



EVAPORISATION: A NEW VAPOR PRESSURE MODEL WITH NEIGHBOUR EFFECTS

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I. Introduction

Vapor pressure of molecules is one of the most important single-molecule properties regulating SOA formation. As this property is not measured for most molecules, it has to be estimated. However, the vapor pressure of polyfunctional molecules is poorly characterized, as is clear from the large variation in vapor pressure estimation by different methods. We are currently developing EVAPORISATION, an estimation method needing only molecular structure as input, which will include local and non-local interactions between functional groups. We identify the different structural characteristics which impact on the vapor pressure. Here we consider carbonyls, alcohols, ethers and esters, for which a relatively large set of data is available.

II. Determining parameters for a vapor pressure model. Work method.

To determine relevant parameters for vapor pressure, we do not directly model vapor pressures but rather vapor pressure *ratios*. By comparing molecules that are identical except in one parameter, one gets the dependence on that parameter only. By minimizing σ_{STD}^2

$$\sigma_{STD}^2 = \frac{1}{n_T N - 1} \sum_{j=1}^{n_T} \sum_{i=1}^N (r_{exp,i}(T_j) - r_{mod,i}(T_j))^2 \quad (1)$$

$$r_{exp,i} = \log_{10} \frac{p_{exp,1,i}^0}{p_{exp,2,i}^0}, \quad r_{mod,i} = (q_{1,i} - q_{2,i}) \left[A + B \left(\frac{1}{298K} - \frac{1}{T} \right) \right] \quad (2)$$

where $q_{1,i}$, $q_{2,i}$ are the number of times this parameter occurs in molecule 1 and 2 respectively. The only exception is the dependence on carbon number, which is determined directly from vapor pressures.

III. Atom number and topology

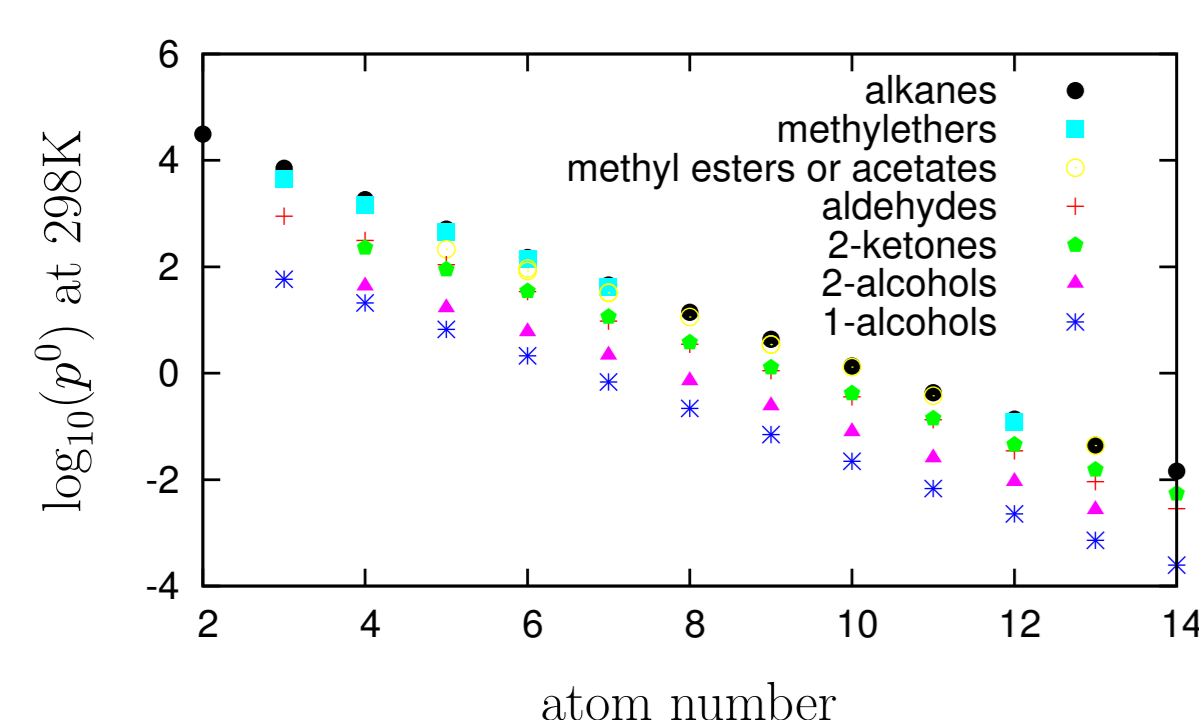


FIGURE 1: Evolution of $\log_{10}(p)$ with atom number for different types of linear zero- and monofunctional molecules.

TABLE 1: Contribution of carbon number and topology to the vapor pressure.

	A	B	N	molecule 1 + ex.	molecule 2 + ex.	p-value	σ_{STD}
Carbon number	-0.48n	254n	104				0.07
Branching at single bond	0.19b	-98b	122	branched, b > 0 2,2-dimethylpropanal (2)	unbranched, b = 0 pentanal	10 ⁻⁷	0.10
Branching at double bond	0.006b _d	-24b _d	15	branched, b _d > 0 2-methylpropene (1)	unbranched, b _d = 0 1-butene	0.89	0.14
Cyclicity	-0.18	50	9	cyclic, R = 1 methylcyclohexane	acyclic, R = 0 3-methylhexane	10 ⁻⁵	0.07
Topological index	0.19t	-99t	134	nonlinear α -pinene, (t = 4 - 2 = 2)	linear 1-decene, t = 0	10 ⁻⁷	0.09

$\log_{10}(p)$ varies linearly with carbon number for different molecule types. As ethers have about the same vapor pressure as the corresponding alkane, in-chain oxygen atoms can be counted as carbon atoms. In the same way, aldehydes and ketones can be grouped together.

Branching number b and ring number R are two main topological descriptors of a molecule. The branching number b is defined here by taking at each carbon atom the number of *single* carbon-carbon or carbon-in-chain-oxygen bonds exceeding 2, as we found that *branching at a double bond* b_d has no impact on vapor pressure.

As the dependence on branching and cyclicity is the same in size but with opposite sign, a single topological index is defined

$$t = b - R \quad (3)$$

This index also works well for more complicated structures, such as terpenes and bicyclohexyl. For example, bicyclohexyl with $t = b - R = 2 - 2 = 0$ has about the same vapor pressure as linear dodecane.

IV. Monofunctional molecules: local structure effects on functional groups

Groups on rings and near the end of chains (i.e. next to CH₃) lower the vapor pressure more. Interestingly, the effect is *quantitatively* the same for different functional groups.

TABLE 2: Impact of functional group position on contribution to vapor pressure.

	A	B	N	molecule 1 + ex.	molecule 2 + ex.	p-value	σ_{STD}
X on ring ^a	-0.59	251	9	cyclic cyclohexanone	acyclic 3-hexanone	4.10 ⁻⁸	0.06
CXCH ₃ ^b	-0.13	57	47	next to CH ₃ propylmethyl ether	not next to CH ₃ diethylether	10 ⁻⁷	0.06

a. X = =O, -OH. Only part of the effect can be explained by topology (see Table 1).
b. X = =O, -OH, -O-, -C(=O)O-, -OC(=O)-.

If a branching is placed next to an COH, this increases the vapor pressure. This is not the case for a carbonyl or ether.

TABLE 3: A molecule where a branching is located next to a functionality, is compared to the corresponding molecule where this is not the case. The total branching number of both molecules is the same.

	A	B	N	molecule 1 ex.	molecule 2 ex.	p-value	σ_{STD}
COC(C)	0.006q	-10q	4	methyl-sec.butyl ether	methylisobutylether	0.92	0.02
C(=O)C(C)	0.02q	-12q	10	2-methylpentanone	4-methylpentanone	0.19	0.09
COHC(C)	0.14q	-66q	12	2-methylcyclohexanol	4-methylcyclohexanol	4.10 ⁻⁴	0.11

Primary alcohols have a lower vapor pressure than secondary alcohols, which have in turn, *by the same factor*, a lower vapor pressure than tertiary alcohols. Hydroperoxides (-OOH) can be considered as equivalent to primary alcohols (-CH₂OH).

TABLE 4: Relations between primary, secondary, tertiary alcohols and hydroperoxides.

	A	B	N	molecule 1 ex.	molecule 2 ex.	p-value	σ_{STD}
OOH/CH ₂ OH	-0.07	-274	3	ethyl hydroperoxide	propanol	0.5	0.13
CH ₂ OH/CHOH ^a	-0.48	263	15	1-butanol	2-butanol	7.10 ⁻⁸	0.11
CHOH/COH	-0.44	280	8	3-methyl- -2-butanol	2-methyl- -2-butanol	10 ⁻⁴ , 0.01 ^b	0.06

a. OH next to CH₃. See Table 2.
b. q = branching difference next to alcohol. See Table 3.

A double bond conjugated with a carbonyl *lowers* the vapor pressure, while combined with an alcohol it *increases* the vapor pressure. No impact for esters or nonconjugated carbonyls. Relatively large errors!

TABLE 5: Effect of double bond on group contribution.

	A	B	N	molecule 1 ex.	molecule 2 ex.	p-value	σ_{STD}
C=CC=O	-0.25	134	14	2-propenal	propanal	0.002	0.25
C=C+C(=O)(nc)	-0.07	-27	8	5-hexenal	hexanal	0.39	0.22
C=C+COH	0.20	-396	12	3-buten-1-ol	butanol	0.006	0.22
C=C+C(=O)O	-0.05	-3	10	ethylpropenoate	ethylpropanoate	0.005	0.07

V. Bifunctional molecules

$\log_{10}(p^0)$ varies nonlinearly with the number of functional groups. For bifunctional molecules, when the two functional groups are far apart, $\log_{10}(p^0)$ is lower than would be expected from taking twice the group contribution as determined for monofunctional molecules. This is a nonlocal, overall (O) effect. Proximity of functional groups will however increase the vapor pressure due to local (L) intramolecular interactions. To determine these interactions, we model

$$\log_{10}(p_b^0) - \log_{10}(p_{m1}^0) - \log_{10}(p_{m2}^0) + \log_{10}(p_z^0) = O + L_1(\text{if neighbours}) + L_2(\text{if second neighbours}) \quad (4)$$

TABLE 6: Interaction factors of functional groups.

	term	A	B	N	σ_{STD}
diols	O	-0.84	-54	29	0.21
	L ₁	0.84	-413		
	L ₂	0.39	-269		
dicarbonyls	O	-0.32	159	15	0.14
	L ₁	1.53	-593		
	L ₂	0.63	-350		
diesters	O	-0.54	71	9	0.27
	L ₁	0.86	-374		
hydroxyketones	O	-0.22	-197	11	0.17
	L ₂	0.42	-479		

with p_b^0 the vapor pressure of the bifunctional molecule, p_{m1}^0 , p_{m2}^0 the vapor pressures of the corresponding monofunctional molecules, and p_z^0 the one of the corresponding zerofunctional molecule. Example: for the bifunctional molecule 1,2-pentanediol, m1=1-pentanol, m2=2-pentanol, z=pentane. Contributing factors are O, L₁.

The interaction factors are in all cases important and vary for different molecules. Approximately $L_2 = L_1/2$.

VI. Polyfunctional molecules

How will the vapor pressure scale with number of functional groups for polyfunctional molecules? This question is difficult to address as room-temperature data on molecules with more than 2 functional groups is scant and relatively imprecise. An important clue is found by plotting $\log_{10}(p^0)$ vs. group number for linear polyols CH₂OH(CHOH)_{n-2}CH₂OH at high temperature (above $n = 3$ no data is available at room temperature).

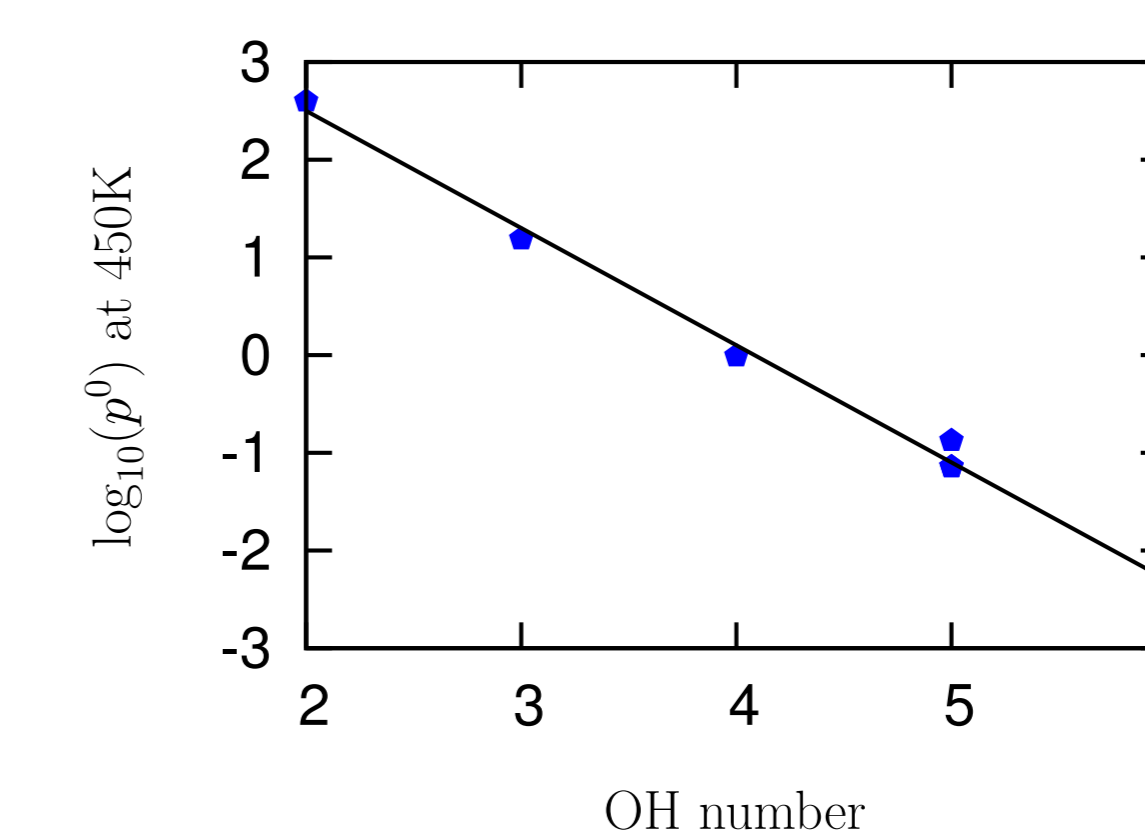


FIGURE 2: Evolution of $\log_{10}(p)$ with OH number for linear polyols.

Hence $\log_{10}(p^0)$ scales linearly with the number of neighbouring COH groups. If we assume this is also true at room temperature and for other groups, this gives an important constraint on the formulation of the vapor pressure model.

VII. Conclusions

- Local structure effects can have an important impact on functional group contribution.
- For bifunctional molecules, one cannot simply sum up the group contributions determined for monofunctional molecules. The vapor pressure will depend on the *combination* and *relative position* of both functional groups.
- For polyfunctional molecules with neighbouring functional groups, there is an indication that $\log_{10}(p^0)$ scales linearly with group number.