Application of the compensated Arrhenius formalism to temperature-dependent fluidity and self-diffusion coefficients of 1-alcohol and 3-alcohol systems

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Abstract

The compensated Arrhenius formalism (CAF) models temperature-dependent self-diffusion coefficients and fluidity (the inverse of viscosity) of protic and aprotic polar liquid systems. The CAF assumes transport to be a thermally activated process, with a corresponding energy of activation, $E_a$. The CAF includes the static dielectric constant in the exponential prefactor of an Arrhenius-like model, which varies with hydrogen bonding in protic systems. We apply the CAF to temperature-dependent fluidity data of 1-alcohol and 3-alcohol systems to investigate the effect of hydrogen bonding on the $E_a$. The CAF results describe the temperature-dependent behavior of both sets of fluidity data—the $E_a$ values are similar, but the exponential prefactors are significantly different due to the differences in hydrogen bonding. The CAF is also applied to temperature-dependent self-diffusion coefficients for 1- and 3-alcohols and compared to the results for fluidity.

Experimental

- Cambridge Viscosity VISCOMLab 4000
- Data taken from 5-85°C in increments of 10°C in N$_2$ glovebox
- All compounds purchased from commercial sources, used as delivered
- Diffusion coefficients determined with a Stejskal-Tanner pulsed field gradient spin-echo sequence using a Varian VNMRS400 MHz NMR
- IR spectra taken with a Bruker IFS66V

Procedure

1. Fluidity and static dielectric constant are both functions of temperature
2. Fluidity is a thermally activated process modeled with an Arrhenius-like expression:
   \[ F(T) = F_0 \exp\left(\frac{E_a}{RT}\right) \]
3. Assume a temperature dependence in the exponential prefactor, $F_0$:
   \[ F(\varepsilon_s, T) = F_0(\varepsilon_s, T) \exp\left(\frac{E_a}{RT}\right) \]
4. Assume all temperature dependence in $F_0$ is due to $\varepsilon_s$:
   \[ F(\varepsilon_s, T) = F_0(\varepsilon_s(T)) \exp\left(\frac{E_a}{RT}\right) \]
5. Create an isothermal reference curve of transport measurements from each family member, here represented by black curve
6. Scale out the prefactor by dividing $F(T)$ by $F_r(T)$
   \[ F(T) = \frac{F_0(\varepsilon_s(T))}{F_0(\varepsilon_s(T))} \exp\left(\frac{E_a}{RT}\right) \]
7. The natural logarithm of the resulting equation is the compensated Arrhenius equation, from which the $E_a$ can be calculated:
   \[ \ln\left(\frac{F(T)}{F_r(T)}\right) = -\frac{E_a}{RT} + \frac{E_a}{R_0} \]
8. The scaling procedure is performed on each family member, and the $E_a$’s are averaged
9. exponential prefactor determined form average activation energy

Results, Discussion, Conclusion

- 1- and 3-alcohols share similar activation energies for any specific mass transport property
- The results are consistent with differences in the hydrogen bonding of 1- and 3-alcohols
- As postulated by the CAF, the differences between $F_0$ of 1- and 3-alcohols correspond to solution structure through the static dielectric constant, due to the differences in hydrogen bonding
- The CAF must be used in order to account for the observed differences in 1- and 3-alcohol mass transport

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