

Course: SIO209

Aerosol-Cloud Interactions

Instructor: Prof. Lynn Russell

Author: **Timothy M. Raymond and Spyros N. Pandis**

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Title:

**Cloud activation of single-
component organic aerosol
particles**

Reviewed by: Odelle Lariviere and Ji Chen

Background Literature

- **Works that this article cited:**
 1. Corrigan et al, 1999 *“Cloud condensation nucleus activity of organic compounds.”*
 2. Eichel et al, *“The solubility of atmospheric aerosol particles and its impact on cloud microphysics”*
 3. Gorbunov et al , 1997 and 1998 *“Water nucleation on aerosol particles containing both organic and soluble inorganic substances.”*
 4. Kohler, 1936 *and we all know what THAT was about...*

- **What did we know before this article?**
 - 1) A large amount of work has been done to develop various theories on CCN activation.
 - 1) Kelvin equation
 - 2) Kohler theory
 - 3) Organic aerosols exist in abundance in the atmosphere.

New Contribution

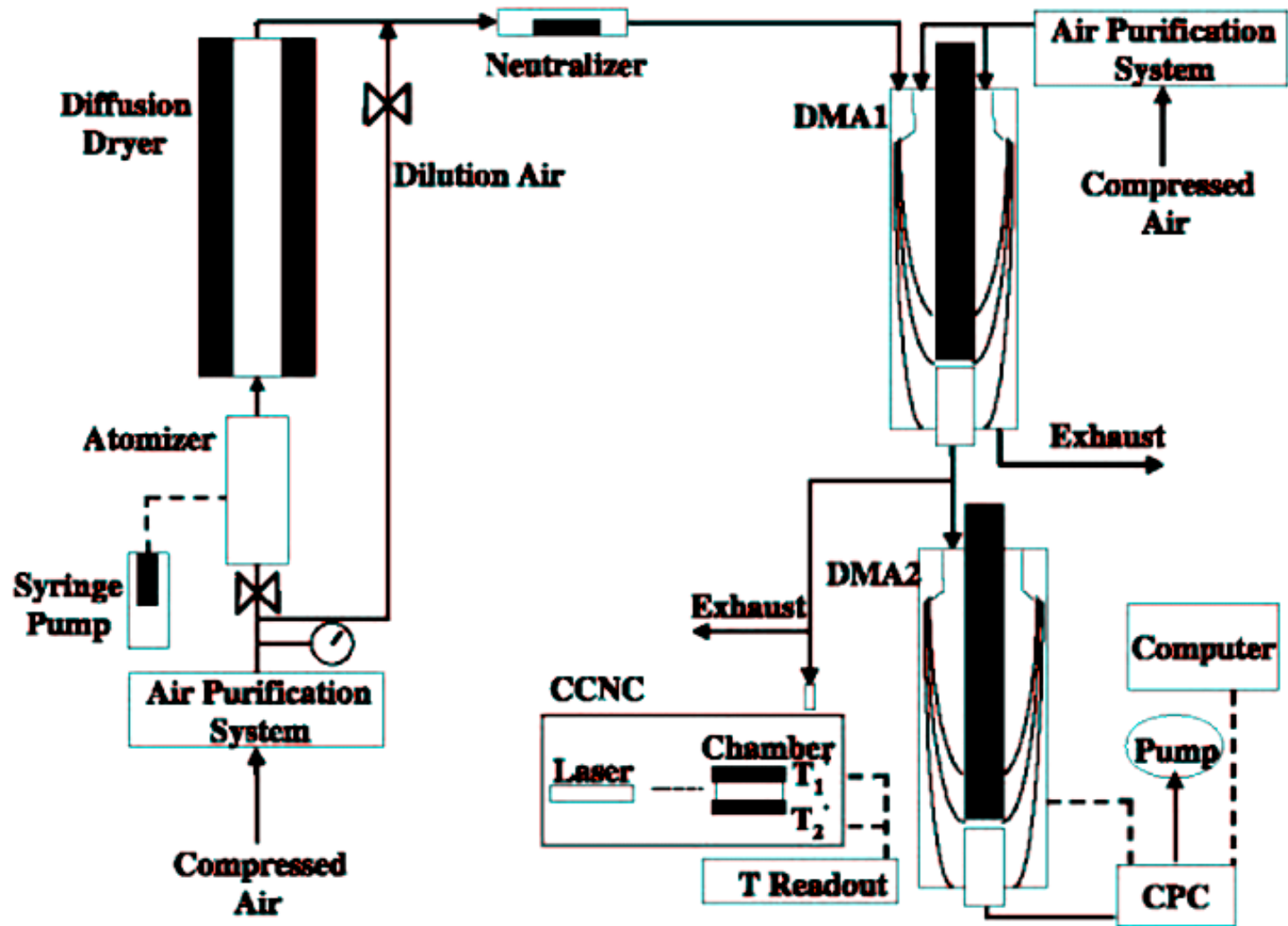
- **Work that this article describes:**
 - 1) Expanding the database of pure organic component CCN activation studies
 - 2) Compare the experimental results with an extension of the Kohler theory that includes an easily obtainable parameter for modeling the system.
 - 1) Solubility
 - 2) Wettability (contact angle with water)

- **What advance was made in this article?**
 - 1) Experimental evidence supporting Kohler theory ... 70 years later.
 - 2) Showed that surfactant properties and morphology can be more of a determinant of good CCN than solubility.
 - 3) Increased our understanding of the relative efficiency of organics to act as CCN.

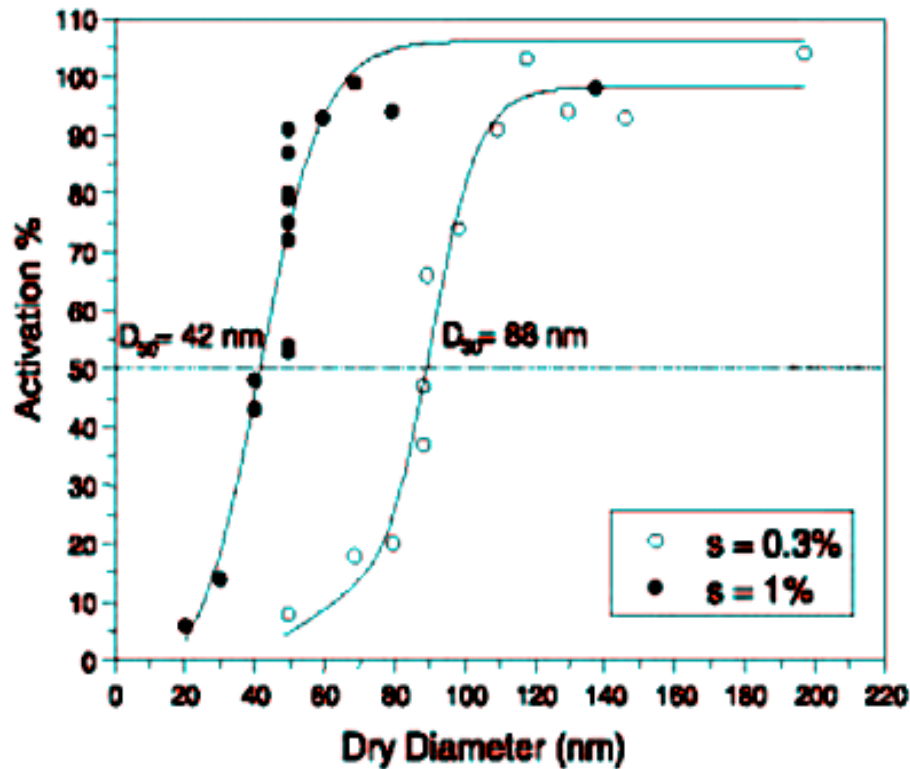
Implications

- **To what other advances did this work lead?**
 - 1) Published in 2002, so these advances are still being worked on.

Experimental Design



Statistics of Activation



- D_{50} is the dry diameter at which half of the particles activate at a given super-saturation.
- Cumulative distribution function from these curves and their respective probability distribution function is how the variance/std dev is calculated.

Determining solubility and surface contact angle with water.

Table 1. Properties of Investigated Compounds at 293 K

Chemical Species	Formula	Purity, ^a %	M_w , g mol ⁻¹	Density, ^b g/cm ³	Solubility, ^c g/100 cm ³ H ₂ O	Surface Tension, ^d dyn cm ⁻¹	Contact Angle With H ₂ O ^e
Adipic acid	C ₆ H ₁₀ O ₄	99+	146.15	1.360	1.76 1.89	66	~0°
Ammonium sulfate	(NH ₄) ₂ SO ₄	99.5	132.14	1.769	76.4 ^f	73 (3.0)	~0°
Cholesterol	C ₂₇ H ₄₆ O	99+	386.66	1.067	<0.002	72	~0°
Glutamic acid	C ₅ H ₉ NO ₄	99+	147.13	1.538	0.66 0.73	71	~0°
Glutaric acid	C ₅ H ₈ O ₄	99	132.12	1.424	107 140	51 (2.0)	~0°
Hexadecane	C ₁₆ H ₃₄	99	226.45	0.773	9 × 10 ^{-8f}		>90°
Hexadecanol	C ₁₆ H ₃₄ O	99	242.45	0.830	3 × 10 ^{-6b}		~45°
Leucine	C ₆ H ₁₃ NO ₂	99+	131.17	1.239	0.88 0.97	70	>90°
Myristic acid	C ₁₄ H ₂₈ O ₂	99.5	228.38	0.866	<0.002	57	>90°
Norpinic acid	C ₈ H ₁₂ O ₄	unknown	172.18	0.8 ^f	4.7	57 (2.0)	
Palmitic acid	C ₁₆ H ₃₂ O ₂	99	256.43	0.853	0.0007 ^f		>90°
Pinic acid	C ₉ H ₁₄ O ₄	unknown	186.21	0.8 ^f	>8.46	45 (4.2)	
Pinonic acid	C ₁₉ H ₁₆ O ₃	98	184.24	0.786	0.64 0.71	53	~0°
Sodium chloride	NaCl	99.5	58.44	2.165	36 ^e	74 (2.0)	~0°
Stearic acid	C ₁₈ H ₃₆ O ₂	99+	284.48	0.847	0.0003 ^f		>90°

^aSigma-Aldrich Chemical Company.

^bCRC Handbook.

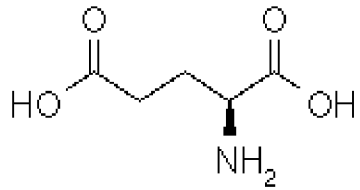
^cThis study.

^dExperimentally determined at saturation concentration except where noted by concentration value in parentheses in g/100 cm³ H₂O.

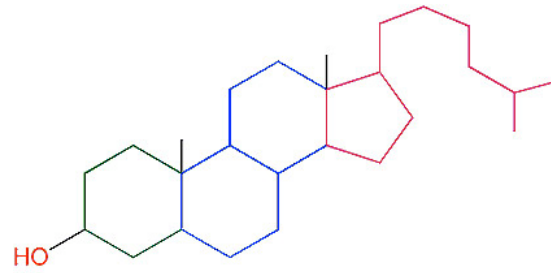
^eSaxena and Hildemann [1996].

^fYaws [1999].

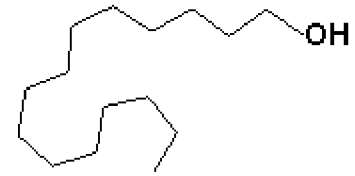
^gEstimated.



Glutamic Acid



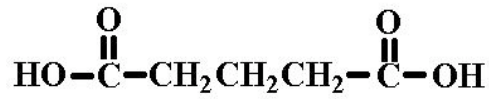
CHOLESTEROL



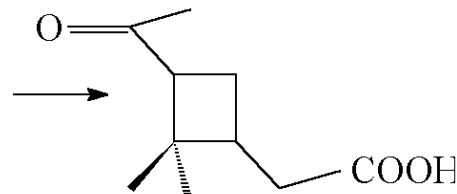
Hexadecanol



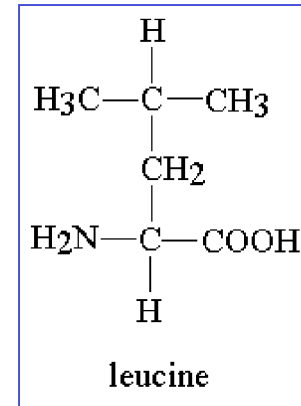
Hexadecane



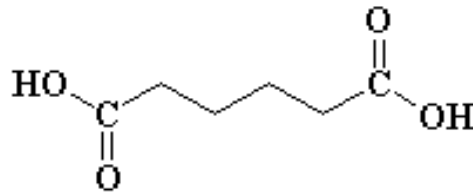
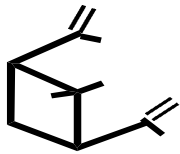
Glutaric acid



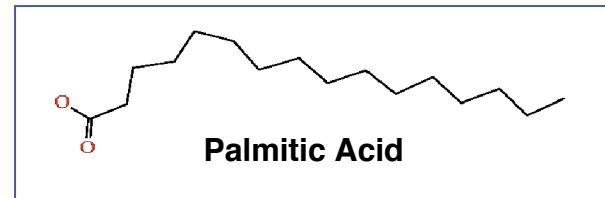
Pinonic acid



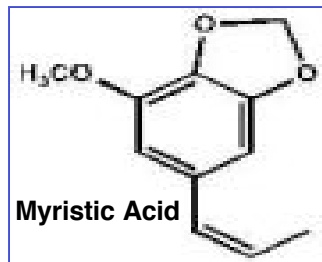
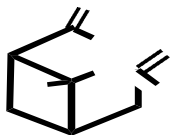
leucine



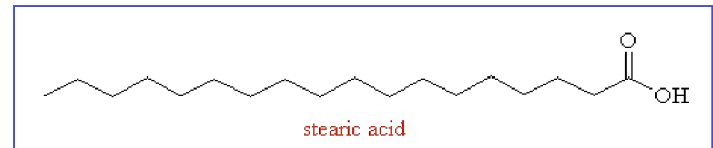
adipic acid



Palmitic Acid



Myristic Acid



stearic acid

Results

Table 2. Activation Diameters for Investigated Compounds^a

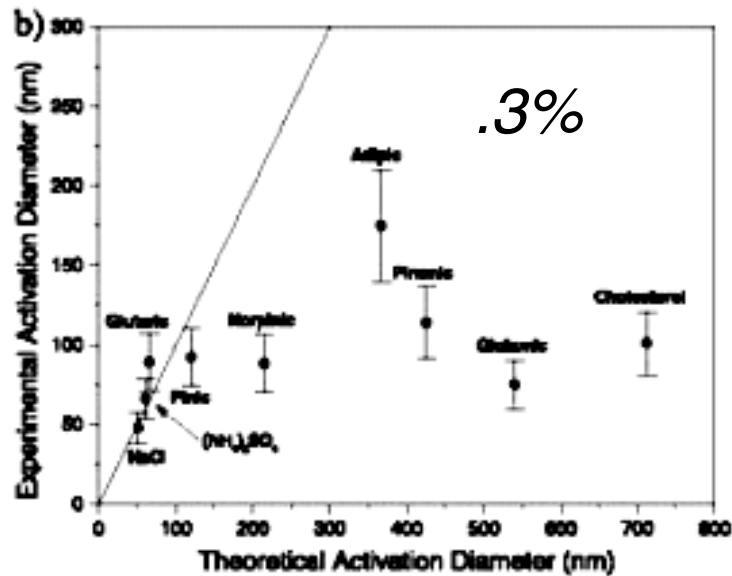
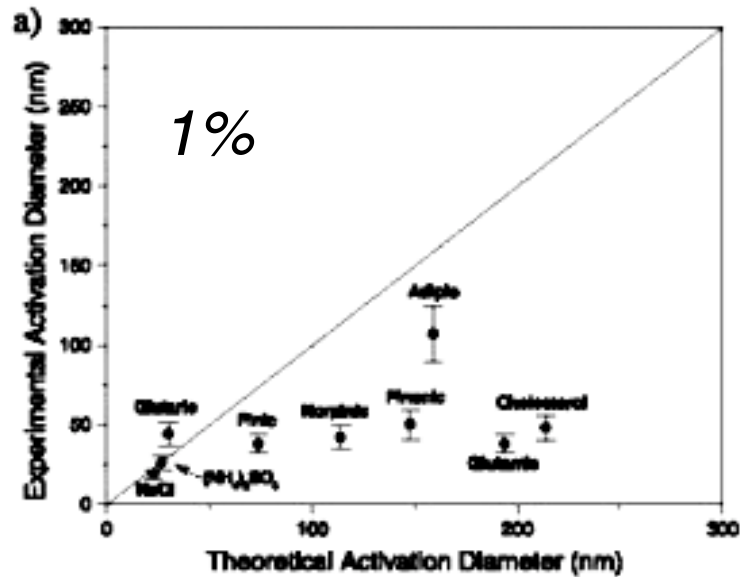
	Measured D_{50} , nm		Predicted			
			D_{K0} , nm		D^* , nm	
	$s - 0.3\%$	$s - 1\%$	$s - 0.3\%$	$s - 1\%$	$s - 0.3\%$	$s - 1\%$
Sodium chloride	48 ± 10	19 ± 3	51	23	51	23
Ammonium sulfate	66 ± 13	26 ± 4	61	27	61	27
Glutaric acid	89 ± 18	44 ± 7	66	30	66	30
Pinic acid	92 ± 18	38 ± 6	80	36	120	74
Adipic acid	175 ± 35	107 ± 18	90	41	368	159
Glutamic acid	75 ± 15	38 ± 6	93	42	541	194
Pinonic acid	114 ± 23	50 ± 9	94	42	426	148
Leucine	>200	200 ± 34	95	43	479	184
Norpinic acid	88 ± 18	42 ± 7	98	44	215	114
Myristic acid	>200	>200	105	47	>700	>200
Hexadecanol	>200	>200	137	62	>700	>200
Hexadecane	>200	>200	138	62	>700	>200
Palmitic acid	>200	>200	139	62	>700	>200
Stearic acid	>200	>200	144	65	>700	>200
Cholesterol	101 ± 20	48 ± 8	148	66	712	214

^a D_{50} , experimental activation diameter; D_{K0} , theoretical activation diameter according to Köhler theory at $T = 293$ K, not accounting for limited solubility; D^* , theoretical activation diameter according to equation (5); s , supersaturation. Error bars determined by standard deviations of multiple runs.

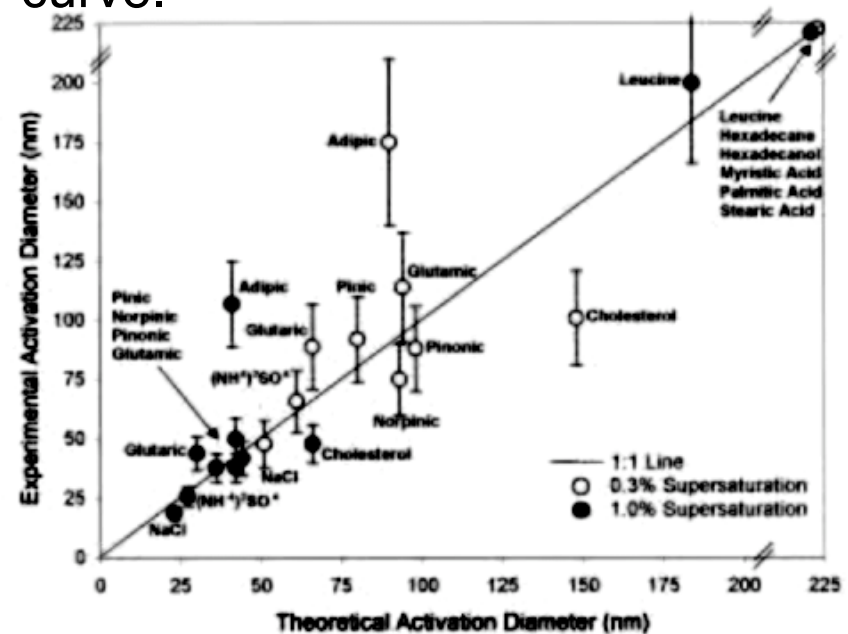
- NaCl and $(\text{NH}_4)_2(\text{SO}_4)$ are found to agree well with Köhler theory.

- Agreement begins to decrease as morphology and surfactant properties dominate solubility in activation efficiency.

- An insoluble particle that is “wetable” behaves as a pure water drop (Kelvin equation)? ie always unstable and will grow if R_c is achieved for a given supersaturation. (Eqn. 5)



- Theory overpredicts activation D.
- For species where solubility is the key factor, experiment agrees with Kohler and extended Kohler theory.
- For those assumed “wetable” agreement generally improves when allowed to follow the Kelvin curve.



Components of Kohler's equation.... (Simplified sort of)

• Kelvin's equation: $S = \exp\left(\frac{2M_{w-s}}{RT_{-s}D}\right)$ (surface tension)

• Raoult's equation: $P = x_{\text{solvent}} P_{\text{pure}}$ (solute effect on a flat surface)

• $x = n_w / (n_w + n_s)$

• $\Delta x = n_w / (n_w + v n_s)$ ('v' is the van't Hoff factor) too simple.

• $\Delta x = \exp(-vMM_-)$ or

• $= \exp[-(v_{-} m_s M_w / M_s) / ((4\pi a^3_{-s} / 3) - m_s)]$

• Kohler: $S = \exp\left[\left(\frac{2M_{w-s}}{RT_{-w}D}\right) - \frac{(v_{-} m_s M_w / M_s)}{((4\pi D^3_{-s} / 3) - m_s)}\right]$

(These equations are from Pruppacher and Klett - equation 5 is

Assumptions, simplifications, and other stuff...

- CCN used to measure number of drops activated was not able to resolve a size distribution for the activated drops.
- There appears to still be some flexibility on the best way to handle the solubility/activity of the solute in the theory
- The proposed modified Kohler equation (#5) appears to overpredict the activation diameter to the same degree that the original underpredicts the activation.
- Use of equation 6 is only supported by results for leucine.

Conclusions

- Insoluble species with contact angle of zero with water may be good CCN.
- Modified Kohler equation should only be used for these cases, however there is still a lot of variance between the species.