Electrochemical Behaviour of Water in Molten $LiNO_3$–KNO_3 Eutectic

By DAVID G. LOVERING,* RICHARD M. OBLATH, and ALAN K. TURNER
(*Chemistry Branch, Royal Military College of Science, Shrivenham, Swindon* SN6 8LA)

Summary Contrary to previous reports, the electroreduction of water in nitrate melts appears to be coupled with nitrite reduction, probably involving an autocatalytic mechanism and an adsorbed intermediate.

A NUMBER of authors[1–6] have reported a cathodic voltammetric wave, anodic to the nitrate reduction wave, at solid microelectrodes, in molten alkali metal nitrate mixtures containing water. Whenever this 'water wave' has been observed either the melt has been conditioned by excessive potential scans into regions of interfering reactions[1–4], *vide infra*, or the electrode has been subjected to arbitrary prebiasing[2,5] or ageing.[2] Additionally, melts have often been overheated during purification procedures,[7] or subsequently aged, leading to thermal decomposition with the production of nitrite ions.[8] Although the 'water wave' has generally been attributed to the direct, diffusion-controlled reduction of water, Jordan[6] preferred to assign the wave to the concomitant reduction of water and nitrate ions (reaction 1).

$$NO_3^- + H_2O + 2e \rightarrow NO_2^- + 2OH^- \qquad (1)$$

More recently nitrate reduction by hydrated electrons has been invoked,[9] particularly to explain a blue coloration near the cathode.

During some recent cyclic voltammetric studies at stationary platinum microelectrodes, in molten $LiNO_3$–KNO_3 eutectic at 145 °C containing added water, we consistently failed to locate the characteristic 'water wave'. Care had been taken to ensure that the melt was not overheated during its preparation; cathodic potential excursions were always terminated prior to the reduction of nitrate ions. We subsequently recorded a single cathodic voltammogram encompassing the nitrate reduction wave, which exhibited its usual shape, but, again, no 'water wave' was evident. However, all cathodic potential scans initiated immediately following this yielded the 'water wave.' Moreover, its wave height was related to the bulk water concentration, as previously reported, and was also proportional to the square-root of the potential sweep-rate.

It appears that water is neither intrinsically cathodically electroactive in the region of the 'water wave' nor electroactive in combination with other melt components including nitrate ions (*cf.* ref. 6). Initially, experiments were conducted in Pyrex glass cells, but quantitatively similar results were observed with polytetrafluoroethylene vessels: thus species of the type $(SiO_2)_xO^{2-}$ are not involved. Furthermore, the results were unchanged with gold microelectrodes, or in an atmosphere of pure oxygen. Hence, it seems unlikely that surface oxides on the electrodes or bulk oxide species produce this wave.

Addition of hydroxide to an anhydrous nitrate melt produced the 'water wave,' but only after the potential had moved into the nitrate reduction region. In contrast, the 'water wave' appeared on all voltammograms following the addition of nitrite to a melt containing water, *i.e.* it was no longer necessary for the potential to encroach upon the nitrate reduction wave region.

Clearly, the presence of nitrite, as well as water, is essential for observation of the 'water wave.' In melts to which nitrite ions have not been added, it is necessary for them to be electrogenerated before the 'water wave' can be recorded (equation 2). Once nitrite ions are available in the melt, the 'water wave' may then be observed according to the proposed equation (3), the stoicheiometry of which

$$NO_3^- + 2e \rightarrow NO_2^- + \text{oxides} \qquad (2)$$

$$H_2O + NO_2^- + 2e \rightarrow 2OH^- + NO^- \qquad (3)$$

is consistent with coulometric results.[6]

This leads to an autocatalytic reaction (4),[10] in line with

$$NO^- + NO_3^- \rightarrow 2NO_2^- \qquad (4)$$

the observed time dependence of the 'water wave,' involving regeneration of nitrite. Monohyponitrite would be lost by dimerisation and side reactions. The mechanism of equation (3) could involve intermediates such as $Pt(NO)_{ads}$, on the grounds of known, strong metal–NO interactions.

The results obtained when hydroxide is added to an anhydrous melt are consequent upon a small back reaction in the equilibrium (5), producing water.[6] The equilibrium

$$O^{2-} + H_2O \rightleftharpoons 2OH^- \quad K_f(250\ °C) \sim 10^{18} \qquad (5)$$

(5) will be driven towards the left-hand side by the simultaneous consumption of H_2O and generation of OH^- according to equation (3).

Spectroscopic studies are necessary to establish whether blue colours observed at the cathode[1,9] are due to hydrated electrons,[9] nitrosyl complexes,[11] or oxides of nitrogen.[12]

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[1] H. S. Swofford, Thesis, Illinois University, Urbana, 1962; H. S. Swofford and H. A. Laitinen, *J. Electrochem. Soc.*, 1963, **110**, 814.

[2] T. E. Geckle, Thesis, Pennsylvania State University, 1964; U.S. Atomic Energy Comm., 1964, TID 21511.

[3] M. Peleg, *J. Phys. Chem.*, 1967, **71**, 4553.

[4] G. J. Hills and P. D. Power, *J. Polarog. Soc.*, 1967, **13**, 71.

[5] P. G. Zambonin, V. L. Cardetta, and G. Signorile *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1970, **28**, 237; *Analyt. Chem.*, 1971, **43**, 1571.

[6] J. Jordan, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1971, **29**, 127.

[7] P. G. Zambonin and J. Jordan, *Analyt. Letters*, 1967, **1**, 1.

[8] R. N. Kust and J. D. Burke, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 333; see also A. F. J. Goeting and J. A. A. Ketelaar, *Electrochim. Acta*, 1974, **19**, 267.

[9] J. Jordan, research colloquium, Imperial College, 9th June, 1976; A. Espinola, Thesis, Pennsylvania State University, 1974.

[10] D. H. Kerridge and J. D. Burke, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1307.

[11] H. E. Bartlett and K. E. Johnson, *Corrosion Sci.*, 1966, **6**, 87.

[12] T. Moeller, 'Inorganic Chemistry,' Wiley, New York, 1952.