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# Self-Diffusivity and Free Volume: an Ideal Binary Mixture

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## 1. Introduction

Small molecules in solution can exhibit a variety of phase behavior, including glass and gel formation, and liquid-liquid phase separation.[1] Predicting these phases requires knowledge of the effective attractions between the solutes in solution, as well as their volume fraction. One method for quantifying the attractions between solutes is to measure the concentration dependence of their self-diffusivity.[2] In general, the steeper the decrease in the self-diffusivity of a solute with increasing concentration, the greater the effective attractions between solutes, and the lower the solubility. However, using this method to compare different molecular species is complicated by the fact that the concentration dependence of the self-diffusivity is influenced by volume exclusion effects. To correct for these effects it is necessary to accurately predict the effect of free volume on the self-diffusivity. We study this relationship by measuring the self-diffusivity of a solute in a solution where it is highly soluble. Under these conditions, we expect that the attractions between solute particles should be of little importance relative to free volume effects, thereby allowing us to quantify the effect of volume exclusion on self-diffusivity.

## 2. Results

We use Pulse Gradient Spin Echo NMR to measure the concentration dependence of the self-diffusivity of citric acid (CA) in ethanol (EtOH), where it is highly soluble. The self-diffusivity measured over a range of concentrations and temperatures is consistent with a simple free volume model,[3] as shown in Fig. 1(a) and (b). Within this model, the free volume available to the diffusing molecules can be decreased either by increasing the concentration of the solute, or by decreasing the temperature. Using this model, we are able to collapse all values of self-diffusivity of both CA and EtOH onto a single line for each species by plotting them as functions of $1/(T/T_g - 1)$ (Fig 1(c)). In this expression $T$ is the absolute temperature, and $T_g$ is the glass transition temperature of the mixture, which is calculated using the Gordon-Taylor equation, and by estimating the thermal expansion coefficient of CA using the Simha-Boyer rule. [4]

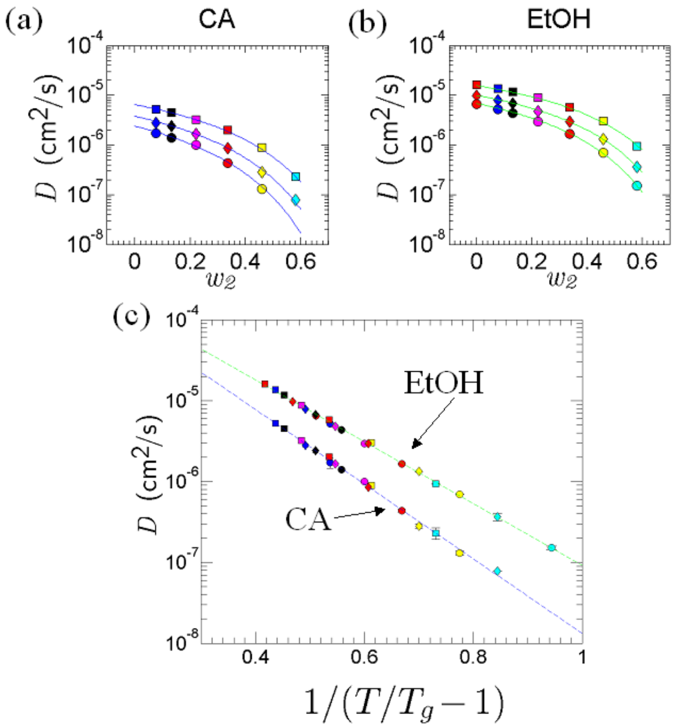


Fig. 1 Self-diffusivity of (a) CA and (b) EtOH as a functions of the weight fraction, $w_2$, of CA, at 8 ºC (spheres), 25 ºC (diamonds), and 50 ºC (squares). Solid lines show fits from the free volume theory. (c) The self-diffusivity data from each species superimpose onto master lines.

**3. Conclusion**

The simple free volume model accurately describes the self-diffusivity of both EtOH and CA over a range of concentrations and temperatures. Self-diffusivity as a function of these two variables superimpose onto a single master curve for each species. These results suggest that free volume models may be useful in separating the effect of attractions from those associated with excluded volume.

**References**

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