INTRODUCTION

Water dissolves in silicate glasses and melts as molecules (Doremus 1969, 1994, 1995; Ernsberger 1977; Bartholomew 1982; Stolper 1982). These dissolved water molecules react with the Si-Al-O network of the glass to form OH groups:

\[-O- + H_2O(d) = 2OH(n)\] (1)

In this equation, \((n)\) means part of the solid glass network (but see discussion below), and \((d)\) means dissolved molecularly in the glass. The symbol \(-O-\) designates an O ion in the glass network; it can be bonded to either Si or Al ions. The exact configuration of the OH groups is controversial. Based on a nuclear magnetic resonance (NMR) study, Kohn et al. (1992) concluded that in nepheline (NaAlSiO₄) and CaAl₂Si₆O₁₇.₃ melts, one H atom is associated with a bridging O atom between Al and Si atoms, and the remaining OH forms molecular NaOH with a Na ion that compensates for the excess negative charge around the Al atom substituted for a Si atom. The more traditional view of the formation of two hydroxyl groups bonded to Al or Si atoms was advocated in a model of Sykes and Kubicki (1993) based on infrared and Raman spectroscopy and molecular orbital calculations. These models were discussed further by Kohn et al. (1994) and Sykes and Kubicki (1994). For the present purpose, the important result from reaction 1 is the equilibrium constant (see Eq. 2), which should be the same for both models. Richet and Polian (1998) have additional ideas on the structure of water in silicate glasses.

The distribution of dissolved water in a haplogranitic glass between molecular water and reacted OH groups, as measured by Sowerby and Keppler (1999) at temperature and pressure, is compared to a Langmuir model. In this model the number of reactive sites in the glass is limited, so as the total water content increases, the concentration of reacted OH groups saturates. The comparison between the model and experimental measurements is good with two fitting parameters. The total water solubility in NaAlSi₃O₈ melts as measured by Holtz et al. (1995) is the sum of molecular water dissolved from the gas phase and reacted OH groups; the concentration of OH groups calculated from these solubility measurements also fits the Langmuir model. The partial molar volumes for water in NaAlSi₃O₈ melts are constant above about 4 wt% total water, but decrease at lower water contents; this dependence can be understood from the speciation measurements.

ABSTRACT

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Water speciation in silicate glasses and melts: Langmuir limited site model

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