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**You said:**

the time-temperature superposition (TTSP) for his SAOS (small-angle oscillatory shear) measurements. Explain TTSP using the Arrhenius dependence of viscosity on temperature. Replace the activation energy by DH – T DS, and T by the Vogel expression (T – T0) to obtain a three-parameter function for viscosity, or relaxation time (~1/viscosity). Relate DH, DS, and T0 to the three parameters in the WLF equation.

**ChatGPT said:**

Time-Temperature Superposition (TTSP) is a fundamental concept in rheology used to extend the range of viscoelastic data by shifting measurements taken at different temperatures to create a master curve. This principle relies on the fact that the material's response at different temperatures can be scaled by a shift factor, aTaT​, which modifies time or frequency.

**Arrhenius Dependence of Viscosity on Temperature**

The Arrhenius equation describes the temperature dependence of viscosity ηη as:

η(T)=η0eEARTη(T)=η0​eRTEA​​

where:

* EAEA​ is the activation energy,
* RR is the universal gas constant,
* TT is the absolute temperature,
* η0η0​ is a pre-exponential factor.

Replacing the activation energy EAEA​ by ΔH−TΔSΔH−TΔS, we obtain:

η(T)=η0eΔH−TΔSRTη(T)=η0​eRTΔH−TΔS​

or rewriting,

η(T)=η0eΔHRTe−ΔSRη(T)=η0​eRTΔH​e−RΔS​

Since relaxation time ττ is proportional to viscosity (τ∼ητ∼η), we can express the relaxation time similarly:

τ(T)=τ0eΔH−TΔSRTτ(T)=τ0​eRTΔH−TΔS​

**Modification Using the Vogel Equation**

The Vogel-Fulcher-Tammann (VFT) equation provides a more accurate description of viscosity in glass-forming materials:

η(T)=η0eBT−T0η(T)=η0​eT−T0​B​

where:

* BB is a material-specific constant,
* T0T0​ is the Vogel temperature.

By comparing the exponential dependencies, we set:

ΔH−TΔSRT=BT−T0RTΔH−TΔS​=T−T0​B​

which implies the following parameter correspondences:

* B≈ΔHRB≈RΔH​,
* T0T0​ accounts for the entropic effects in a manner analogous to the Kauzmann temperature where configurational entropy vanishes.

**Connection to the WLF Equation**

The Williams-Landel-Ferry (WLF) equation, which describes the temperature dependence of the shift factor aTaT​, is given by:

log⁡aT=−C1(T−Tr)C2+(T−Tr)logaT​=C2​+(T−Tr​)−C1​(T−Tr​)​

where C1C1​ and C2C2​ are empirical constants, and TrTr​ is a reference temperature.

Comparing with the Vogel equation, we identify:

* C1≈Bln⁡(10)RC1​≈ln(10)RB​,
* C2≈(Tr−T0)C2​≈(Tr​−T0​),
* T0T0​ plays a role similar to the temperature where the viscosity diverges.

Thus, TTSP is validated through the VFT equation, which refines the Arrhenius approach by incorporating a divergence temperature T0T0​. This approach explains why the WLF equation provides a better fit for polymer relaxation dynamics than a simple Arrhenius model.