and MPN (—); b) in mixed solvent systems with different ratios of water and DMSO, using a three-electrode cell equipped with a platinum working electrode (1.6 mm diameter) and two platinum wires as the counter and reference electrodes, at a scan rate of 50 mV s^{-1} .

Comparison of the S_e values for $[\text{Co}(\text{bpy})_3][\text{NTf}_2]_{2/3}$ and $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ redox couples in DMSO, MPN or IL (Table 2) shows that in this case the counter ion has no significant effect. In contrast, using different solvents in the electrolyte preparation revealed a strong dependence of S_e on the nature of solvent. $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ in DMSO gave an S_e of 2.65 mV/K, which is the highest S_e for 0.01 M cobalt-based redox couple

reported thus far.^[4a, 4b, 14] The S_e for this redox couple in MPN is also higher than that measured in water or IL. Replacement of DMSO with water resulted in a significant decrease in S_e , to 1.22 mV/K. This is consistent with our previous observations,^[15] where a low S_e for $[\text{Co}(\text{bpy})_3]\text{Cl}_{2/3}$ in water (1.21 mV/K) was observed while developing quasi-solid state cellulose-based electrolytes.

As introduced above, the S_e of transition metal complexes has previously been correlated to the charge density of the redox ions and the solvent acceptor number.^[5-6] Assessing this possible trend for the cobalt complex studied here, and considering the difference in acceptor number of DMSO (19.3),^[16] $[\text{C}_2\text{mim}][\text{NTf}_2]$ (27.4)^[17] and water (54.8),^[16-17] it was observed that $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ in a solvent with a larger acceptor number results in a smaller S_e . This is also consistent with early reports,^[3a] that $[\text{Co}(\text{bpy})_3]^{2+/3+}[\text{ClO}_4]_{2/3}$ and $[\text{Co}(\text{phen})_3]^{2+/3+}[\text{ClO}_4]_{2/3}$ redox couples in organic solvents have a larger reaction entropy than in water, and lower acceptor number organic solvents result in more positive ΔS values. In that early work, it was found that the smallest entropy change for $[\text{Co}(\text{bpy})_3]^{2+/3+}$ and $[\text{Co}(\text{phen})_3]^{2+/3+}$ (22 cal. $\text{K}^{-1} \text{mol}^{-1}$, $S_e = 0.92$ mV/K) was measured in water, while the largest values of ΔS were found in non-aqueous solvents, especially in aprotic media (e.g. ~ 57 cal. $\text{K}^{-1} \text{mol}^{-1}$, $S_e = 2.38$ mV/K in nitromethane).^[3a] The authors suggested^[3a] that the change in S_e with solvent is related to the relative ability of the 3+ ion to “disturb the bulk solvent structure and re-orientate solvent molecules within its vicinity” compared to the 2+ ion and that there is more solvent polarization (“ordering”) in the vicinity of the complex for non-aqueous solvents compared with the same process in water.^[3a] However, it was also noted that there is a diverse range of influences on these solvent effects.

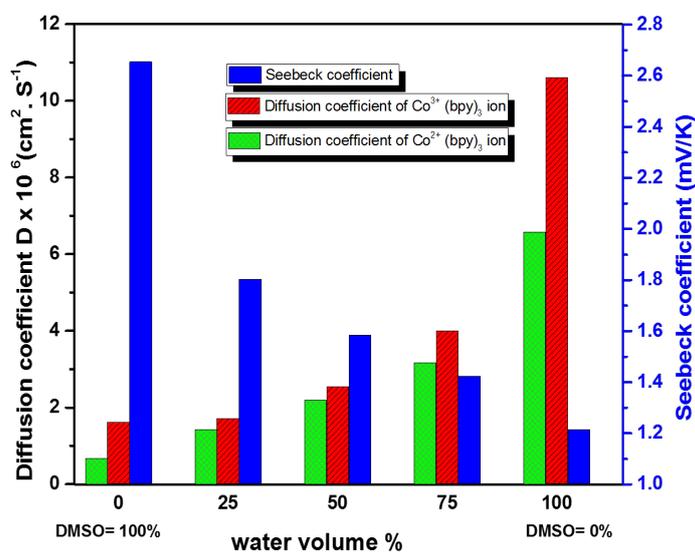


Figure 2 Seebeck coefficient and diffusion coefficient of $[\text{Co}(\text{bpy})_3]^{2+/3+}$ ions in different ratios of water/ DMSO.

In the present work, as the largest decrease in S_e of the cobalt redox couple was observed using water as the solvent instead of DMSO, in order to further understand this effect and determine any trend with solvent composition, solutions of $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ in mixed solvent systems were prepared using different ratios of water and DMSO. It was found that the addition of water to the DMSO decreases the value of the S_e of $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ (Figure 2, Table S1) but not in a completely linear trend. Electrochemical analysis of the mixed solvent system shows that the reversibility of $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ and the current density are improved by increasing the ratio of added water to DMSO (Figure 1b). This observation is supported by the ion diffusion coefficients (Figure 2) which also increased with water addition, as a result of the lower viscosity of water than DMSO. This trend in thermodynamics and transport behaviour with solvent composition is important for understanding the thermocell performance of these different solvent systems, which reflect a balance between these different parameters, as discussed further below.

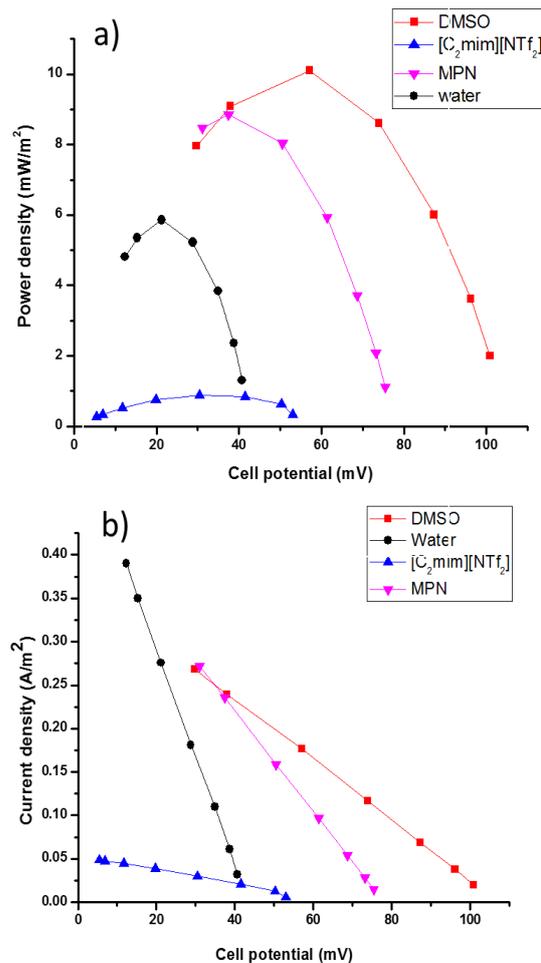


Figure 3 a) Power density and b) current density of thermocells containing 0.01 M [Co(bpy)₃][BF₄]_{2/3} in different solvents: water (—), DMSO (—), [C₂mim][NTf₂] (—) and MPN (—) (T_{cold}= 20 °C, T_{hot}= 60 °C).

Table 2 The effect of solvent and redox couple counter ion on the Seebeck coefficient of 0.01 M cobalt-based electrolytes.

Redox couple	Solvent	Seebeck coefficient (mV/K)
Co(bpy) ₃ [NTf ₂] _{2/3}	DMSO	2.51 ± 0.02
[Co(bpy) ₃][BF ₄] _{2/3}	DMSO	2.65 ± 0.02
[Co(bpy) ₃][NTf ₂] _{2/3}	MPN	2.05 ± 0.02
[Co(bpy) ₃][BF ₄] _{2/3}	MPN	1.95 ± 0.06
[Co(bpy) ₃][NTf ₂] _{2/3}	[C ₂ mim][NTf ₂]	1.52 ± 0.03
[Co(bpy) ₃][BF ₄] _{2/3}	[C ₂ mim][NTf ₂]	1.54 ± 0.01
[Co(bpy) ₃][NTf ₂] _{2/3}	Water	-*
[Co(bpy) ₃][BF ₄] _{2/3}	Water	1.22 ± 0.04

*Not soluble in water

Performance of thermocells containing the $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ redox couple in different solvent systems

Thermocell performance (Figure 3) was studied by holding the two electrodes at different temperatures ($T_{\text{cold}} = 20\text{ }^\circ\text{C}$, $T_{\text{hot}} = 60\text{ }^\circ\text{C}$), applying a sequence of external resistances, measuring the voltage and thus calculating the power and current output.^[4a] The DMSO-based electrolyte gave higher power density than the three other electrolytes (Figure 3a), while the aqueous electrolyte had larger current density, resulting from higher ion diffusivity (Figure 3b, Table 1). This demonstrates the trade-off between different factors, such as S_e and mass transport that determine the thermocell performance. The higher power output of the cell with the DMSO-based electrolyte can be attributed to the higher S_e of the cobalt redox couple in DMSO compared to that in other solvents. In contrast, although the S_e of $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ in the IL is higher than that in water, the power output of the cell with the IL-based electrolyte is much lower due to the mass transfer resistance arising from the higher viscosity of the IL-based electrolyte.^[4b]

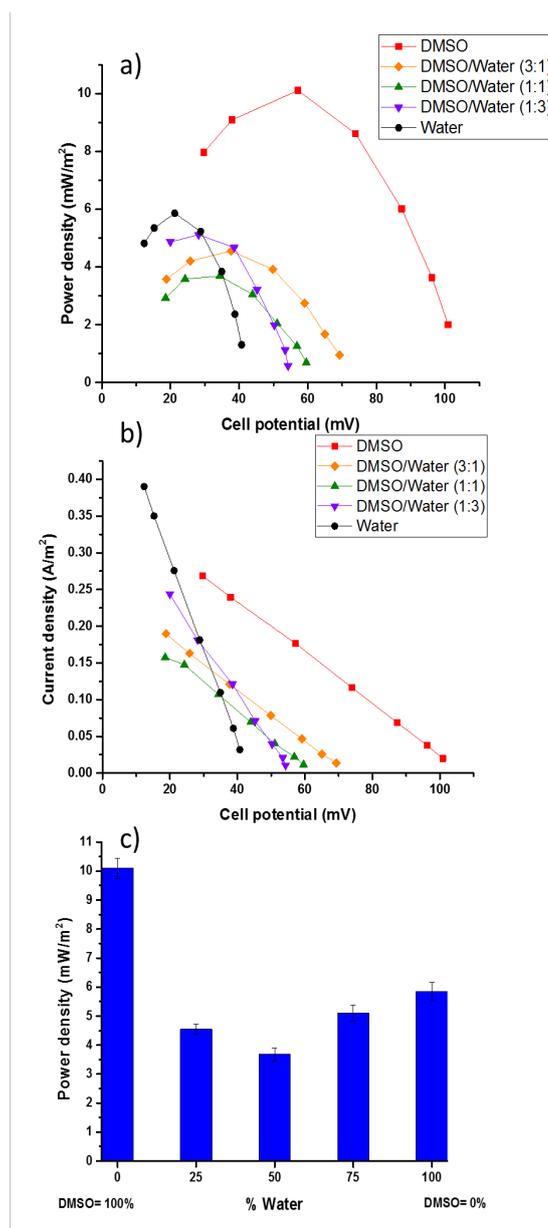


Figure 4 a) Power and b) current output of the cell containing 0.01M of $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$ in mixed solvent (water/ DMSO) in different solvent ratios, and c) the effect of the ratio of water on maximum power density of cell ($T_{\text{cold}} = 20\text{ }^\circ\text{C}$, $T_{\text{hot}} = 60\text{ }^\circ\text{C}$).

To overcome the mass transfer problem in viscous ILs, the ILs can be mixed with high boiling molecular solvents. Addition of organic solvents such as DMSO, MPN and propylene carbonate to ILs can improve the power and current density of thermocells with the $\text{Co}(\text{bpy})_3^{2+/3+}$ couple by decreasing the mass transport resistance.^[4b,18] Here, in spite of the observed improvement in ion diffusivity in mixed water/DMSO solvent systems with increasing amounts of added water, the performance of the thermocells with the mixed solvents did not show the same trend (Figure 4). The highest power density of 10 mW/m² was produced using DMSO as solvent. Addition of 25 and 50 % of water led to a sharp decrease in the power density of the cell (Figure 4c), which is attributed to the decreased S_e . Further increase in the water content led to a slight rise in S_e . Overall the power produced by thermocells with mixed electrolyte systems was less than either of the two individual solvent systems (DMSO or water). Thus, the cell performance did not benefit from a combined advantage of high S_e in DMSO and high ion diffusivity in the aqueous system. In summary, it can be concluded that although addition of water to DMSO improves the mass transfer and reversibility, the smaller S_e in water has the biggest impact on the overall cell performance. This again serves to highlight the importance of understanding and optimising S_e when developing new thermocell electrolytes.

The effect of solvent on the Seebeck coefficient of the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple

To further study the effect of solvent on S_e , the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple, which has a negative S_e (between -1.43 and -1.77 mV/K in water depending on the concentration of redox couple),^[19] was chosen for comparison with the positive S_e $\text{Co}(\text{bpy})_3^{2+/3+}$ system. Solutions of 0.01 M $\text{K}_{3/4}\text{Fe}(\text{CN})_6$ in water or in mixtures of water and a range of aprotic and protic organic solvents (DMSO, MPN, isopropanol and ethylene glycol) at a volume ratio of 3:1 were prepared. The miscibility of these organic solvents with water, and their relatively high boiling point, make them good candidates for thermocell systems. As the $\text{K}_{3/4}\text{Fe}(\text{CN})_6$ redox couple is not soluble in organic solvents, it is not possible to prepare a solution in pure organic solvents or in mixed water/organic solvent systems with high ratios of organic solvent. To overcome this, replacement of the K^+ counter-ions with Et_4N^+ and NH_4^+ was investigated as a route to increasing the solubility in higher ratio organic solvent/water systems. Thus, the $(\text{Et}_4\text{N})_3/(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ redox couple was investigated in thermocells for the first time, used to prepare 0.01 M redox concentration in water and in mixed water/DMSO at ratios of 3:1 and 1:1.

The results in Table 3 show that the higher the ratio of DMSO, the smaller the S_e in the mixed solvents. Unlike the cobalt redox couple electrolytes discussed above, the largest (most negative) S_e for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple was measured in water, and addition of organic solvents to water resulted in a smaller S_e . The smallest change is seen with the addition of protic solvents, particularly ethylene glycol, and the biggest effect with MPN. This likely reflecting the amount that the hydration/solvation shell of the redox couple is changed in the mixed solvent systems compared to that in pure water, which is more pronounced upon addition of aprotic solvents. The addition of organic solvents to aqueous solution of the $(\text{Et}_4\text{N})_3/(\text{NH}_4)_4\text{Fe}(\text{CN})_6$ redox couple also decreased S_e , with the effect being greater at higher DMSO concentrations.

Table 3 The effect of organic solvent addition on the Seebeck coefficient of homogeneous solutions of 0.01 M $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple in water

Solvent	Redox couple (0.01 M)	Seebeck coefficient (mV/K)
Water	$\text{K}_{3/4}\text{Fe}(\text{CN})_6$	-1.68 ± 0.02
Ethylene glycol : Water (1:3)	$\text{K}_{3/4}\text{Fe}(\text{CN})_6$	-1.64 ± 0.01
Isopropanol : Water (1:3)	$\text{K}_{3/4}\text{Fe}(\text{CN})_6$	-1.42 ± 0.02
DMSO : Water (1:3)	$\text{K}_{3/4}\text{Fe}(\text{CN})_6$	-1.31 ± 0.01
MPN : Water (1:3)	$\text{K}_{3/4}\text{Fe}(\text{CN})_6$	-1.22 ± 0.01
Water	$(\text{Et}_4\text{N})_3/(\text{NH}_4)_4\text{Fe}(\text{CN})_6$	-1.68 ± 0.03
DMSO : Water (1:3)	$(\text{Et}_4\text{N})_3/(\text{NH}_4)_4\text{Fe}(\text{CN})_6$	-1.32 ± 0.02
DMSO : Water (1:1)	$(\text{Et}_4\text{N})_3/(\text{NH}_4)_4\text{Fe}(\text{CN})_6$	-1.00 ± 0.01

This decrease in S_e is opposite to that of the effect reported for 0.4 M $K_{3/4}Fe(CN)_6$ using a mixed solvent system containing 80 wt% water and 20 wt% of an organic solvent such as methanol, ethanol and DMSO.^[8] This is attributed to differences in the solubility of the $(Et_4N)_3/(NH_4)_4Fe(CN)_6$ redox couple used here, which forms a homogeneous solution, compared to the potassium salt that we observed to form a precipitate upon addition of organic solvent.

In summary, investigation of the $[Co(bpy)_3]^{2+/3+}$ and $Fe(CN)_6^{3-/4-}$ redox couples in different solvent systems showed, surprisingly, that the direction of change in S_e (and thus reaction entropy change) upon addition of organic solvent to water is the same for both couples despite the different signs of S_e . Increasing the amount of water in the $[Co(bpy)_3]^{2+/3+}$ systems, decreases the S_e . However, for $Fe(CN)_6^{3-/4-}$, increased water content makes S_e more negative. The origins of these effects were further investigated spectroscopically, as discussed below.

UV-vis and IR studies of redox couples in different solvents

The results discussed above clearly demonstrate that the Seebeck coefficients of redox couples is strongly dependent on the solvent. As the Seebeck coefficient is affected by the solvation shell around the redox ions,^[3, 5] spectroscopic techniques can be used to probe these interactions between the redox ions and solvent and understand their influence on S_e .^[8]

Solutions of 0.1 M $K_3Fe(CN)_6$ in water and mixed solvents were used. $K_4Fe(CN)_6$ has lower solubility than $K_3Fe(CN)_6$, and it was not possible to prepare 0.1 M solution of $K_4Fe(CN)_6$ in some mixed solvent systems (water/DMSO or water/isopropanol). Therefore, only 0.1 M solutions of $K_4Fe(CN)_6$ in pure water, mixed water/MPN and mixed water/ethylene glycol were studied by FT-IR. Solutions of 0.1 M $[Co(bpy)_3][BF_4]_2$ and of $[Co(bpy)_3][BF_4]_3$ in DMSO and in mixed solvents were also studied by FT-IR. Due to the solubility constraints, solutions of $[Co(bpy)_3][BF_4]_2$ or $[Co(bpy)_3][BF_4]_3$ complexes in water were studied at 0.05 M.

The effect of solvent was investigated by studying the peaks in the FT-IR spectra attributed to the CN ligands in $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$, at 2115 and 2037 cm^{-1} , respectively.^[20] Spectra of $K_3Fe(CN)_6$ solutions in water or mixed solvents showed that addition of MPN or DMSO causes a small change in the CN group's peak position (Figure 5 a), indicating a small change in the solvation shell. Hydrogen bonding between water and the CN groups in aqueous solutions leads to a red shift in the CN peak compared to when less hydrogen bonding is present. Thus, addition of non-protic solvents such as DMSO to the aqueous solution decreases the strength of interaction between water and CN groups, resulting in a blue shift.^[21] The addition of protic solvents (ethylene glycol and isopropanol) causes a small change in the CN peaks of $K_3Fe(CN)_6$, with a more significant effect from adding aprotic solvents. Although the relationship is not linear (Figure 5 c), it can be concluded that more hydrogen bonding between the protic solvents, especially water, and the CN groups of the redox couple contributes to a more negative Seebeck coefficient. Similarly, for the $K_4Fe(CN)_6$ solutions in water and mixed solvent systems, a small change in the CN group peak position to lower wavenumbers was observed after addition of both protic (isopropanol) and non-protic (MPN) solvent (Figure 5 b).

For the tris-2, 2'-bipyridine cobalt complexes, the peaks in the FT-IR spectra due to the pyridyl rings were used to investigate the effect of solvent. The stretching vibrations and in-plane bending peaks of pyridyl rings in $Co(bpy)_3$ are reported at ~ 1600 – 1400 cm^{-1} and ~ 1020 cm^{-1} , respectively.^[22] However, the FT-IR spectra of $[Co(bpy)_3][BF_4]_2$ and $[Co(bpy)_3][BF_4]_3$ in different solvent systems do not clearly show the characteristic peaks from the pyridyl rings due to the overlapping with solvent peaks (Figure S1). Therefore, ultraviolet-visible (UV-Vis) spectroscopy was used to investigate 0.1 mM solutions of $[Co(bpy)_3][BF_4]_2$ or $[Co(bpy)_3][BF_4]_3$ in pure organic solvent (DMSO), water or mixed water/organic solvents. 1 mM solutions of $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$ were also prepared, in pure water or mixed water/organic solvents. Since the $[Co(bpy)_3]$ solution is very highly absorbing in the UV-Vis, a diluted solution (0.1 mM) of $[Co(bpy)_3][BF_4]_2$ or $[Co(bpy)_3][BF_4]_3$ was used for UV-Vis analysis.

Prior studies of $Co(bpy)_3Cl_2$ in water have reported intra-ligand π - π^* absorption at 305, 295 and 243 nm, and at 319 and 307 nm for solution of $Co(bpy)_3Cl_3$ in water.^[23] Here, the UV-Vis spectra of solutions of $[Co(bpy)_3][BF_4]_2$ and $[Co(bpy)_3][BF_4]_3$ in water, DMSO and mixed solvents

showed that the absorption peaks in the 200-250 nm range have a strong dependence on solvent. Addition of DMSO led to a red shift and a decrease in the intensity of absorbance in this range (Figure 6). The observed change can be attributed to the replacement of some of the water with organic solvent in the solvation shell around the bpy ligands, which affects the intra-ligand $\pi-\pi^*$ absorption in $\text{Co}(\text{bpy})_3$. For solution of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ in water, absorption in the 200-230 nm range is reported as metal to ligand charge transfer (MLCT), and absorption in 258-400 nm range are attributed to ligand to metal charge transfer (LMCT) and d-d transitions.^[24] The UV-Vis results (Figure S2), show that the addition of DMSO or MPN to aqueous solutions of $\text{K}_3\text{Fe}(\text{CN})_6$ or $\text{K}_4\text{Fe}(\text{CN})_6$ causes a red shift and decrease in intensity of the MLCT, indicating a decrease in the interactions (such as hydrogen bonding) between the solvent and ligands. This is consistent with prior reports that the MLCT in $\text{Fe}(\text{CN})_6$ complexes appears at a shorter wavelength when CN groups are involved in hydrogen bonding.^[25] Importantly, this trend in peak position with solvent composition is the same as is observed in the $\text{Co}(\text{bpy})_3^{3-/4-}$ system (Figure 6), supporting the observation that the direction of entropy change upon organic solvent addition is the same. However, unlike the effect of aprotic solvents (MPN and DMSO), addition of ethylene glycol or isopropanol to the $\text{K}_4\text{Fe}(\text{CN})_6$ in water did not significantly change the absorption in this range, possibly because the extent of hydrogen bonding is relatively unchanged by these protic solvents.

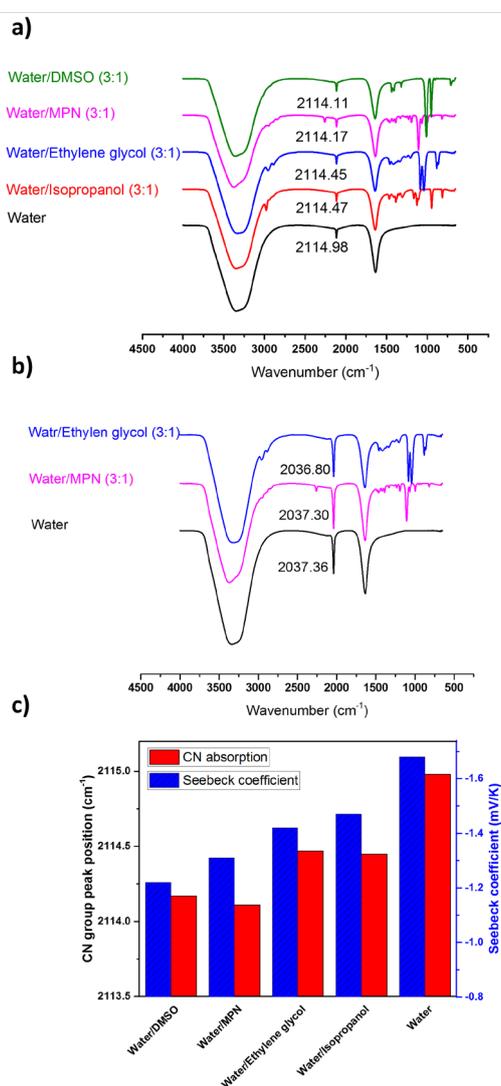


Figure 5. FT-IR absorption of 0.1 M solution of a) $\text{K}_3\text{Fe}(\text{CN})_6$ and b) $\text{K}_4\text{Fe}(\text{CN})_6$ in different solvents; c) relationship between Seebeck coefficient of $\text{K}_3/\text{K}_4\text{Fe}(\text{CN})_6$ redox couple and CN peak position of $\text{K}_3\text{Fe}(\text{CN})_6$ in water and mixed water/organic solvents (3:1 v/v).

This observation was cross-checked using different ratios of DMSO and water to dissolve $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. In the case of $K_4Fe(CN)_6$ solution (Figure S3a), addition of even a small portion of DMSO results in a large decrease in the MLCT peak. Increasing the ratio of DMSO in the $K_3Fe(CN)_6$ solution (Figure S3b) leads to a decrease in absorption and a clear red shift in the MLCT. The observed changes in UV-Vis results show that the addition of organic solvents to water has affected the solvation shell around the redox ions, attributed to a decreasing in the hydrogen bonding between the water and redox ions, which is detrimental to the Seebeck coefficient of the $Fe(CN)_6^{3-/4-}$ redox couple.

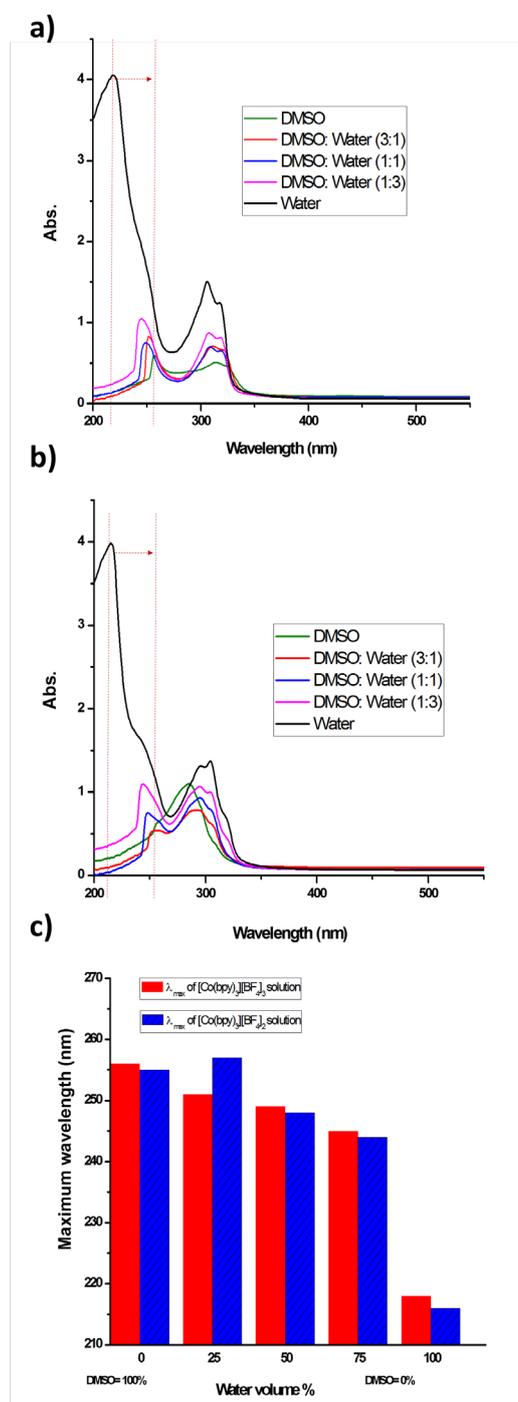


Figure 6. UV-Vis spectra of a) 0.1 mM $[Co(bpy)_3][BF_4]_3$ and b) $[Co(bpy)_3][BF_4]_2$ in different solvents; and c) the effect of solvent on the absorption peak of 0.1 mM $[Co(bpy)_3][BF_4]_3$ (red) and $[Co(bpy)_3][BF_4]_2$ (blue) in the 200-250 nm range.

Conclusions

In order to investigate the influence of solvent on the Seebeck coefficient and thermocell performance of different redox electrolytes, redox couples designed to impart high solubility across different solvent systems were studied: $[\text{Co}(\text{bpy})_3][\text{BF}_4]_{2/3}$, which has a large positive S_e , and $(\text{Et}_4\text{N})_3/(\text{NH}_4)_4\text{Fe}(\text{CN})_6$, which has a large negative S_e . The electrochemical, transport and spectroscopic properties were studied across a range of aqueous and non-aqueous solvents and mixtures. This revealed that, depending on the nature of the redox couple and the sign of the S_e , the nature of the solvent affects S_e in different ways. While organic solvents are more desirable to achieve a larger and more positive S_e for the $\text{Co}(\text{bpy})_3$ redox couple, the largest (most negative) S_e for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple was measured in water without any organic solvent. Although a large S_e is desirable for achieving a high voltage and power output, fast mass transport of the redox couple is also needed for high thermocell power. For different cobalt redox couples in water, organic solvents and mixed solvent systems, the highest ion diffusivity was measured in water as a result of the lower viscosity. This was also reflected in the current density of the CVs. However, both S_e and the diffusivity of redox ions, which have different trends with solvent composition, affect the performance of a thermocell. Thus, in spite of the lower diffusion coefficient of cobalt complexes in organic solvents than in water, a higher power was produced using organic solvents due to their higher S_e .

Spectroscopic studies show that the interaction between the solvent and the redox ions strongly affect S_e . The FT-IR and UV-Vis spectra show changes in the strength of interactions between the solvents and the different redox couples. The addition of organic solvent to the $\text{Fe}(\text{CN})_6^{3-/4-}$ aqueous system produced a decrease in the strength of interactions between the redox couple and the solvent, which corresponds to S_e becoming less negative. In contrast, the highest S_e for the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ systems was found in the organic solvent systems without any added water. Interestingly, for both types of redox couple, the addition of organic solvent resulted in a red shift in the UV-vis spectra and a blue shift in the FT-IR, indicating a decrease in solvent/ligand interactions. This is consistent with the observation that effect of organic solvent addition results in the same *direction* of change of S_e (i.e. more positive). This indicates that for higher S_e $\text{Co}(\text{bpy})_3$ systems, decreasing the solvent-redox couple interaction is important for large values of S_e , while the opposite is true for developing ferri/ferrocyanide-based systems with a more negative S_e .

Conflicts of interest

There are no conflicts to declare.

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