The effect of intermolecular forces and entropy on viscosity, vapor pressure and evaporation in hydrocarbon oils

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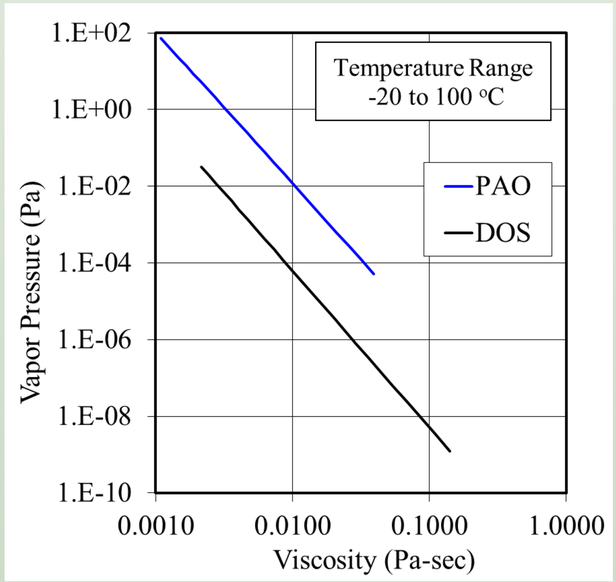
Motivation

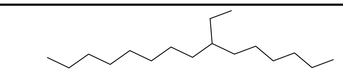
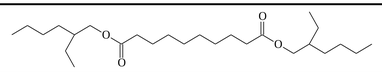
Hydrocarbon base oil provide the starting point for lubricant formulations. The fundamental problem addressed in this work is the relationship between viscosity and vapor pressure of base oil.

Needs for low viscosity/low vapor pressure oils.
- Increase efficiency of motors, engines, and drivetrains
- Lower friction and evaporation loss

Problem:
- Low viscosity -> leads to high vapor pressures

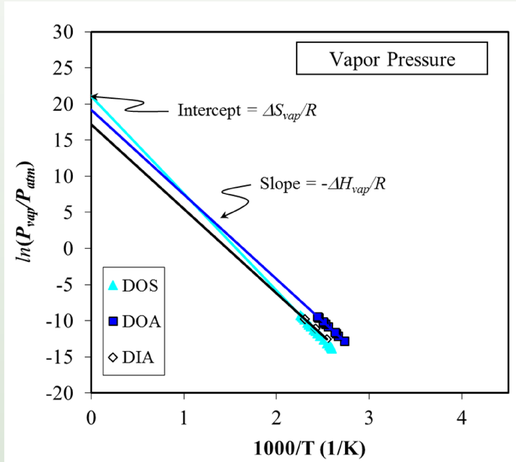
Vapor Pressure vs. Viscosity for Two Base Oils

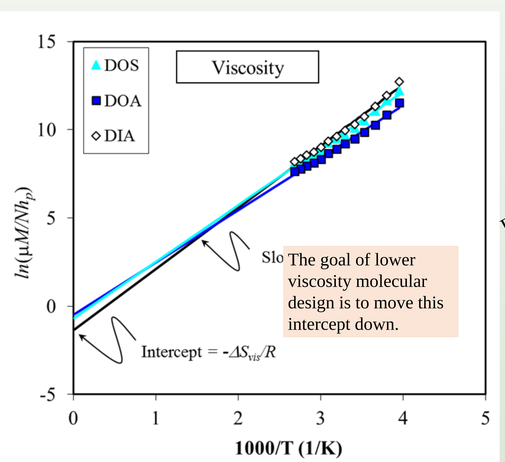


Acronym	Molecular Weight (g/mol)	Structure
PAO	240	
DOS	427	

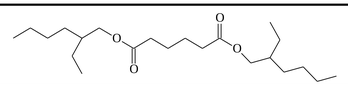
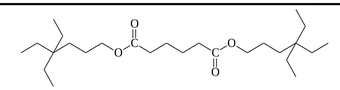
"Arrhenius" plots for Vapor Pressure and Viscosity

The slope and intercept determine the vapor pressure and viscosity





The goal of lower viscosity molecular design is to move this intercept down.

Acronym	Molecular Weight (g/mol)	Structure
DOA	371	
DIA	427	

"Shape Factor": $n = \frac{\Delta E_{vap}}{\Delta E_{vis}} > 1$

(Ewell and Eyring, 1937)

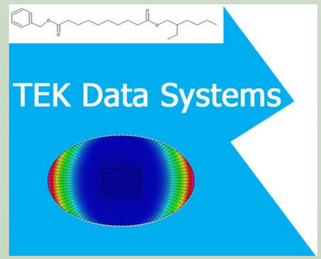
The slope and intercept of the Arrhenius plot are fixed by the activation entropy ΔS and energy $\Delta H = \Delta E + \Delta(PV)$ for vaporization and for flow.

P_{vap} vapor pressure, P_{atm} atmospheric pressure, μ kinematic viscosity, M molecular weight, N Avogadro's number, h_p

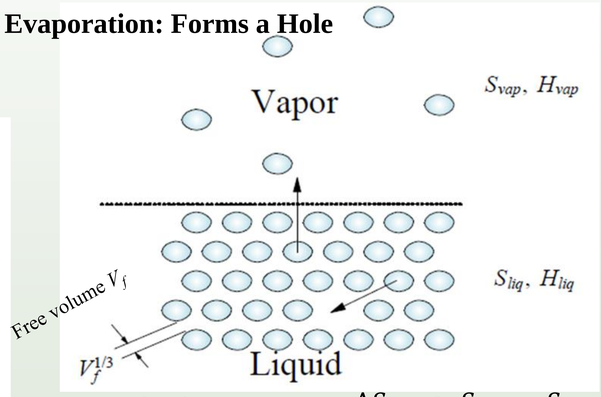
Combining the vapor pressure and viscosity activation energies, the molecular shape factor is provided by the vaporization ΔE_{vap} and flow ΔE_{vis} activation energies (determined by the number and type of atoms and oil polarity)

References

1 T. E. Karis & H. S. Nagaraj (2000) Evaporation and Flow Properties of Several Hydrocarbon Oils, TRIBOLOGY TRANSACTIONS, 43:4, 758-766, DOI: 10.1080/10402000008982405
2 R.H.Ewell & H.Eyring (1937) Theory of Viscosity of Liquids as a Function of Temperature and Pressure , Journal of Chemical Physics, Princeton, NJ
3 S.Q.A. Rizvi, Petroleum-Derived Hydrocarbon Base Oils, Fuels and Lubrications Handbook ©2016, pg 292
4 J.H. Hildebrande(1939), Liquid Structure and Entropy of Vaporization, Journal of Chemical Phyiscs, Berkeley, CA
5 W. Kauzmann & H. Eyring (1940) The Viscous Flow of Large Molecules, J.AM Chemistry Society Vol. 62. Princeton, NJ

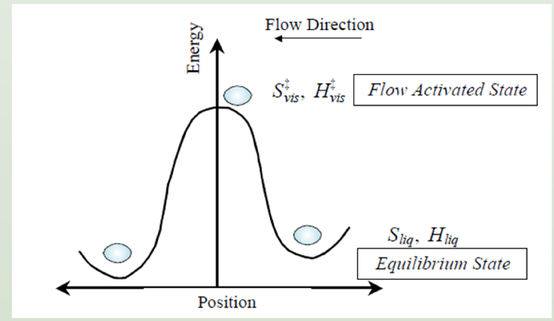


Evaporation: Forms a Hole



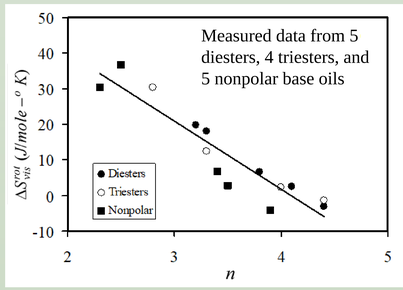
vaporization entropy $\Delta S_{vap} \approx S_{vap} - S_{liq}$

Flow: Changes Position



flow activation entropy $\Delta S_{vis} = \Delta S_{vis}^{trans} + \Delta S_{vis}^{rot}$

Flow Activation Rotational Entropy ΔS_{vis}^{rot} vs. Shape Factor n



Molecules with a higher vaporization energy have a higher viscosity because they the gain less or lose more rotational entropy as they transition to a hole in the liquid.

Conclusion

Lubricant base oils with lower viscosity and vapor pressure should be designed to gain more entropy as they translate between the neighboring molecules in the liquid. This can most likely be accomplished by designing a molecular structure with a greater flow rotational activation entropy and lower vaporization entropy.