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Technical Note: Estimating fusion properties for polyacids

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Estimating fusion properties for polyacids

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Abstract

Organic aerosol (OA) components are generally assumed to be liquid-like. Hence, to describe the partitioning of these components, the liquid vapor pressure of these components is desired. Polyacids and functionalized polyacids can be a significant part of OA. But often, measurements are available only for solid state vapor pressure, which can differ by orders of magnitude from their liquid counterparts. To convert such a sublimation pressure to a subcooled liquid vapor pressure, fusion properties (two out of these three quantities: fusion enthalpy, fusion entropy, fusion temperature) are required. Unfortunately, experimental knowledge of fusion properties is sometimes missing in part or totally, hence an estimation method is required. Several fusion data estimation methods are tested here against experimental data of polyacids. Next, we develop a simple estimation method, specifically for this kind of compounds, reducing significantly the estimation error.

1 Introduction

Diacids can be a significant part of OA, according to both field measurements and smog chamber experiments (Limbeck et al., 2001; Baboukas et al., 2000; Claeys et al., 2007; Yu et al., 1999). Due to the multicomponent nature of OA it is often glassy or liquid-like at ambient temperature even if the individual components are crystalline solids when in pure state, as was recently demonstrated for a mixture of diacids (Cappa et al., 2008b). To describe the partitioning of a compound to the aerosol, its liquid vapor pressure is required. Vapor pressures of polyacids have been measured since decades (Bradley and Cotson, 1953; Arshadi, 1974) but recently work in this area has intensified, with several publications in only this year (Booth et al., 2010, 2011; Frosch et al., 2010; Soonsin et al., 2010; Pope et al., 2010).

Unfortunately, pure diacids are solid at ambient temperature. To obtain the liquid vapor pressure, one could extrapolate from measurements above the melting point T_{fus},

but as T_{fus} can be a few hundred Kelvin above the temperature of interest, this approach is very prone to error. Some groups have measured the vapor pressure of the liquid diacid in a mixture with water (Zardini et al., 2006; Riipinen et al., 2007; Koponen et al., 2007; Pope et al., 2010; Soonsin et al., 2010). In that case, also the activity coefficient is needed in order to determine the vapor pressure of the pure diacid, which can be calculated using empirical methods (Peng et al., 2001; Hansen et al., 1991). Other groups have measured the solid vapor pressure (Cappa et al., 2007, 2008a; Booth et al., 2010, 2011; Frosch et al., 2010; Ribeiro da Silva et al., 2000, 2001; Salo et al., 2010; Bilde and Pandis, 2001; Bilde et al., 2003; Soonsin et al., 2010). However, there can be orders of magnitude difference between measurements of different groups on the same compound (e.g. for sebacic acid, 3 orders of magnitude between Cappa et al., 2007 and Salo et al., 2010), way above the reported experimental errors (typically 30–50%). It has been speculated that this might be due to the experimental technique employed (Cappa et al., 2007; Pope et al., 2010) or to the physical nature of the diacids (Zardini et al., 2006; Soonsin et al., 2010; Salo et al., 2010) (presence of defects; partially or completely liquid/amorphous character). Soonsin et al. (2010) have measured supercooled liquid vapor pressures with only a very small water content, and vapor pressures of the saturated solution, which allows the derivation of the vapor pressure of the pure liquid and solid, respectively.

Even if a given experimental sublimation pressure can be considered accurate, one still needs fusion data to obtain a subcooled liquid vapor pressure (Prausnitz et al., 1999):

$$\ln\left(\frac{p_l^0}{p_s^0}\right) = \frac{\Delta S_{fus}}{R}\left(\frac{T_{fus}}{T} - 1\right) - \frac{\Delta C_{p,sl}}{R}\left(\frac{T_{fus}}{T} - 1 - \ln\left(\frac{T_{fus}}{T}\right)\right) \quad (1)$$

with p_l^0, p_s^0 the vapor pressures of the liquid and solid state, respectively, R the ideal gas constant, ΔS_{fus} the entropy of fusion and $\Delta C_{p,sl}$ the difference between solid and liquid heat capacity. The fusion temperature, enthalpy of fusion ΔH_{fus} and entropy of fusion are related by

$$\Delta H_{\text{fus}} = T_{\text{fus}} \Delta S_{\text{fus}} \tag{2}$$

Although the second term in Eq. (1) can be significant for large values of the difference $T_{\text{fus}} - T$, it will generally be much less important than the first term. Moreover, as $\Delta C_{p,\text{sl}}$ is frequently unavailable experimentally, it is often estimated from ΔS_{fus} (e.g., Booth et al., 2010). Therefore, the availability of measured or estimated fusion data appears critical. However, it occurs often that fusion data is unavailable, or only the fusion temperature is known (Ribeiro da Silva et al., 2000; Monster et al., 2004; Frosch et al., 2010). General estimation methods for T_{fus}, ΔH_{fus} (Joback and Reid, 1987; Marrero and Gani, 2001; Zhao and Yalkowsky, 1999) or ΔS_{fus} (Myrdal and Yalkowsky, 1997; Jain et al., 2004a) give significant errors for diacids, as we will show below. Therefore, a new simple estimation method is developed specifically for this class of compounds.

2 Literature data

In Table 1 we present experimental fusion data for polyacids and keto or hydroxy polyacids, taken from Roux et al. (2005); Booth et al. (2011, 2010). In case also solid-solid transitions were present, always the sum over all fusion data was taken:

$$\Delta H_{\text{fus,tot}} = \sum_i \Delta H_{\text{trans},i}, \text{STD} = 1.7\,\text{kJmol} \tag{3}$$

$$\Delta S_{\text{fus,tot}} = \sum_i \Delta S_{\text{trans},i}, \text{STD} = 2.8\,\text{J(molK)} \tag{4}$$

$$T_{\text{fus,tot}} = \frac{\Delta H_{\text{fus,tot}}}{\Delta S_{\text{fus,tot}}}, \text{STD} = 4.1\,\text{K} \tag{5}$$

The standard deviations (STD) were obtained by comparing overlapping data for linear diacids from Cingolani and Berchiesi (1974); Hansen and Beyer (2004); Booth et al. (2010); Roux et al. (2005). At 298.15 K, these experimental errors correspond to an uncertainty of 0.36 on $\log_{10} \frac{p_l^0}{p_s^0}$ or a factor of 2.3 on $\frac{p_l^0}{p_s^0}$. Also the derived property

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$$\omega = \frac{\Delta S_{\text{fus}}}{R \ln 10} \left(\frac{T_{\text{fus}}}{T} - 1 \right) \tag{6}$$

$$= \frac{\Delta H_{\text{fus}}}{R \ln 10} \left(\frac{1}{T} - \frac{1}{T_{\text{fus}}} \right) \tag{7}$$

evaluated at 298.15 K is given in Table 1. Roughly speaking and excluding oxalic acid, ω is about 1 for odd-numbered linear diacids and 2 for even-numbered linear diacids.

For oxalic acid, T_{fus} reported by Booth et al. (2010) conflicts with the transition data reported by Linstrom and Mallard and Thalladi et al. (2000). It is possible that Booth et al. (2010) found a solid-solid transition point rather than a fusion point (Booth 2010, personal communication). Furthermore, Soonsin et al. (2010) have measured the vapor pressure of both solid and supercooled liquid oxalic acid, and found two orders of magnitude difference. This would result in a ω of about 2, much more than the value of 0.12 calculated from the data of Booth et al. (2010), but corresponding satisfactorily with those of the other even-numbered linear diacids. However, interpretation of experimental data is hampered due to uncertainty regarding the precise structure of the solid oxalic acid (Soonsin et al., 2010). Therefore, we exclude oxalic acid in our comparison analysis of experimental with modeled data.

For some diacids, only T_{fus} is reported, but not ΔH_{fus} or ΔS_{fus}. Table 2 presents melting points taken from Ribeiro da Silva et al. (2000, 2001); Monster et al. (2004); Frosch et al. (2010); Bilde and Pandis (2001).

3   Testing existing estimation methods

The methods considered are presented in Table 3. Both the methods of Joback and Reid (1987) (JR) and Marrero and Gani (2001) (MG) are group contribution methods providing both T_{fus} (JR(T), MG(T)) and ΔH_{fus} (JR(H), MG(H)). While the former is relatively simple, the second is a detailed method involving first, second and third order groups. The method of Myrdal and Yalkowsky (1997) (MY) and the more recent variant

of Jain et al. (2004a) (JYY) estimate ΔS_{fus} from the number of torsional bonds and rotational symmetry of the molecule. Although the method of Zhao and Yalkowsky (1999) (ZY), and its more recent variant (Jain et al., 2004b) (JYY), are formally ΔH_{fus} group contribution methods, they are rather T_{fus} estimating methods, as the group contributions are fitted to experimental fusion points, with the entropy of fusion fixed by the MY method. In Table 4, the bias, the mean absolute error MAE and the standard deviation STD are presented.

$$\text{bias} = \frac{1}{N} \sum_{i=1}^{N} \left(f_i^{est} - f_i^{exp} \right) \tag{8}$$

$$\text{MAE} = \frac{1}{N} \sum_{i=1}^{N} \left| f_i^{est} - f_i^{exp} \right| \tag{9}$$

$$\text{STD} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} \left(f_i^{est} - f_i^{exp} \right)^2} \tag{10}$$

The JR(T) method gives a very large error on the fusion temperature. This can be ascribed to the fact that this method considers T_{fus} as a sum of group contributions, and this gives large overestimations for larger molecules (up to 275 K for citric acid). Clearly, the JR(T) method is not suitable to estimate fusion point of polyacids. We note that a similar failure occurs for the estimation of boiling points by the JR method (Stein and Brown, 1994). The ZY(T) and MG(T) methods perform best for fusion temperature, while the more recent version of ZY(T), JYY(T), actually performs worse.

Notwithstanding its high detail, the MG(H) method performs worse than the JR(H) method in estimating fusion enthalpy, and has a relatively high bias. For fusion entropy estimation, the MY(S) and JYY(S) method have a similar precision, but the last one (Jain et al., 2004a) has the highest bias.

For the calculation of ω, it is possible that no experimental fusion data are available and hence the estimation of two fusion properties is necessary. Combinations with JR(T) give a large positive bias for ω due to the large overestimation of T_{fus}. This method will not be considered further. The combinations MG(T) + MY and MG(T) + JR(H) perform the best in terms of low bias and STD, with the first having the smallest bias. Better estimation is possible when one fusion property is already known. This is typically the fusion temperature. Best results are obtained when employing MY(S) in combination with the experimental fusion temperature. Note that the more recent version of this method, JYY(S), performs worse.

Even in the best case, the MAE and STD of ω remains quite substantial. The methods are general purpose and are apparently not well suited to polyacids. Therefore, we developed a simple specialized method, based on the experimental data from Table 1.

4 Development of a new estimation method

As is well known, the fusion data of linear diacids follow an even-odd alternation (Roux et al., 2005). Using the data from Table 1, excluding oxalic acid, one obtains

$$\#CH_2 \quad \text{odd}:$$

$$\frac{\Delta H_{\text{fus}}}{\text{Jmol}^{-1}} = 16\,464 + 1909 \cdot \#CH_2, STD = 6 \times 10^2 \tag{11}$$

$$\frac{\Delta S_{\text{fus}}}{\text{JK}^{-1}\text{mol}^{-1}} = 40.91 + 5.81 \cdot \#CH_2, STD = 1.1 \tag{12}$$

$$\#CH_2 \quad \text{even}:$$

$$\frac{\Delta H_{\text{fus}}}{\text{Jmol}^{-1}} = 25\,704 + 2657 \cdot \#CH_2, STD = 3 \times 10^2 \tag{13}$$

$$\frac{\Delta S_{\text{fus}}}{\text{JK}^{-1}\text{mol}^{-1}} = 52.45 + 8.11 \cdot \#CH_2, STD = 1.0 \tag{14}$$

where #CH$_2$ denotes the number of methylene groups. Using correlation Eq. (13), a T_{fus} of 490 K would be predicted for oxalic acid, even higher than the fusion point reported by Linstrom and Mallard,Thalladi et al. (2000). This gives further argument that the fusion point reported by Booth et al. (2010) could be a solid-solid transition point.

No such clear correlation of fusion enthalpy or entropy with carbon number exists for the nonlinear polyacids. For example, for the cyclic diacids, the diacids with the highest carbon number have the lowest ΔH_{fus} and ΔS_{fus}, while the other three have very similar values. Instead, we use as independent variable the effective torsional bond number τ (Dannenfelser and Yalkowsky, 1996). Also the number of nonacid functional groups (keto and hydroxy groups), and the identification of the molecule as a linear even-numbered chain, are taken as independent variables. Our estimation method has then the following form

$$\Delta H_{fus}^{est} = a_1 + a_2\tau + a_3 i_{even} + a_4(n_{OH} + n_{CO}) \qquad (15)$$

$$\Delta S_{fus}^{est} = a_1 + a_2\tau + a_3 i_{even} + a_4(n_{OH} + n_{CO}) \qquad (16)$$

with $i_{even} = 1$ if the molecule is a linear even-numbered chain and 0 otherwise, and n_{OH} and n_{CO} the number of hydroxy and keto groups, respectively. In Table 5 the optimal parameters, obtained by linear regression, are given, as well as the STD and MAE, and the prediction sum of squares (PRESS). This last statistical diagnostic is based on the leave-one-out principle and is calculated by

$$\text{PRESS} = \sqrt{\frac{1}{N-1} \sum_i^N \left(f_{(i)}^{est} - f_i^{exp} \right)^2} \qquad (17)$$

where f_i^{exp} is an experimental measurement and $f_{(i)}^{est}$ a model calculation, using parameters fitted to all experimental data *except f_i^{exp}*. In this way, PRESS is a measure of the predictive power of the model, while MAE and STD merely show how well the model can fit the observations. It is always higher than the STD. Cyclicity as an extra independent variable was tested but this did not improve the PRESS.

Comparing the PRESS of Table 5 with the STD of Table 3, it is clear that this new model performs much better than the methods considered in Sect. 3. This should of course not be a surprise, as these methods have a much wider scope, and most experimental data used to develop this model are more recent than these methods.

5 If $T_\mathrm{fus}^\mathrm{exp}$ is available, this leads to an important improvement of the estimation of ω. It makes thereby not much difference whether ΔS_fus or ΔH_fus is used in conjunction with $T_\mathrm{fus}^\mathrm{exp}$.

When testing our method on the molecules of Table 2, an STD of 31 K is obtained, relatively close to the PRESS obtained from the data of Table 1. This confirms the

10 robustness of our model, as the data of Table 2 was in no way included in the development of our method.

5 Predicting fusion data for some compounds

In Table 6 we present the fusion data estimations for the compounds in Table 2. The lowest ω is predicted for pinic acid, and the highest for 4-oxo pimelic acid.

15 ## 6 Conclusions

To derive subcooled liquid vapor pressure from solid vapor pressure, knowledge of the fusion properties is necessary. Several fusion property estimation methods are tested for polyacids, having possibly keto- or hydroxy groups. Best results are obtained by combining the experimental fusion temperature with the method of Myrdal

20 and Yalkowsky (1997), and estimating the fusion temperature with Marrero and Gani (2001) if it is not available. We have also developed a simple method to estimate the fusion properties for this kind of compounds, with a smaller error compared to the other methods.

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Table 1. Experimental fusion data of several polyacids.

Acid	$\frac{T_{fus}}{K}$	$\frac{\Delta H_{fus}}{kJ\,mol^{-1}}$	$\frac{\Delta S_{fus}}{J\,K^{-1}\,mol^{-1}}$	ω
Linear diacids even carbon number				
Oxalic	370[a*]	3.424[a*]	9.25[a*]	0.12
Succinic	458[a]	31.259[a]	68.25	1.91
Adipic	423[a]	35.891[a]	84.85	1.86
Suberic	407.94[b]	41.8[b]	102.47	1.97
Sebacic	403.59[b]	47.0[b]	116.46	2.15
Linear diacids odd carbon number				
Malonic	406[a]	18.739[a]	46.16	0.87
Glutaric	369[a]	22.043[a]	59.74	0.74
Pimelic	366.23[b]	25.2[b]	68.81	0.82
Azelaic	371.56[b]	30.41[b]	81.84	1.05
Branched noncyclic diacids				
Methyl malonic	403[a]	30.746[a]	76.29	1.40
Methyl succinic	383[a]	9.980[a]	26.06	0.39
2-methyl glutaric	349[a]	30.259[a]	86.70	0.77
3-methyl glutaric	356[a]	27.351[a]	76.83	0.78
Cyclic diacids				
1,1-cyclopropane	413[c]	17.4[c]	42.13	0.85
1,1-cyclobutane	433.2[c]	16.8[c]	38.78	0.92
1,2-cyclopentane	428.6[c]	19.1[c]	44.56	1.02
1,3-cyclohexane	439.0[c]	12.9[c]	29.39	0.73
Keto and hydroxy di- and triacids				
2-oxo succinic	437[a]	50.382[a]	115.29	2.80
2-oxo glutaric	386[a]	34.693[a]	89.88	1.38
3-oxo glutaric	397[a]	45.895[a]	115.61	2.00
2-hydroxy malonic	428[a]	30.619[a]	71.54	1.63
2-methyl,2-hydroxy succ.	379[a]	35.697[a]	94.19	1.33
2-hydroxy succinic	403[a]	29.031[a]	72.04	1.32
2,3-dihydroxy succinic	480[a]	62.723[a]	130.67	4.16
Citric acid	427[a]	43.455[a]	101.77	2.30

[a] Booth et al. (2010)
[b] Roux et al. (2005)
[c] Booth et al. (2011)
[*] For oxalic acid, Linstrom and Mallard and Thalladi et al. (2000) report a solid-solid transition point at 393.2 K and a fusion point at 463–464 K, which are both significantly higher than the fusion point reported by Booth et al. (2010).

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Table 2. Melting points of diacids, where no fusion enthalpy or entropy is available.

Acid	T_{fus}/K	Source
Dimethyl malonic	464.6	Ribeiro da Silva et al. (2000)
Ethyl malonic	385.8	
Butyl malonic	377.2	
2,2-dimethyl glutaric	356.6	Ribeiro da Silva et al. (2001)
2,2-dimethyl succinic	372	Monster et al. (2004)
3,3-dimethyl glutaric	377	
3-methyl adipic	367	
Pinic	343	Bilde and Pandis (2001)
4-oxo pimelic	416	Frosch et al. (2010)

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Table 3. Fusion property estimation methods considered in this work.

Notation	Source	Form[a]
JR(T)	Joback and Reid (1987)	$T_{\text{fus}}^{\text{JR}} = \sum_i n_i g_i$
JR(H)	Joback and Reid (1987)	$\Delta H_{\text{fus}}^{\text{JR}} = \sum_i n_i g_i$
MG(T)	Marrero and Gani (2001)	$e^{T_{\text{fus}}^{\text{MG}}} = \sum_i n_i g_i$
MG(H)	Marrero and Gani (2001)	$\Delta H_{\text{fus}}^{\text{MG}} = \sum_i n_i g_i$
MY(S)	Myrdal and Yalkowsky (1997)	$\Delta S_{\text{fus}}^{\text{MY}} = g_1 + g_2 \ln\sigma + g_3 \tau$[b]
JYY(S)	Jain et al. (2004a)	$\Delta S_{\text{fus}}^{\text{J}}$: as $\Delta S_{\text{fus}}^{\text{MY}}$
ZY(T)	Zhao and Yalkowsky (1999)	$T_{\text{fus}}^{\text{ZY}} = \frac{\sum_i n_i g_i}{\Delta S_{\text{fus}}^{\text{MY}}}$
JYY(T)	Jain et al. (2004b)	$T_{\text{fus}}^{\text{J}} = \frac{\sum_i n_i g_i}{\Delta S_{\text{fus}}^{\text{J}}}$

[a] g_i represent parameter values, n_i the frequency of group i.
[b] σ is the rotational symmetry number (Dannenfelser and Yalkowsky, 1996) and τ the effective torsional bond number (Myrdal et al., 1996).

Table 4. Performance of different estimation methods on the experimental fusion data of Table 1.

	Method	Bias	MAE	STD
T_{fus}/K^a	JR(T)	95, 107	96, 107	111, 125
	ZY(T)	13, 17	35, 29	49, 46
	JYY(T)	16, 4	43, 37	62, 61
	MG(T)	−1.2, 7.3	26, 36	32, 56
$\dfrac{\Delta H_{fus}}{kJ\,mol^{-1}}$	JR(H)	−1.7	9.0	12
	MG(H)	−6.8	11	13
$\dfrac{\Delta S_{fus}}{J K^{-1} mol^{-1}}$	MY(S)	4.4	20.9	26.3
	JYY(S)	−7.0	20.3	26.4
ϖ, fully estimated	JR(T + H)	0.63	0.89	1.05
	ZY(T) + MY(S)	0.15	0.68	0.82
	JYY(T + S)	−0.03	0.69	0.95
	MG(T + H)	−0.33	0.49	0.78
	JR(H) + MY(S)	−0.53	0.80	1.08
	MG(H) + MY(S)	−1.42	1.54	1.84
	MG(T) + JR(H)	−0.11	0.50	0.75
	MG(T) + MY(S)	0.05	0.53	0.75
ϖ, with T_{fus}^{exp}	JR(H)	−0.12	0.45	0.67
	MG(H)	−0.33	0.51	0.72
	MY(S)	0.03	0.41	0.57
	JYY(S)	−0.18	0.41	0.62

[a] The second value is obtained by testing on the data of Table 2.

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Table 5. Parameters and statistic diagnostics of the new estimation method.

	a_1	a_2	a_3	a_4	MAE	STD	PRESS
$\dfrac{\Delta H_{\text{fus}}^{\text{est}}}{\text{Jmol}^{-1}}$	16 388	2213	11 533	18 698	4.2×10^3	5.8×10^3	6.5×10^3
$\dfrac{\Delta S_{\text{fus}}^{\text{est}}}{\text{JK}^{-1}\text{mol}^{-1}}$	40.40	7.16	16.81	38.37	10.00	14.00	16.00
T_{fus}/K, from $\Delta H_{\text{fus}}^{\text{est}}$, $\Delta S_{\text{fus}}^{\text{est}}$					18.00	23.00	27.00
ω, from $\Delta H_{\text{fus}}^{\text{est}}$, $\Delta S_{\text{fus}}^{\text{est}}$					0.28	0.40	0.50
ω, from $\Delta H_{\text{fus}}^{\text{est}}$, $T_{\text{fus}}^{\text{exp}}$					0.19	0.27	0.31
ω, from $\Delta S_{\text{fus}}^{\text{est}}$, $T_{\text{fus}}^{\text{exp}}$					0.17	0.25	0.28

Table 6. Estimated ΔH_{fus}, ΔS_{fus} and ω for the compounds of Table 2.

Acid	$\dfrac{\Delta H_{\text{fus}}^{\text{est}}}{\text{Jmol}^{-1}}$	$\dfrac{\Delta S_{\text{fus}}^{\text{est}}}{\text{JK}^{-1}\text{mol}^{-1}}$	ω, from $\Delta S_{\text{fus}}^{\text{est}}, T_{\text{fus}}^{\text{exp}}$
Dimethyl malonic	18 601	47.56	1.39
Ethyl malonic	20 815	54.72	0.84
2,2-dimethyl succinic	20 815	54.72	0.71
3-methyl adipic	25 241	69.03	0.83
2,2-dimethyl glutaric	23 028	61.87	0.63
3,3-dimethyl glutaric	23 028	61.87	0.85
Butyl malonic	25 241	69.03	0.96
Pinic	19 708	51.14	0.40
4-oxo pimelic	45 046	110.98	2.29