Anion-exchange membranes for alkaline polymer electrolyte fuel cells: Comparison of pendant benzyltrimethylammonium- and benzylmethylimidazolium- head-groups

Oliver I. Deavin, Sam Murphy, Ai Lien Ong, Simon D. Poynton, Rong Zeng, Henryk Herman and John R. Varcoe

Additional Methodology

Synthesis of the radiation-grafted ETFE-g-poly(vinylbenzyltrimethylammonium hydroxide) benchmark AAEM (PVBTMA-OH⁻)

Poly(ethylene-co-tetrafluoroethylene) films (Nowoflon ET-film, Nowofol Kunstoffprodukte GmbH, Germany, 50 µm thick) were subject to electron-beam (4.5 MeV) irradiation in air to a total dose of 70 kGy (7 MRad). The irradiated ETFE films were then stored at -36 ± 2°C until required for reaction. The first chemical stage of the synthetic process was to immerse the e-beamed ETFE into a N_2-purged solution [consisting of 20%vol vinylbenzyl chloride monomer (Dow Chemicals, 97% Lot # YB27012U01, 1.26:1 ratio of *meta:para* isomers, 172 ppm water), 1%vol Surfadone and 79%vol propan-2-ol] and then heat at 60°C for 72 h. Intermediate ETFE-g-poly(vinylbenzyl chloride) membranes (**ETFE-g-PVBC)** were obtained as brittle translucent white films after thorough washing in toluene at 60°C and removal of the last traces of the toluene in a vacuum oven at 70°C for 5 h. The second stage of the reaction was to immerse the **ETFE-g-PVBC** in aqueous trimethylamine (TMA, 50%mass, Acros Organics) at ambient temperature for at least 5 h. The resultant ETFE-g-poly(vinylbenzyltrimethyl-ammonium chloride) anion-exchange membranes (**PVBTMA-Cl⁻**) were obtained as pale brown/orange transparent films after thorough washing in, and heat treatment at 50°C for at least 12 h in, deionised water (at least Grade II).

Ion-exchange to the relevant alkaline anion form (i.e. hydroxide) was achieved by immersion of the **PVBTMA-Cl⁻** membranes in aqueous solutions (1 mol dm⁻³) of the relevant anion (i.e. KOH to yield the hydroxide form **PVBTMA-OH⁻** AAEM) for at least 1 hour (with at least 3 replacements of the solution in this time period to ensure rigorous anion-exchange).

Ion-exchange capacities

Multiple samples of each membrane were treated in aqueous potassium chloride (1 mol dm⁻³) for at least 1 hour (with at least 3 replacements of the solution in this time period) to ensure the anions in the membrane were all Cl⁻. After thorough washing with deionised water (at least Grade II) at room temperature, the membrane samples dried for at least 4 days in a relative humidity

(RH) = 0% desiccator that contained anhydrous $CaCl_2$ as desiccant. The dried membrane samples were then quickly reweighed and each sample of membrane was immersed in aqueous sodium nitrate (50 cm³, 2 mol dm⁻³) for at least 24 h in separate polypropylene pots (glass would have risked a potential halide and analytical interference). After addition of aqueous nitric acid (3 cm³, 2 mol dm⁻³), the solutions, still containing the membrane samples, were titrated with aqueous silver nitrate (0.02000 ± 0.00006 mol dm⁻³) titrant. The titration endpoint was determined from the maximum gradient of the voltage *vs.* titrant volume plot and this endpoint corresponds the amount of Cl⁻ anions in the membrane samples (1:1 titration).

Vibrational spectroscopy

Routine FT-Raman spectra were recorded on a Perkin-Elmer System 2000 FT-Raman/near-IR spectrometer with a laser power of 1435 ± 5 mW and a resolution of 4 cm⁻¹. Samples, either liquids or solids, were directly mounted in the beam in glass vials at ambient temperature and pressure. The Raman spectra of the as-synthesised coloured anion-exchange membranes, in the Cl⁻-form, were recorded with the membranes being hydrated with a trace of water in the vials to prevent the laser burning the samples. The advantages for this type of research in using Raman, as opposed to infra red spectroscopy, is that the samples do not have to be dried (as Raman is relatively insensitive to the presence of water), no special sample preparation is required, and that the technique is highly quantitative. The significance of these advantages will be apparent in the Raman chemical stability studies described below and in the main paper.

IR spectroscopy was carried out upon a Perkin-Elmer Spectrum BX FT-IR Spectrometer. To get a complete picture of the membranes both transmission and attenuated total reflectance (ATR) FT-IR methods were used. This was due to three reasons: (1) The strong bands in the transmission FT-IR of these membranes saturate and key detail is lost; (2) The intensity of the bands with ATR is a function of wavenumber and key details of weak bands at high wavenumbers (*e.g.* the C-H stretches at *ca.* 3000 cm⁻¹) are lost; and (3) We wanted to keep sample preparation to a minimum to minimise the risk of degradation. Spectra were recorded on relative humidity RH = 0% desiccator dried membrane samples: The membrane was pressed between sodium chloride (NaCl) discs for the transmission FT-IR spectra.

ATR spectra were recorded using a Specac Mk II Golden Gate attachment containing a Diamond 45° ATR window and a Sapphire anvil. The scan range was 4000-600 cm^{-1} with a resolution of 4 cm^{-1} and with averaging over 64 repeat scans for FT-IR ATR and 16 repeat scans for transmission FT-IR.

Solid state NMR

The ^{13}C and ^{15}N solid state NMR spectra (cross polarisation, 6.8 kHz magic-angle spinning) were obtained on a Varian VNMRS spectrometer (^{1}H resonance of 400 MHz) using neat trimethylsilane and nitromethane respectively as external shift references. ^{19}F solid state NMR spectra (direct excitation, 15 kHz magic-angle spinning with no-decoupling) were obtained on a Varian Unity Inova spectrometer (^{1}H resonance of 300 MHz) using CFCl$_3$ as an external shift reference. To record spectra of the anion-exchange membranes, the samples were dried in the open atmosphere, to remove excess water, before measurement.

The features of, and assumptions involved with, the FT-Raman-based method for head-group chemical stability testing of model compounds

The Raman chemical stability studies on model small molecules were outlined in the main paper. The experimental design used allows for the following features:

1   Once sealed, carbon dioxide can be prevented from entering the vials and hence it can be guaranteed that the chemical stabilities of the compounds are being measured in the desired solution (e.g. the potassium hydroxide is not converting the lower pH carbonate or bicarbonate solutions during the experiment, which would affect the alkaline stabilities being measured);

2   Carbonate anions have a strong Raman signal at 1067 cm^{-1} (the C-O symmetric stretch) and so this can be used as an internal check for excessive potassium carbonate formation during the experiment (in case vial sealing was inadequate);

3   The concentrations of the alkaline solution species, *e.g.* KOH, do not vary due to evaporation of water from the solutions;

4   The degradation products cannot escape and so there is a chance that they can be directly identified. This will aid the identification of degradation pathways, if this is desired.

5   If the experiments show that a particular head-group is highly stable, then the concentration of the alkali solution and the temperature can be increased (obviously still below 100°C) in order to develop accelerated stability test protocols; *e.g.* aqueous KOH (10 mol dm^{-3}) and temperatures of 80°C could be used. This ensures the elucidation of chemical stabilities on a reasonable experimental timeframes (weeks/months rather than years if a highly stable anion-exchange head-group is identified).

6   The technique is highly amenable to chemometric methods, especially when the measurements are conducted with a large number of replicates.

The main disadvantages of the technique include:

1   The chemical stabilities are only being probed with the head-groups in a highly hydrated form;

2   It is difficult to measure quality Raman spectra (adequate signal to noise ratio) of the membranes in this type of experiment (with 1 × excess of alkaline solution) as the Raman signals are too weak without undesirable long measurements using a considerable number of scans (recall S/N improvement is proportional to the square root of the number of scans). A new Raman spectrometer will be available soon that will address this problem, and modifying this technique to study the degradation of actual (insoluble) AAEMs will be the focus of a future study (with different anion-exchange head-groups).

The assumptions involved in the technique include:

1   The Cl$^-$ spectator anions present do not affect the chemical stability;

2   The stabilities of the head-groups on these model small molecules do not significantly vary from the stabilities of these head-groups when they are polymer bound (i.e. the head-groups would have more restricted mobilities); the *absolute* stabilities of the different head-groups may vary when polymer-bound compared to in small molecule form but the *relative* stabilities are unlikely to be affected.

3   The laser beam is not degrading the compounds and is not causing significant heating of the sample solutions during the collection of the scans; this risk is only partially mitigated by the use of aqueous solutions (water as the heat-sink) and by only conducting 32 scans (takes about 10 min on the FT-Raman instrument used - this latter point is another reason why it is currently difficult to conduct these experiments on the AAEMs themselves).
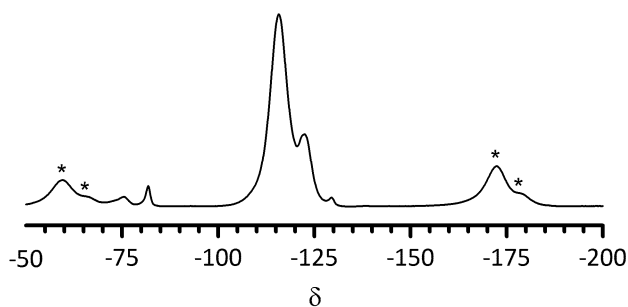
Additional Data

Solid state NMR spectra

Fig. S1 ^{19}F solid state NMR spectrum of the **PVBMI-Cl** anion-exchange membrane. The signals marked * are spinning sidebands.
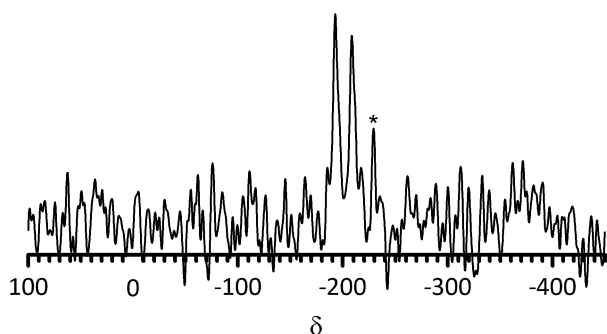

Fig. S2 ^{15}N NMR solid state NMR spectrum of the **PVBMI-Cl** anion-exchange membrane. The apparent signal at $\delta = -230$ (*) is statistically indistinguishable from the background noise.

Infrared spectra

The FT-IR spectra (ATR and transmission) of **PVBMI-Cl** yields bands that are present in the intermediate ETFE-g-poly(VBC) membrane (not shown): e.g. the strong ETFE CF_2 bands in the range $1000 - 1400$ cm^{-1}. Additional bands are also present and are diagnostic of the benzylmethylimidazolium head-groups: 2114 (C=N – particularly diagnostic in the transmission FT-IR spectrum), 1634 (C=N, C=C), 1574 (C-C, C-N), 1456 (C-H alkyl deformation) and 1163 (C-H aromatic ring deformation).[1]
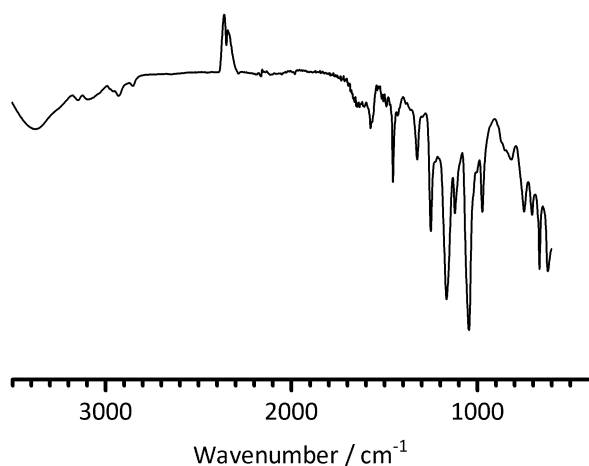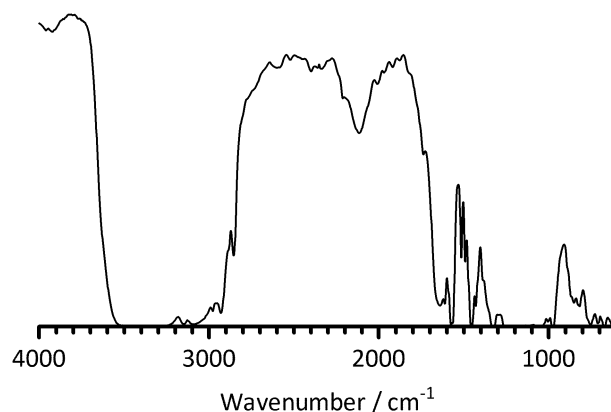

Fig. S3 The ATR FT-IR spectrum of **PBMI-Cl**.

Fig. S4 The transmission FT-IR spectrum of **PBMI-Cl**.

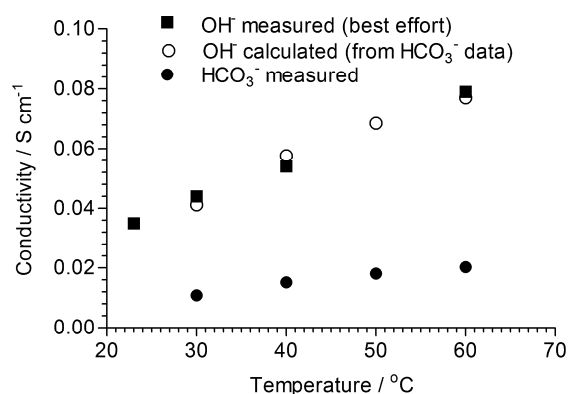### Additional data for conductivity method validation

Fig. S5 The bicarbonate and hydroxide ion conductivities (2-probe – from impedance spectroscopy data[2] for a sample of ETFE-g-poly(vinylbenzyl-trimethylammonium)-type AAEM. Validation of the hypothesis suggested by Hickner *et al*:[3] The hydroxide conductivities of AAEMs can be estimated by measuring the bicarbonate conductivities (easiest to do and least affected by contact with CO_2) and then multiplying by 3.8.

Chloride precipitation titration data for an anion-exchange membrane (containing both quaternary and tertiary groups)
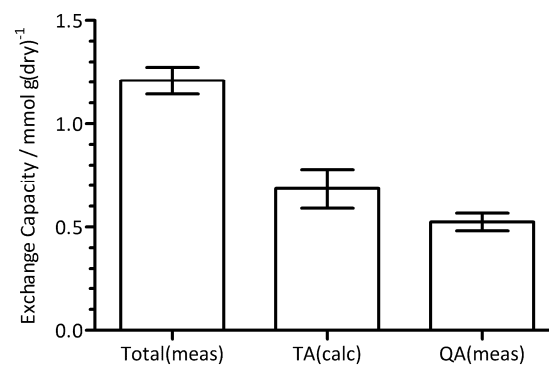

Fig. S6 The total, quaternary –ammonium, and tertiary amine exchange capacities of a radiation-grafted AAEM synthesised from ETFE-g-poly(vinylbenzyl chloride) radiation-grafted membrane and *N,N,N′,N′*-tetramethyldiaminomethane (Me$_2$N-CH$_2$-NMe$_2$) amination agent [the full study will be published in due course]. Error bars are the confidence intervals at the 95% confidence level ($n = 4$).

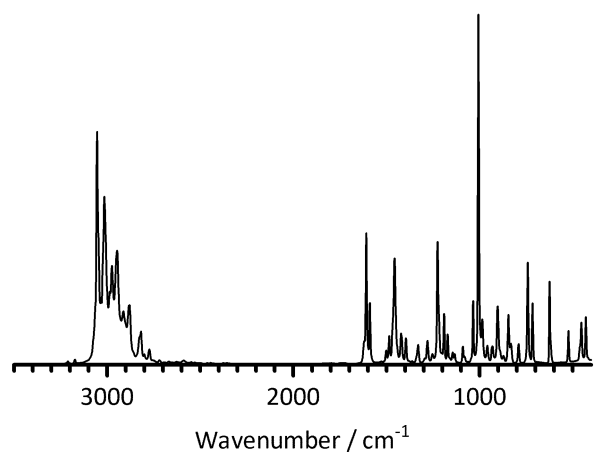**Additional FT-Raman data related to the small molecule stability tests**

Fig. S7 The FT-Raman spectrum of solid (as received) benzyltrimethylammonium chloride (**BTMA**). Top spectrum is full range, bottom spectrum is scaled to match the Raman stability data presented in the main article. The y-axis is scaled to height of the ring breathing mode at 1005 cm^{-1} for presentation purposes.
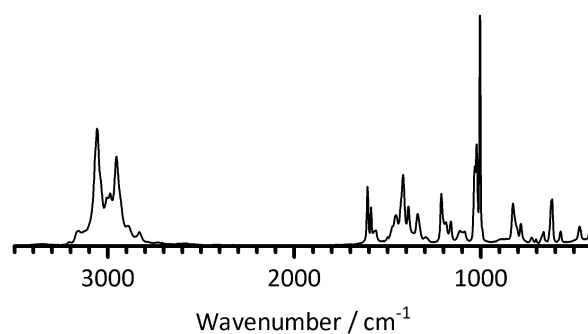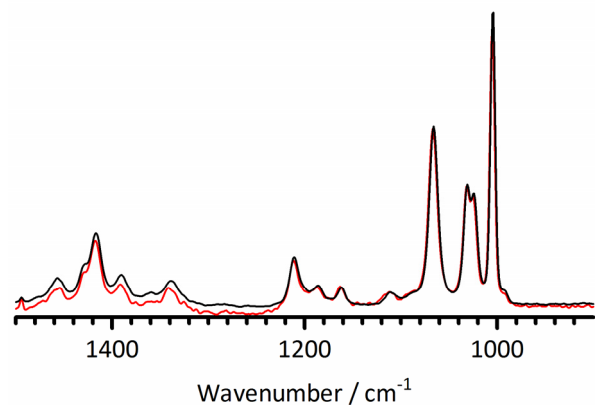

Fig. S8 The FT-Raman spectrum of solid (as received) 1-benzyl-3-methylimidazolium chloride (**1B3MI**). Top spectrum is full range, bottom spectrum is scaled to match the Raman stability data presented in the main article. The y-axis is scaled to height of the ring breathing mode at 1005 cm^{-1} for presentation purposes.
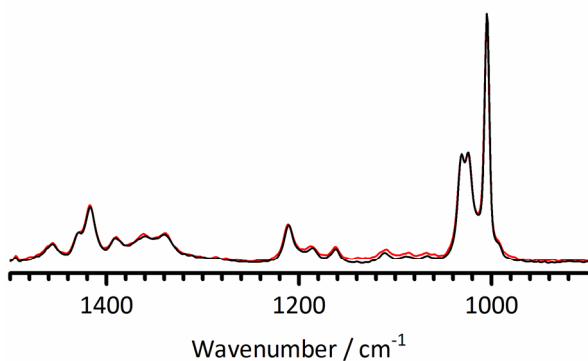

Fig. S9 The FT-Raman spectra of **1B3MI** dissolved in aqueous K_2CO_3 (1 mol dm^{-3}) and treated at 60°C for 0 (red) and 32 (black) days. Spectra were normalised to the ring breathing mode at 1005 cm^{-1}. The additional peak [*cf.* the KOH(aq) tests] at 1065 cm^{-1} is due to the CO_3^{2-} species in solution. Note: 128 scans and a 1:2 **1B3MI**:K_2CO_3 ratio were used.

Fig. S10 The FT-Raman spectra of **1B3MI** at dissolved in aqueous NaHCO$_3$ (1 mol dm^{-3}) and treated at 60°C for 0 (red) and 32 (black) days. Spectra were normalised to the ring breathing mode at 1005 cm^{-1}. Note: 128 scans and a 1:2 **1B3MI**:NaHCO$_3$ ratio were used.
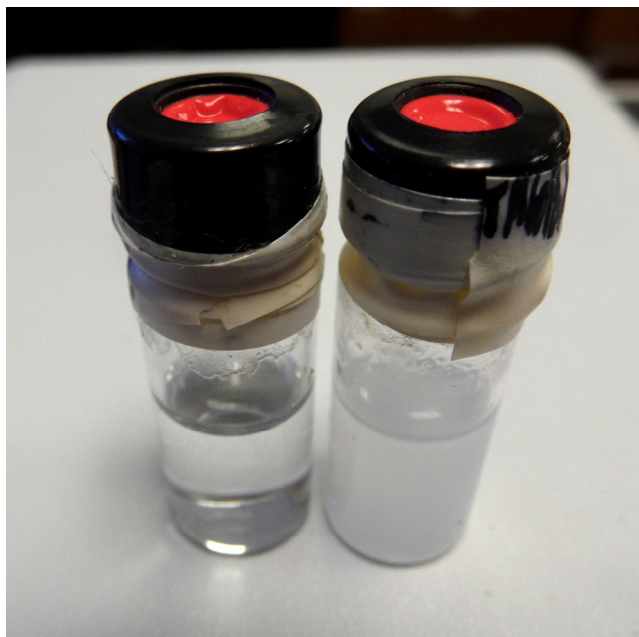
Fig. S11 Photograph of **BTMA** in the different solutions after treatment at 60°C for several weeks: Left = Deionised water (control experiment) and Right = aqueous KOH (1 mol dm^{-3}). Note the white precipitate in the KOH experiment.
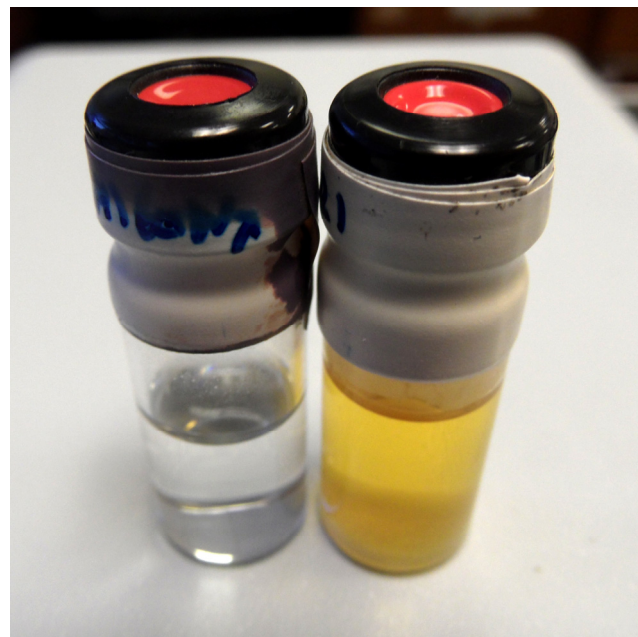

Fig. S13 Photograph of **1-butyl-3-methylimidazolium chloride** in the different solutions after treatment at 60°C for several weeks: Left = Deionised water (control experiment) and Right = aqueous KOH (1 mol dm^{-3}). Note the solution colour change and white precipitate in the KOH experiment.

References to ESI

1 T. Erdmenger, J. Vitz, F. Wiesbrock and U. Schubert, *J. Mater. Chem.*, 2008, **18**, 5267.
2 J. R. Varcoe, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1479; J. R. Varcoe, R. C. T. Slade, E. Lam How Yee, S. D. Poynton, D. J. Driscoll and D. C. Apperley, *Chem. Mater.*, 2007, **19**, 2686.
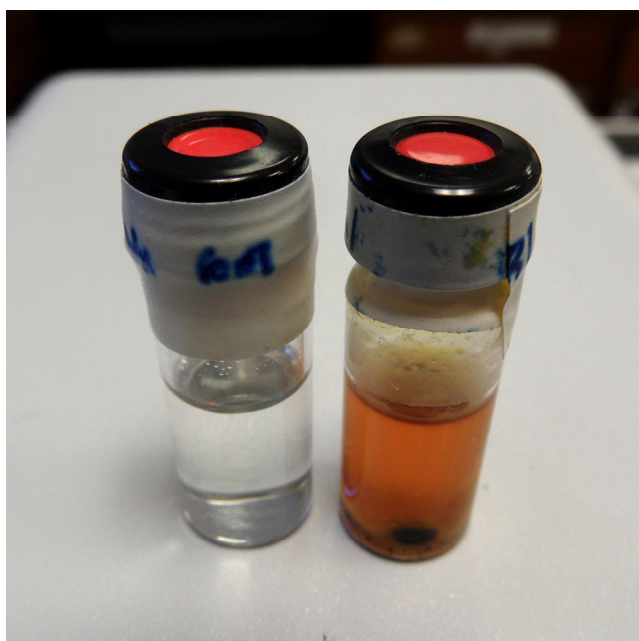3 J. Yan and M. A. Hickner, *Macromolecules*, 2010, **43**, 2349.

Fig. S12 Photograph of **1B3MI** in the different solutions after treatment at 60°C for several weeks: Left = Deionised water (control experiment) and Right = aqueous KOH (1 mol dm^{-3}). Note the solution colour change and mixed white and black precipitate in the KOH experiment.