

Supporting file

S. 1 The characterization data for the synthesized ILs

S. 2 Bode plots for mild steel in 2M HCl solution containing of pure ionic liquids; HMIIm Cl, BMIm Cl and EMIm Cl

S. 3 Nyquist and Bode plots for mild steel in 2M HCl solution containing of BMIm Cl (1%w)+SDS and EMIm Cl (1%w)+SDS mixtures

S. 4 The potentiodynamic polarization curves for mild steel in 2M HCl solution in the presence of various concentrations of BMIm Cl, EMIm Cl and their mixtures with SDS

S. 1

HMIIm Cl¹

For the synthesis a 250 mL flask, equipped on a magnetic stirrer and condenser, was used. The substances 1-methylimidazolium (0.4 mol) (Merck 99 %) and 1-chlorohexane (0.5 mol) (Aldrich 98 %, used as received) were charged. The reaction mixture was stirred at a temperature of 70°C for 12 h. 1-chlorohexane has been removed by extraction with hexane, ethyl acetate, and diethyl ether. Product was dried in vacuum (0.38 mol, yield 95 %). ¹H NMR (500 MHz, CDCl₃) δ: 0.873 (t, 3H), 1.31 (multiplet, 6H), 1.918 (quintet, 2H), 4.137 (s, 3H), 4.328 (t, 2H), 7.524 (d, 1H), 7.730 (d, 1H), 10.57 (s, 1H). ¹³C NMR (500 MHz, CDCl₃) δ: 13.92, 22.37, 25.90, 30.28, 31.09, 36.57, 50.07, 122.00, 122.83, 137.88.

BMIm Cl²

To a dry round-bottomed flask under nitrogen atmosphere 40 mL (0.49 mol) of 1-methylimidazole and 51 mL (0.49 mol) n-butylchloride were added. The reaction mixture was stirred at 75-85 °C for 72 h. The resulting pale yellow, viscous liquid was washed with ethyl acetate. The remaining ethyl acetate was removed by drying on a vacuum line overnight to afford 1-butyl-3-methylimidazolium chloride. ¹H-NMR (300 MHz, CDCl₃) δ: 0.80 (t, 3 H, ³J_{HH} = 7.3), 1.23 (m, 2 H), 1.75 (m, 2 H), 3.98 (s, 3 H), 4.19 (t, 2 H, ³J_{HH} = 7.4), 7.46 (s, 1 H), 7.63 (s, 1 H), 9.55 (s, 1 H) ; ¹³C NMR (75 MHz, CDCl₃) δ: 13.6, 19.6, 32.3, 36.6, 49.8, 122.3, 124.0, 137.8.

BMIm BF₄³

To a dry round-bottomed flask under nitrogen, 0.5 mmol [BMIm][Cl] was dissolved in 250 mL of water and 79 mL (0.635 mol) of 50% aqueous HBF₄ was added dropwise over 60 min. The reaction was stirred for an additional 12 h at ambient temperature and was then extracted with CH₂Cl₂ (2*200 mL). The organic layer was washed with water (50 mL aliquots) until the aqueous washes were no longer acidic. The ionic liquid was dried in a vacuum oven overnight at 80-90 °C to afford 96.6 g (95% Yield) of a pale yellow liquid that was used without further purification. ¹H-NMR (500 MHz, CDCl₃) δ: 8.83 (1H, s), 7.36 (1H, t, J=1.7 Hz), 7.31 (1H, t, J=1.7 Hz), 4.05 (2H, t, J=7.5 Hz), 3.81 (3H, s), 1.67 (2H, m), 1.15 (2H, m), 0.73 (3H, t, J=7.3 Hz).

BMIm Br²

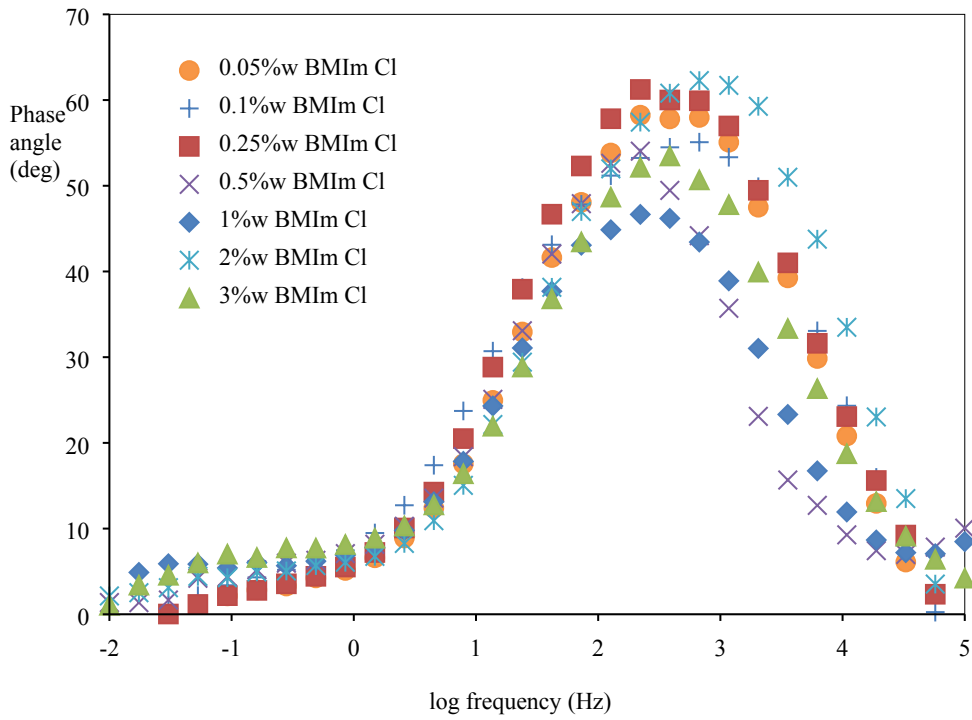
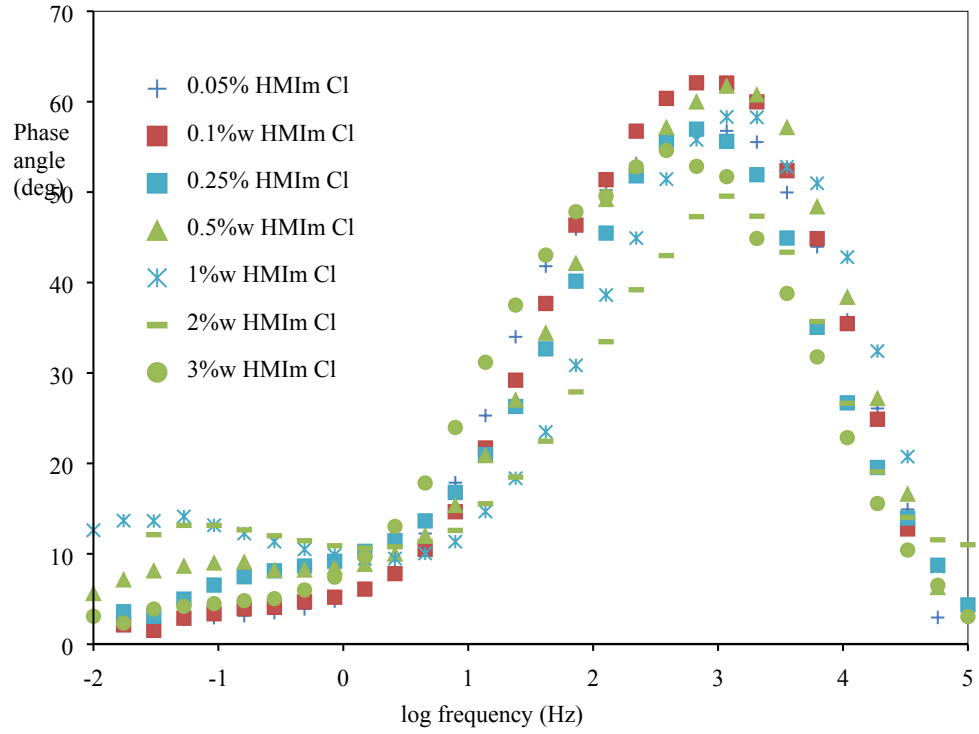
A solution of 1-methylimidazole (16 ml, 0.20 mol) in toluene (25 ml) was prepared and cooled in an ice/water bath. To this was added slowly 1-bromobutane (25 ml, 0.23 mol) with stirring. After addition, the mixture was allowed to warm to room temperature, then heated at reflux for 24 h, and then crystallized. The solid was purified by recrystallization from acetonitrile to give a colorless, crystalline solid (38 g, 0.17 mol, 86% Yield). ¹H NMR (500 MHz, CDCl₃) δ: 9.23 (s, 1H), 7.77 (d, 1H, J=1.2 Hz), 7.70 (d, 1H, J=1.2 Hz), 4.13 (t, 2H, J=7.4 Hz), 3.81 (s, 3H), 1.70 (quintet, 2H, J=7.4 Hz), 1.19 (sextet, 2H, J=7.4 Hz), 0.82 (t, 3H, J=7.4 Hz).

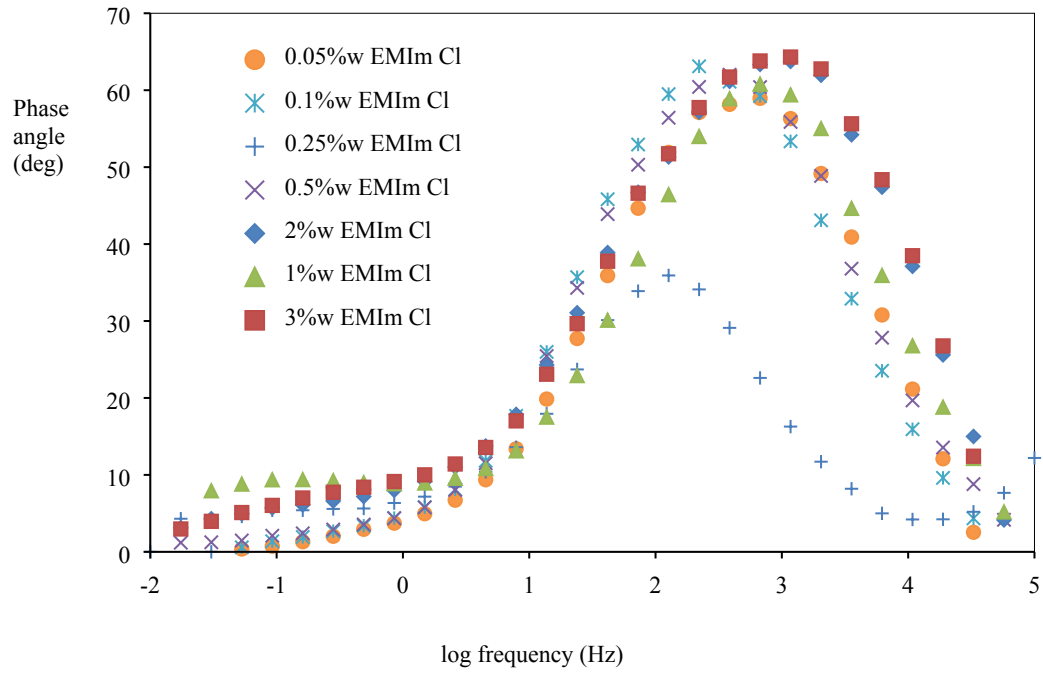
BMIm PF₆³

The respective metal salt (0.32 mol), required to give the desired ionic liquid, was added to a solution of either [BMIM]Cl or [BMMIM]Cl (0.29 mol) in dichloromethane and stirred for 24 hours. The suspension was filtered to remove the precipitated chloride salt and the organic phase repeatedly washed with small volumes of water (ca. 30 cm³) until no precipitation of AgCl occurred in the aqueous phase on addition of a concentrated AgNO₃ solution. The organic phase was then washed a further two times with water to ensure complete removal of the chloride salt. The solvent was removed in vacuo and the resulting ionic liquid stirred with activated charcoal for 12 hours, after which the ionic liquid was passed through a short alumina column(s) (acidic and/or neutral) to give a colourless ionic liquid, which was dried at ca. 100°C in vacuo for ca. 24 hours or until no visible signs of water were present in the IR spectrum. Yields generally 70 to 80 %. ¹H-NMR (300 MHz, Chloroform-*d*) δ: 8.68 (1H, s, NCHN), 7.22 (1H, m, CH₃NCHCHN), 7.14 (1H, m, CH₃NCHCHN), 4.16 (2H, t, J=7.4 Hz, NCH₂(CH₂)₂CH₃), 3.90 (3H, s, NCH₃), 1.86 (2H, m, NCH₂CH₂CH₂CH₃), 1.31 (2H, m, N(CH₂)₂CH₂CH₃), 0.98 (3H, t, J=7.3 Hz, N(CH₂)₃CH₃). Mass spectrum (FAB +ve) m/z: 139 (M-PF₆)⁺

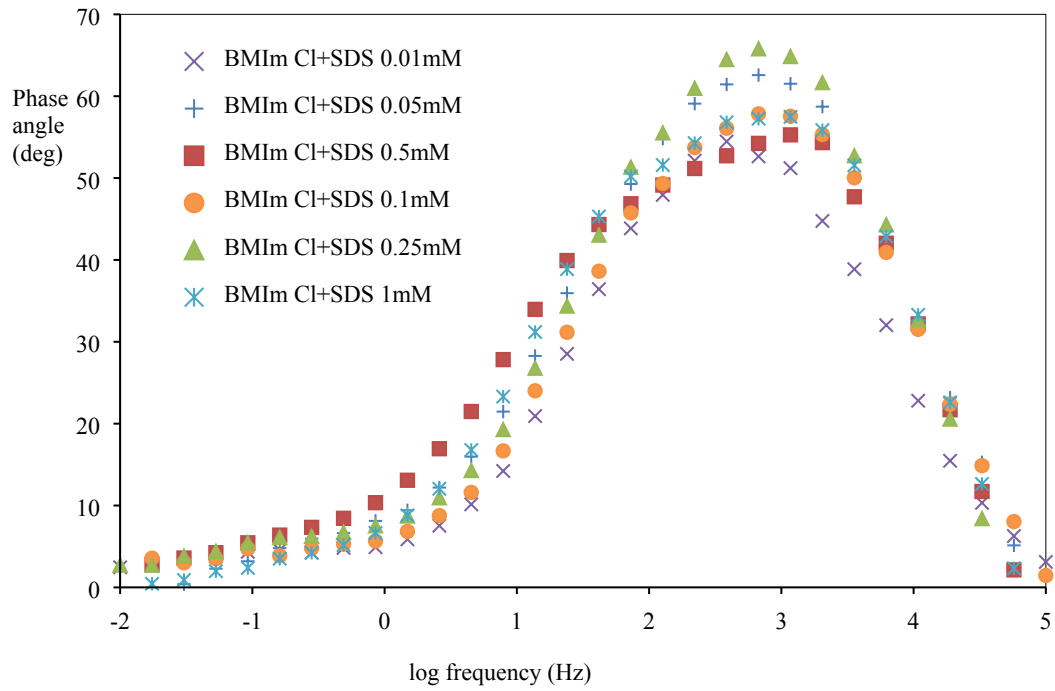
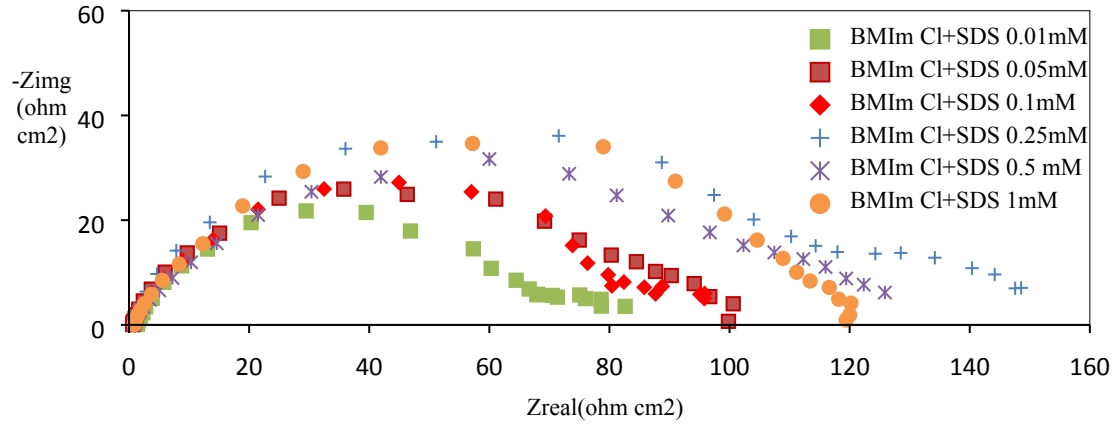
- (1) Mizuuchi, H.; Jaitely, V.; Murdan, S.; Florence, A. T. *Europ. J. Pharm. Sci.* **2008**, *33*, 326.
- (2) Creary, X.; Willis, E. D. *Org. Synth.* **2005**, *82*, 166.
- (3) Palimkar, S. S.; Siddiqui, S. A.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. *J. Org. chem.* **2003**, *68*, 9371.

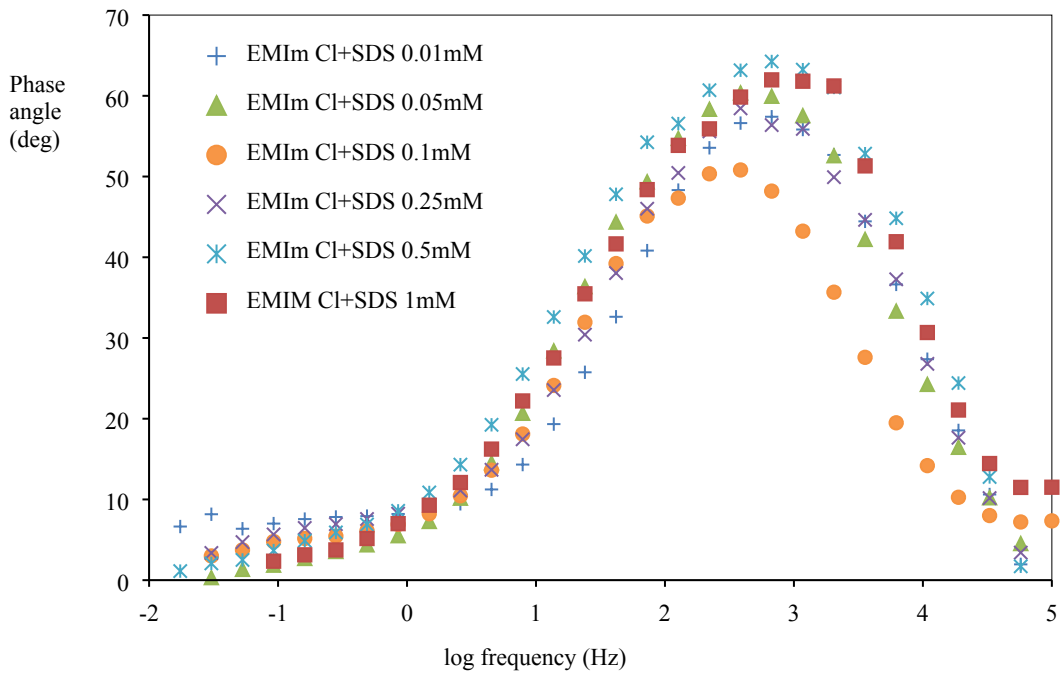
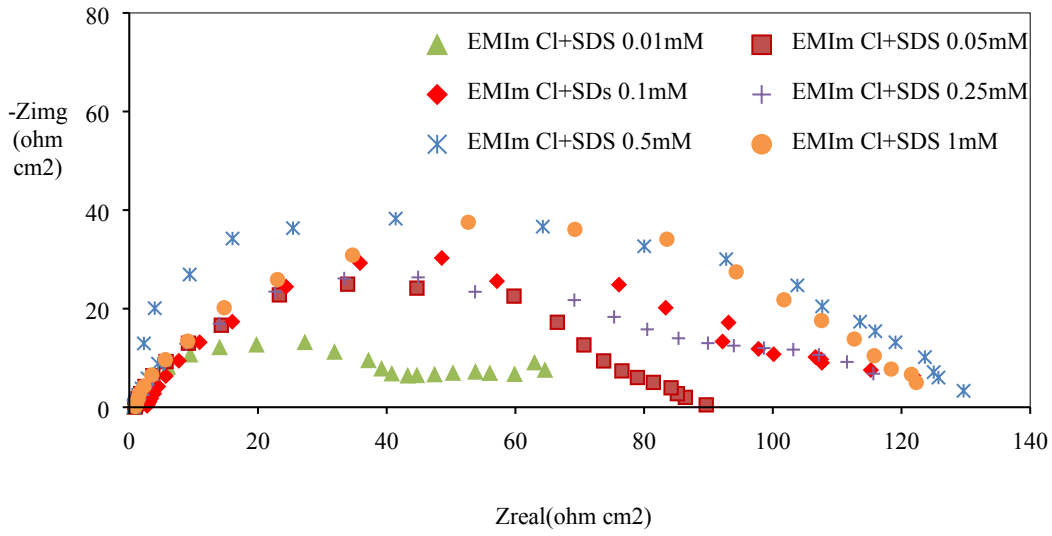
S. 2





S. 3





S. 4

