ELECTROCHEMISTRY OF CATIONS IN DIOPSIDIC MELT: DETERMINING DIFFUSION RATES AND REDOX POTENTIALS FROM VOLTAMMETRIC CURVES

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Abstract

We have used Stationary Electrode Polarography to measure properties of ions in diopsidic melt whose electrochemical behavior is more complicated than that of a simple, reversible reduction within the range of potential between reduction and oxidation of the silicate in the melt. Criteria for obtaining diffusion coefficients and thermodynamic properties from these more complex voltammetric curves are discussed for each cation studied, including criteria to establish whether the values obtained represent equilibrium conditions. Diffusion coefficients were measured in diopsidic melt for cations of Eu, Mn, Cr, In and Ru, and enthalpies and entropies of reduction for the cations V(V), Cr^{3+}, Mn^{2+}, Mn^{3+}, Fe^{2+}, Cu^{2+}, Mo(VI), Ru^{3+}, In^{3+}, Sn(IV), and Eu^{3+}. Free energies of reduction in melts of different extents of polymerization appear to be controlled mainly by cation entropy.