

Diffusivity-viscosity relations

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It is widely "believed" that diffusivity of a component or species in liquids is inversely proportional to the liquid viscosity. Some equations are much celebrated (e.g. the Einstein and Eyring equations) and other less so (e.g. the Sutherland and Glasstone equations) [1]. The equations are often of the form: $D = kT/(\eta L)$, where D is diffusivity; k is Boltzmann constant; T is temperature; η is viscosity; and L takes the form of $6\pi a$ (Einstein), $4\pi a$ (Sutherland), $2a$ (Glasstone), and λ (Eyring), where a is the radius and λ is roughly the jumping distance of the diffusing species. The difference between the equations is no more than a factor of 10. Comparison of experimental data with the relations show:

(1) The Eyring equation applies well to ^{18}O diffusion in dry jadeite, diopside, dacite, and basalt melts (e.g. [2, 3]) but fails for ^{18}O diffusion in hydrous rhyolitic melt [4]. Because most natural silicate melts are hydrous, the applicability of the Eyring equation is hence limited.

(2) The Einstein equation applies roughly to aqueous solutions [1], but does not apply to the molecular species such as H_2O , Ar, and CO_2 in hydrous rhyolitic melt [5-8] even when speciation effect is taking into account.

(3) The activation energy (E) for viscosity often decreases with T (e.g. [9, 10]) whereas E for diffusion is often constant, or increases with T (e.g. [11]). The opposite trends in how E depends on T imply that diffusivity and viscosity are not inversely proportional.

In summary, none of the celebrated diffusivity-viscosity relations is generally applicable. The causes of the failures will be explored.

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Probing the cassiterite (110)-water interface structure with X-ray scattering method

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In earlier studies we reported the rutile [TiO_2] (110)-water interface structures [1]. Cassiterite [SnO_2], which is isostructural to rutile but with a significantly different bulk dielectric constant, has been recently studied both theoretically and experimentally to explore the intrinsic factors affecting the oxide-water interface structures and properties. Yet lack of the direct atomic level structure information hindered the thorough investigation of the systematic behavior, which is important to understand the interfacial processes. The earlier interfacial structure study revealed the structure along the surface normal direction but with ambiguities [2]. In this study, the single crystal cassiterite (110)-water interface structure was measured with high resolution surface X-ray scattering method (crystal truncation rod). 3D interfacial structure, including the relaxations of the atoms on the crystal surface and the adsorbed water molecule distribution at the interface, were determined. The similarities and the differences between the cassiterite-water and rutile-water interfaces and their implications are discussed.

[1] Zhang *et al.* (2007) *Surf. Sci.* **601**, 1129-1143. [2] Vlcek *et al.* (2007) *Langmuir* **23**, 4925-4937.