The partial molar volume of Fe$_2$O$_3$ in alkali silicate melts: Evidence for an average Fe$^{3+}$ coordination number near five

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ABSTRACT

High-temperature (867–1534 °C) density measurements were performed in air on 10 liquids in the Na$_2$O-Fe$_2$O$_3$-FeO-SiO$_2$ (NFS) system and 5 liquids in the K$_2$O-Fe$_2$O$_3$-FeO-SiO$_2$ (KFS) system using Pt double-bob Archimedean method. Replicate measurements indicate an average reproducibility of 0.22%. Compositions (in mol%) range from 4 to 18 Fe$_2$O$_3$, 0 to 3 FeO, 18 to 39 Na$_2$O, 25 to 37 K$_2$O, and 43 to 67 SiO$_2$. Errors in the gram formula weight are ~0.4%. The molar volumes were fitted to a linear compositional model, which gives a compositionally independent partial molar volume (±2σ) for the Fe$_2$O$_3$ component ($\bar{V}_{\text{Fe}_2\text{O}_3}$) of 41.52 ± 0.34 cm$^3$/mol and zero thermal expansivity. The average residual to the fit is ±0.36% for our 57 measurements on 15 liquids at various temperatures. The value for $\bar{V}_{\text{Fe}_2\text{O}_3}$ in silicate liquids when Fe$^{3+}$ is in fourfold vs. sixfold coordination is estimated to be −45.5 ± 1 vs. −34 ± 1 cm$^3$/mol, respectively. Thus, the fitted value of 41.5 cm$^3$/mol appears to reflect an average Fe$^{3+}$ coordination number between 4.5 and 5.0, which is consistent with recently published X-ray absorption fine structure (XAFS) spectroscopy and molecular dynamics (MD) simulations on Fe$^{3+}$-bearing silicate glasses. In the literature, Fe$^{3+}$ is inferred to be present in trigonal bipyramidal sites, in contrast to the square pyramidal sites for Ti$^{4+}$. The lack of a strong compositional or temperature dependence for $\bar{V}_{\text{Fe}_2\text{O}_3}$ in these alkaline silicate liquids, in contrast to what is observed in the literature for $\bar{V}_{\text{Ti}_2\text{O}_3}$ in similar melts, may reflect the different geometries for Fe$^{3+}$ and Ti$^{4+}$.

INTRODUCTION

Iron is the only major element in natural silicate melts with more than one oxidation state. To model magmatic processes, thermodynamic descriptions of silicate melts must include precise information on both the Fe$_2$O$_3$ and FeO components. The structural role of Fe$_2$O$_3$ and FeO in magmatic liquids strongly influences how the Fe-redox ratio varies as a function of composition, temperature, pressure, and oxygen fugacity. Although it has long been known that Fe$^{3+}$ may occur in both four- and sixfold coordination in silicate glasses, only recently has a precise information on both the Fe$_2$O$_3$ and FeO components. The thermodynamic descriptions of silicate melts must include pre-

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