

Supplementary Material

Hydrogels Containing the Ferri/Ferrocyanide Redox Couple and Ionic Liquids for Thermocells

Matthew Russo,^a Holly Warren,^b Geoffrey Spinks,^b Douglas R. MacFarlane,^c and Jennifer M. Pringle^{a,d}

^a) Deakin University, ARC Centre of Excellence for Electromaterials Science, Institute for Frontier Materials, 221 Burwood Highway, Burwood, VIC 3125, Australia.

^b) ARC Centre of Excellence for Electromaterials Science, University of Wollongong Innovation Campus, North Wollongong, Australia.

^c) School of Chemistry, Monash University, Wellington Road, Clayton, VIC 3800, Australia.

^d) Corresponding author. Email: jenny.pringle@deakin.edu.au

Electrolyte Preparation

Potassium ferricyanide ($K_3Fe(CN)_6 \cdot 3H_2O$), potassium ferrocyanide ($K_4Fe(CN)_6$), 1-butyl-3-methylimidazolium methanesulfonate (purity $\geq 95\%$), and the polyvinyl alcohol ($M_w=85,000-124,000$ 99+% hydrolyzed) were purchased from Sigma Aldrich and used as received. The ionic liquid 1-ethyl-3-methylimidazolium methanesulfonate (purity $\geq 95\%$) was purchased from Merck and used as received.

The aqueous $K_3Fe(CN)_6/K_4Fe(CN)_6$ solutions were prepared by dissolving equimolar amounts of each complex in deionized water. The concentrations of these solutions varied from 0.01 M to the saturation point of 0.4 M. The ionic liquid and water mixtures were prepared by first mixing deionized water and the ionic liquid in either a 1:3 or 1:1 volume ratio (i.e. 1 mL of ionic liquid with 3 mL of water, or 2 mL of ionic liquid with 2 mL of water). Then equimolar amounts of $K_3Fe(CN)_6/K_4Fe(CN)_6$ ions were dissolved in the mixed solvent solution.

Polyvinyl Alcohol ($M_w=85,000-124,000$, 99+% hydrolyzed) was purchased from Sigma Aldrich and was used at four different weight percentages (2.5, 5, 7.5, and 10 wt% PVA in water). These percentages were chosen to observe the feasibility of PVA as the gelling agent, and to discover of the quantity of polymer that gave optimal physical properties. The PVA hydrogels were then synthesized with 0.05M $K_3Fe(CN)_6/K_4Fe(CN)_6$ redox couple incorporated into the gel at the same weight percentages of polymer to compare the physical properties before and after redox couple addition (Figure S1). Hydrogel synthesis was performed by first weighing the liquid solution (water or 0.05 M redox couple in water) and then adding the appropriate amount of PVA based on the desired weight percentage (2.5, 5, 7.5, 10 wt%). The solutions containing the PVA granules (and 0.05 M $K_3Fe(CN)_6/K_4Fe(CN)_6$) were then heated to $\sim 85^\circ C$ and magnetically stirred at ~ 300 RPM in an oil bath on a hot plate before being placed in an oven at $70^\circ C$ overnight to ensure homogenous and complete dissolution of the PVA. The homogenous solutions containing PVA were then left to cool to room temperature before being placed in a freezer at $-20^\circ C$ for 24 hours, a freeze-thawing method previously reported for PVA hydrogel synthesis.^[1] The samples were then removed from the freezer and thawed to room temperature, producing physically crosslinked PVA gels both with and without redox couple present.

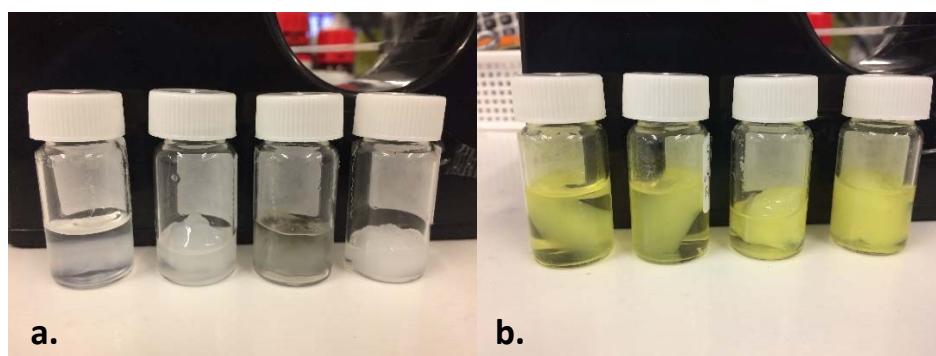


Figure S1. Images of the 2.5, 5, 7.5, and 10 wt% (Left to Right) PVA hydrogels containing pure distilled water (a.) and with 0.05 M $Fe(CN)_6^{3-/4-}$ redox couple (b.).

The IL containing PVA gels were synthesized by first creating the ionic liquid/water mixtures for both 1:3 and 1:1 v/v ratios of ionic liquid to aqueous redox couple. The PVA was then added at 10 wt% to the ionic liquid/water mixture. This solution was placed in an oil bath at $\sim 85^\circ C$ with continuous stirring at ~ 300 RPM. The freeze-thawing technique was again used to produce PVA hydrogel electrolytes with both 1:3 and 1:1 ratios of ionic liquid:water, in the presence of the 0.05 M $Fe(CN)_6^{3-/4-}$ redox couple. These hydrogels containing IL were more rigid, and changes in color based on IL content were observed (Figure S2).

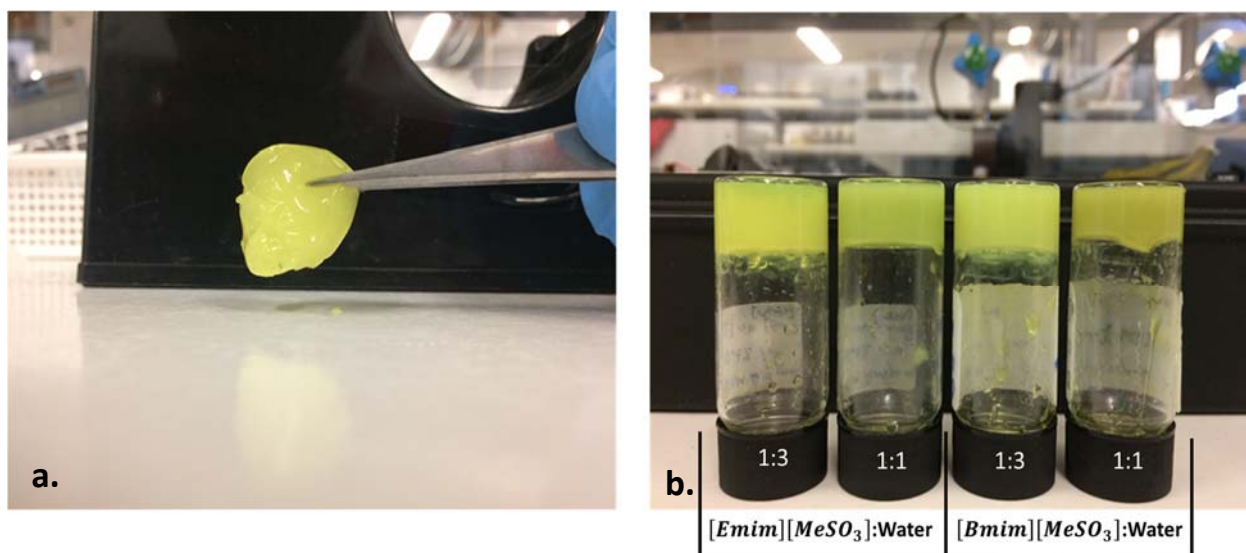


Figure S2. Images of 10 wt% PVA hydrogels containing aqueous $0.05\text{M Fe(CN)}_6^{3-/4-}$ (a.), and 1:3, 1:1 v/v ratios of $[\text{C}_2\text{mim}][\text{MeSO}_3]$ and $[\text{C}_4\text{mim}][\text{MeSO}_3]$ with water containing $0.05\text{ M Fe(CN)}_6^{3-/4-}$ (b).

In order to synthesize the sodium carboxymethyl cellulose (Cmc) hydrogels, $0.4\text{M K}_3\text{Fe(CN)}_6/\text{K}_4\text{Fe(CN)}_6$ or $0.1\text{M K}_3\text{Fe(CN)}_6/\text{K}_4\text{Fe(CN)}_6$ with a 1:3 v/v ratio of $[\text{C}_2\text{mim}][\text{Dca}]:\text{water}$ were first used to create the concentrated solvents. Using a sonication bath at approximately $70\text{ }^\circ\text{C}$, the appropriate amount of Cmc powder was added to the solvent. After the powder was dissolved, the sample was heated in an oven overnight at 70°C to ensure homogenous dispersion of Cmc. The samples were then removed and left to cool to room temperature, creating soft hydrogels containing $0.4\text{M Fe(CN)}_6^{3-/4-}$ redox couple. Figure S3 shows the Cmc hydrogels synthesized at 6 wt% Cmc with $0.4\text{M Fe(CN)}_6^{3-/4-}$, 10 wt% Cmc with $0.4\text{M Fe(CN)}_6^{3-/4-}$, and 6 wt% Cmc containing a 1:3 v/v ratio of $[\text{C}_2\text{mim}][\text{Dca}]:\text{water}$ with $0.1\text{ M Fe(CN)}_6^{3-/4-}$.

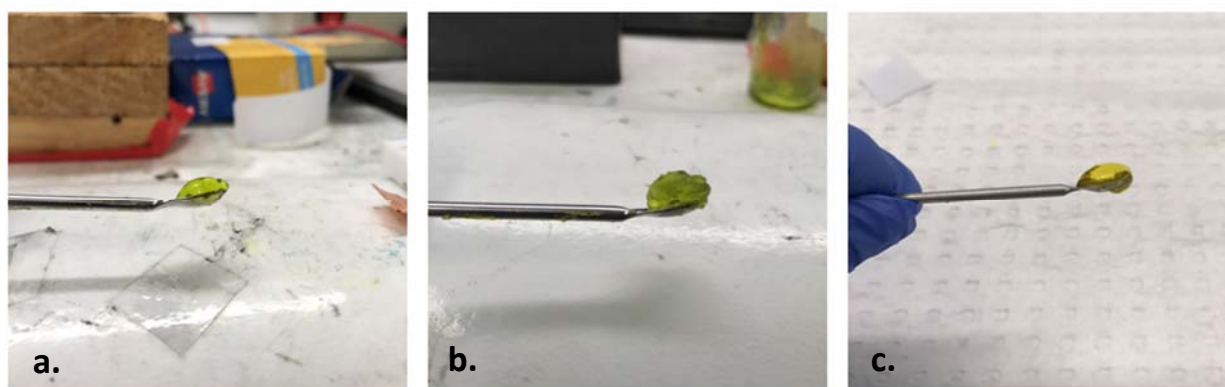


Figure S3. Sodium carboxymethyl cellulose (Cmc) hydrogels containing (a.) 6 wt% Cmc and $0.4\text{ M Fe(CN)}_6^{3-/4-}$, (b.) 10 wt% Cmc and $0.4\text{ M Fe(CN)}_6^{3-/4-}$ and (c.) 6 wt% Cmc 1:3 ratio $[\text{C}_2\text{mim}][\text{Dca}]$ and $0.1\text{ M Fe(CN)}_6^{3-/4-}$.

The 4.5% w/v and 6% w/v Polyacrylamide (PAAm) hydrogels (10 g) were prepared as follows: 450 mg (or 600 mg) acrylamide (AAm) powder (Sigma, Australia) was added to 10 mL of a 0.1% w/v solution

of N,N'-methylenebisacrylamide (MBAAm, Sigma, Australia) and shaken until fully dissolved. 50 μ g Ammonium persulfate (APS, Sigma, Australia) was added to the solution and stirred until fully dissolved. To initiate cross-linking 30 μ L N,N,N',N'-tetramethylethylenediamine (Novachem, Australia) was added to the solution, swirled to fully mix and poured into a petri-dish to allow curing to take place (1 hour). The Polyacrylamide (PAAm) hydrogels were then soaked in the redox active liquid electrolyte to create hydrogel electrolytes for thermocell applications. The PAAm hydrogels were synthesized at 4.5 and 6 wt% polymer, and soaked in 0.4 M $\text{Fe}(\text{CN})_6^{3-/4-}$, as well as in 0.1 M $\text{Fe}(\text{CN})_6^{3-/4-}$ containing a 1:3 v/v ratio of $[\text{C}_2\text{mim}][\text{Dca}]$:water (Figure S4). After soaking in liquid electrolyte overnight, these hydrogels changed color, taking on the color of the solvent, and exhibited no leakage of the liquid component even upon agitation of the hydrogel. In addition, the PAAm hydrogels were easily handled with tweezers and displayed good flexibility.

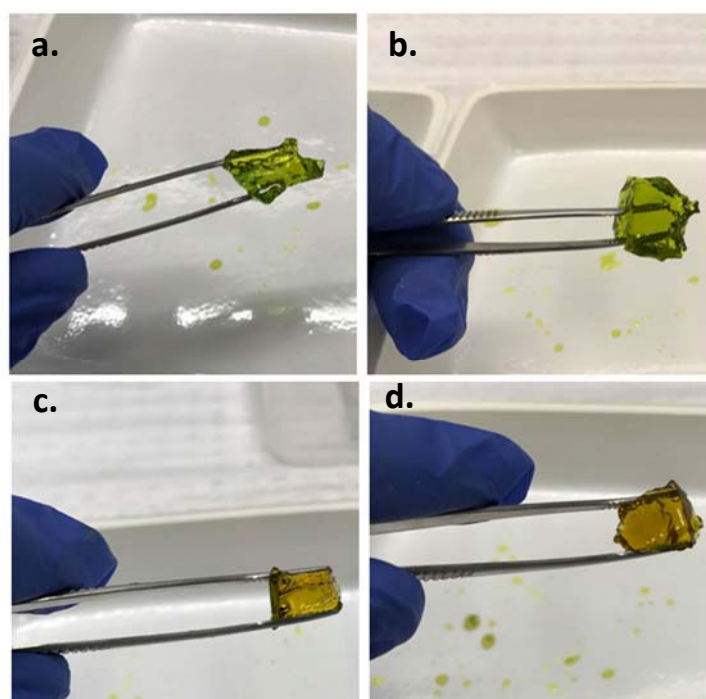


Figure S4. Polyacrylamide (PAAm) hydrogels at 4.5 wt% PAAm and 6 wt% PAAm containing 0.4 M $\text{Fe}(\text{CN})_6^{3-/4-}$ (a & b), and hydrogels containing 4.5 wt% PAAm and 6 wt% PAAm with 0.1 M $\text{Fe}(\text{CN})_6^{3-/4-}$ and a 1:3 v/v ratio of $[\text{C}_2\text{mim}][\text{Dca}]$:water (c & d).

The HydroMed D series hydrogels were synthesized by dissolving polymer granules in a mixture of ethanol (90 %) and distilled water (10 %). The solution was sealed and left in an oven at 65 $^{\circ}\text{C}$, with hourly increments of stirring until a homogenous polymeric solution was obtained. Once fully dissolved and homogenous, the solution was cast into a petri dish and left in the fume hood in order to evaporate the ethanol/water mixture from the polymer melt. Once dried, the cast polymer film was

placed in the solution containing 0.4M $K_3Fe(CN)_6$ / $K_4Fe(CN)_6$ for approximately one hour, or until a fully swollen hydrogel was formed.

Seebeck coefficient measurements

The Seebeck coefficients of electrolyte candidates were measured using two vials joined by a tube containing the same electrolyte, as previously reported by Abraham *et al.*^[2] Two platinum wires were used as electrodes to measure the potential difference between the hot side and the cold side. The temperature of the heating block (heated using a cartridge heater inserted into the block) was increased in a stepwise function (5°C every 30 minutes) from 30-65 °C increasing the overall temperature gradient of the system in constant intervals.

Thermoelectrochemical cell (Thermocell) testing

Thermocell tests were conducted using a Teflon cell containing an internal pocket for electrolyte housing that is 9 mm in diameter and 1 cm in length, between two platinum disk electrodes each with a surface area of 2.55 cm². Two temperature sensors were used, one placed in contact with each electrode in order to monitor the temperature gradient across the device. The hot side of the cell was maintained at 35°C and the cold side was maintained at 20°C in order to keep a steady ΔT of 15°C. A Bio-Logic SP-200 potentiostat was used, which measures the potential across the cell, while simultaneously controlling the external resistances that are chosen and implemented by the user. For the liquid electrolytes, the whole cell was cooled, and both electrodes were heated to different temperatures (20 and 35 °C).

The hydrogel electrolytes were tested in the thermocell using the same experimental setup as reported in the supplementary information document by Jin *et al.*,^[3] using both a peltier cooler and a brass heating block to apply the temperature gradient (20 and 35 °C). However, this work utilized the same Teflon cell electrolyte housing and platinum electrodes previously used for the liquid electrolyte experiments (Figure S5), rather than the plastic frame and nickel foil electrodes used in the work by Jin *et al.*

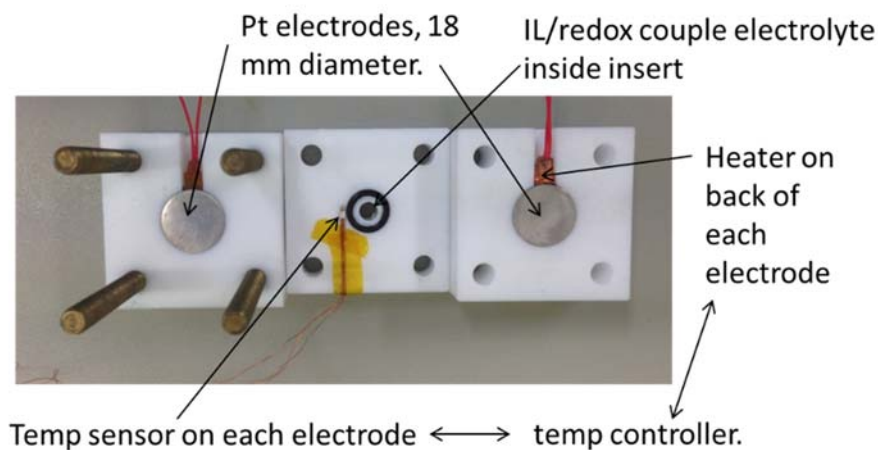


Figure S5. Thermocell performance experimental setup

To conduct the thermocell performance experiments for the hydrogel electrolytes, good contact between the platinum disk electrodes and the electrolyte must be ensured. The middle insert of the cell was first placed on the bottom piece with one electrode in place. The PVA, Cmc, and PAAM hydrogels were then placed into the electrolyte housing in contact with the bottom electrode. The samples were cut or added allowing for excess hydrogel to protrude out of the middle insert. Therefore, when the top electrode was screwed down, contact between the electrolytes and both electrodes was made. After each experiment the cell was taken apart and examined to ensure proper contact was achieved.

Rheology experiments

Rheology experiments were carried out using the Anton Paar MCR301 rheometer and rheoplus software. Experiments were conducted by measuring the storage modulus of the material with respect to temperature. This was done starting with 10 °C and increasing by 5 °C at each interval until reaching a final temperature of 40 °C. This final temperature was chosen because the thermocell operating temperatures are 20 and 35 °C, allowing for a thorough analysis of the hydrogel over the whole temperature range.

The rheometer was first initialized by setting the zero gap, or the vertical distance from the platform to the interface geometry when there is no sample present. Once this was completed, samples of precise thickness (~ 5 mm) were prepared and measured, with diameters matching the Parallel plate interface geometry used for gel measurements and were placed on the rheometer platform. The parallel plate was lowered to the specific y-axis height based on the thickness of each sample and the normal force was zeroed. The experiment was set to perform each storage modulus measurement

twice at each temperature, with a one-minute rest period between each temperature step to allow the gel and the platform to equilibrate at each increment.

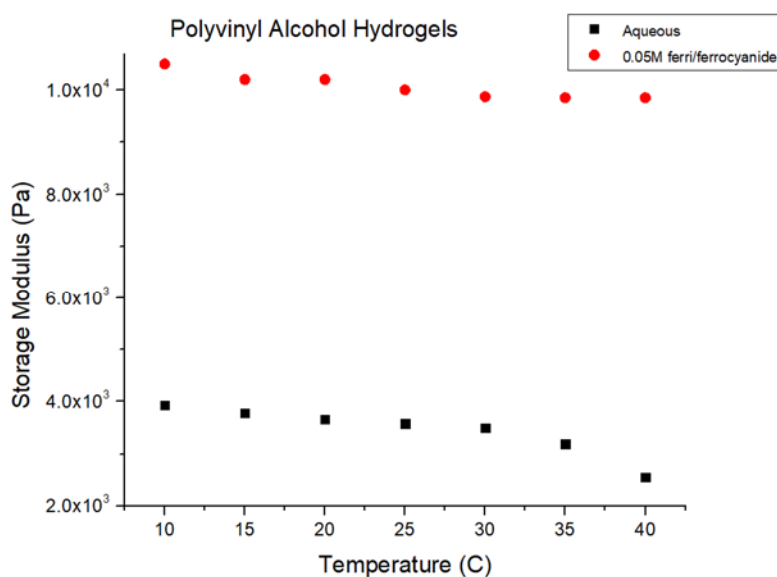


Figure S6. Storage Modulus (Pa) values for PVA hydrogels containing water (black) and 0.05M aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$ in water (red).

Cyclic voltammetry

Cyclic Voltammetry experiments were performed using a glassy carbon working electrode, while platinum wires were used as the reference and auxiliary electrodes. The choice of reference electrode across multiple different IL based electrolyte systems is a recognized challenge in the field of electrochemistry.^[4] This work involved the investigation of electrochemical reversibility, rather than the electrochemical window measurements that require very accurate potential measurements. Thus, here platinum quasi-reference electrodes were chosen for assessment of the reversibility to provide consistency across the different electrolytes, and good contact with the hydrogels, rather than frit-containing reference electrodes. Before each experiment, the glassy carbon working electrode was polished using 0.3 μm Aluminium nanoparticles soaked into a polishing pad and was then washed to ensure a high quality active surface area. To test the reversibility of the redox processes for $\text{K}_3\text{Fe}(\text{CN})_6^{3-}$ / $\text{K}_4\text{Fe}(\text{CN})_6^{4-}$ within the hydrogel electrolytes considered here, the potential was swept from -0.5 to 0.5 V. This potential sweep was performed at five different scan rates (25, 50, 75, 100, and 125 mV s^{-1}) to investigate any changes in peak-to-peak separation.



Figure S7. 3-electrode cell used for Diffusion coefficient and Cyclic voltammetry experiments

Proper contact between the hydrogel electrolytes and the electrodes within the cell was achieved based on the physical properties of each sample. The Cmc and PAAm hydrogels have soft morphologies, allowing for the electrodes to be simply pushed into the sample to ensure proper contact. However, the PVA hydrogels do not possess the same physical properties. As a result, these samples were first melted into a homogenous liquid and were added to the cell. The electrodes were then placed into the cell in contact with the liquid solution. The cell was left at room temperature for roughly two hours or until the liquid solution was completely solidified, achieving thorough contact between the hydrogel and the electrodes.

Diffusion coefficient measurements

Diffusion coefficients were measured and calculated using a combination of chronoamperometry experiments and the Cottrell equation,^[5] as shown below:

$$D_j^{1/2} = \frac{K\pi^{1/2}}{nFAC_j^*} \quad \text{Eq. (S1)}$$

Where, n is the number of electrons, F is Faraday's constant, A is the surface area of the working electrode, C_j^* is the concentration of the electroactive species, and D_j is the diffusion coefficient to be calculated. K is the slope of the linear plot of I (A) vs $t^{1/2}$ obtained from the chronoamperometry experiments.

These experiments were conducted using a three-electrode cell and Potentiostat. The working electrode used was a platinum disk with radius ($r = 0.08 \text{ cm}^2$), and platinum wires as the counter and reference electrodes. Before and after each experiment the working electrode was washed and polished using $0.3 \text{ }\mu\text{m}$ Aluminium nanoparticles and a damp polishing pad, while the counter and reference electrodes were washed and cleaned. Each potential step experiment was performed five times and an average of the diffusion coefficient values for each ion was taken.

Viscosity measurements

Table S1. Viscosity values for 0.05M $\text{Fe}(\text{CN})_6^{3-/4-}$ in the following electrolyte solvents taken at 20 °C

Electrolyte Solvent (v/v IL:Water)	Viscosity (mPa s)
<i>Water</i>	1.08
$[\text{C}_2\text{mim}][\text{MeSO}_3]$ (1:3)	2.02
$[\text{C}_4\text{mim}][\text{MeSO}_3]$ (1:3)	2.19
$[\text{C}_2\text{mim}][\text{MeSO}_3]$ (1:1)	4.59
$[\text{C}_4\text{mim}][\text{MeSO}_3]$ (1:1)	4.81

The viscosities were determined using the rolling ball method at 20°C for the 0.05M $\text{Fe}(\text{CN})_6^{3-/4-}$ samples in water and 1:3 or 1:1 mixtures of water and $[\text{C}_2\text{mim}][\text{MeSO}_3]$ or $[\text{C}_4\text{mim}][\text{MeSO}_3]$. A capillary diameter of 2.5 mm and an angle of 60° were used (Anton Paar Lovis 2000ME). The instrument determined the dynamic viscosity, taking the density into account, as determined at the above mentioned temperatures, measured using an Anton Paar DMA5000 density meter.

References

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