SHORT PAPER

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Electrical conductivities of manganate-permanganate mixtures: new mixed-valence manganate(VI)–(VII) salts $Ba_3(MnO_4)_4$ and $BaK(MnO_4)_2$†

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Mixed-valent salts $Ba_3(MnO_4)_4$ and $BaK(MnO_4)_2$ are indicated by maximal 1:1 mixed-component conductivities, as governed by Marcus reorganisation energies.

Recent single-crystal preparations[1,2] of the mixed-valent salt $KMnO_4.K_2MnO_4$ or $K_3(MnO_4)_2$, hitherto known only as microcrystalline powder,[3-6] allowed the determination of a detailed X-ray diffraction (XRD) structure[1] confirmed at low temperature by neutron diffraction,[7] of the hopping electron-transfer (ET) mechanism of conductivity,[1] and of the (limited) delocalisation of the transferable electron.[7] The data indicate a borderline Class-I/Class-II mixed valent, in the Robin–Day classification.[8] Such mixed-valents with moderate electrical conductivities represent a solid-state equivalent of the outer-sphere ET mechanism for ions in solution, to which the Marcus[9,10] theory is addressed; Marcus theory was shown to be applicable to the solid mixed valent system.[4,5]

The early studies[3] employed solid $KMnO_4$ + K_2MnO_4 mixtures in continuously varied proportions, each ground separately then together for compaction into discs for conductimetry. The admixture of a mixed-valence partner to a salt can generate fractional amounts of a particular mixed-valent compound of enhanced conductivity (contrast the doping enhancement arising in band semiconductors). A sharp conductivity maximum is observed[3] at the 1:1 composition, because the number of electron-hopping partners is maximized in the pure MnO_4^-:MnO_4^{2-} compound. The electrical properties (conductivity, its activation energy, and the ET rate from dielectric relaxometry) of the compacted mixed-valent salt[3,4] were found to be identical with those of the single-crystal material.[1]

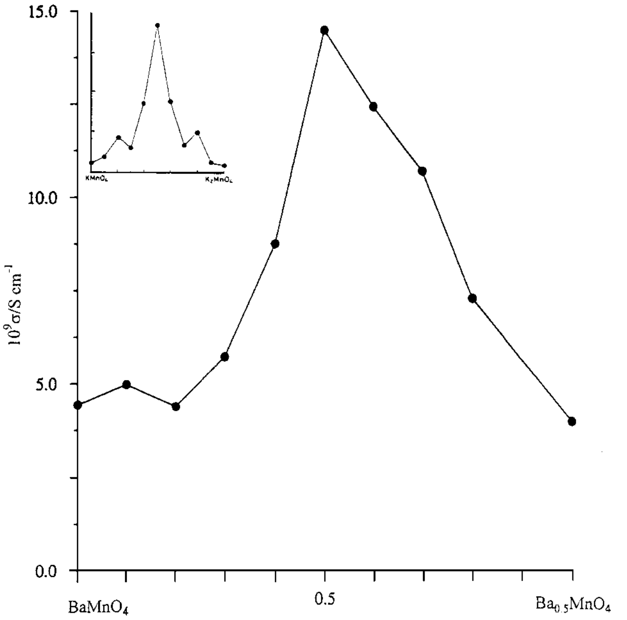

Fig. 1 Conductivities σ of compacted mixtures plotted against mole fractions of $BaMnO_4$ and $Ba_{0.5}MnO_4$ (the latter formulation symmetrising the scale with respect to the anions). Inset: previous results[3] for $KMnO_4$ + K_2MnO_4 showing maximum at 1:1, the established composition for the compound $K_3(MnO_4)_2$.

Further mixed-valents incorporating the MnO_4^-/MnO_4^{2-} system, in single-crystal form, have proved elusive *e.g.* $BaMnO_4$ has been difficult to introduce because of its insolubility, non-aqueous solvents proving no better than water, molten nitrates failing because of redox equilibria with the Mn species. Mixed valence in Ba salts was therefore tested by the mixed-salt conductimetry method,[3] seeking maxima corresponding to simple-fractional compositions in compacted solid-state mixtures now of $BaMnO_4$ and $Ba(MnO_4)_2$ in varying proportions.

In a second mixed-valent series, $KMnO_4$ was used as the valence partner to $BaMnO_4$.

Experimental

$Ba(MnO_4)_2$ and $BaMnO_4$ prepared as in the literature[11] were made into valence-mixture discs of progressive compositions for conductimetry at 22 °C following the established procedure.[3]

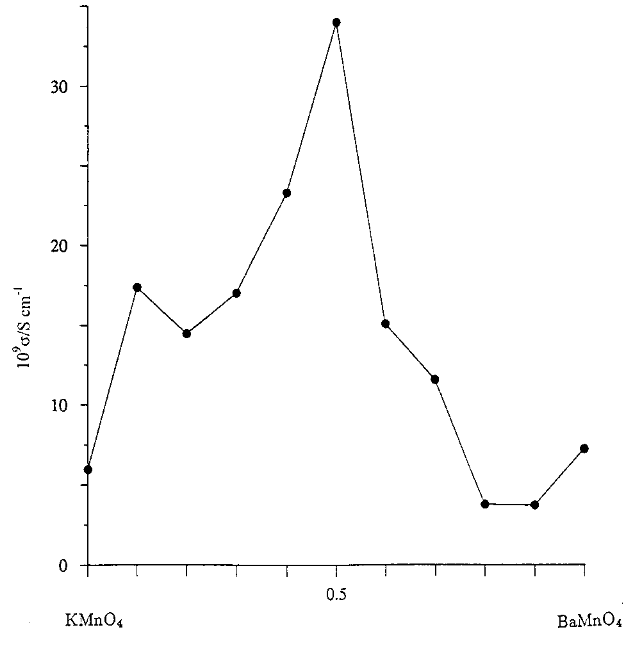

Fig. 2 Conductivity of compacted mixtures plotted against mole fractions of $KMnO_4$ and $BaMnO_4$ again showing a maximum at 1:1.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

$KMnO_4$, recrystallised after filtration, dried and ground separately then with various proportions of $BaMnO_4$, yielded a second set of valence mixtures.

Results and Discussion

The conductivity σ for $Ba(MnO_4)_2/BaMnO_4$ mixtures is a maximum at 1:1 MnO_4**:**MnO_4^{2-}, Figure 1, identically to the $KMnO_4/K_2MnO_4$ case shown in the inset. (Deviations from monotonous decrement or increment either side of the maximum arise from the ± 5–10% variability expected[3,4] in measurements on any one mixture, from *e.g.* incomplete randomness of mixing and related effects.) The mixed-valence compound $Ba(MnO_4)_2\{BaMnO_4\}_2$ or $Ba_3(MnO_4)_4$ is thus indicated, following the $K_3(MnO_4)_2$ case[3] later confirmed in single-crystal form.[1,2]

The mixtures of $BaMnO_4$ with $KMnO_4$, Figure 2, again show maximal conductivity at the 1:1 MnO_4^-**:**MnO_4^{2-} composition, demonstrating a further mixed-valent salt $BaK(MnO_4)_2$.

Compaction conductivities are $K_3(MnO_4)_2$ [110] >>$BaK(MnO_4)_2$ [3.4] >$Ba_3(MnO_4)_4$ [1.45] (with values of $10^8\sigma/S\ cm^{-1}$ in square brackets). Structural information is needed to understand the relative conductivities, but incorrect inferences[5,6] for compacted powder $K_3(MnO_4)_2$ disfavour diffraction studies of the new compounds as compactions. To rationalise the sequence, consider the reorganisation energies[10] for each system. These activation-energy terms are required to place species adjacent to the transfer centres, here MnO_4^- and MnO_4^{2-}, at locations intermediate to their initial and final dispositions. The energies may be represented as parabolas with respect to the required motion(s) for initial and final states in the theories of Marcus[9,10] for the solution case, and of Mott[12] for hopping-mechanism semi-conductors. In solids, re-organisation energies will undoubtedly be governed by the lattice energies of the mixed-valence compounds, as the (here cationic) relocations preceding or accompanying the ET event take place against the lattice energy. With similar structures in the three salts, *mutatis mutandis*, lattice energy will increase with increasing dication content, here Ba^{2+}, hence accounting for the observed sequence. The implied constancy of $MnO_4^- – MnO_4^{2-}$ separations in the three salts is not crucial, as follows. Ba^{2+} would in general confer *closer* anion–anion distances than would K^+, resulting in enhanced ET rates (due to greater transfer-orbital overlap) contrary to observation; variations in this separation thus seem of secondary importance.

To conclude, conductivity maxima at equimolar MnO_4^- and MnO_4^{2-} in valence mixtures provide compelling evidence of the formation of true mixed-valence salts $BaK(MnO_4)_2$ and $Ba_3(MnO_4)_4$, following the case of the K^+ salt confirmed by single-crystal evidence. The conductivities follow the expected sequence of lattice energies via their effects on the reorganisation energies preceding/accompanying ET.

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