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Ideal Solubility of a Solid Solute: Effect of Heat Capacity Assumptions

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The ideal solubility of a solid solute is given by

$$\log X = -\frac{\Delta S_f}{2.3\,R}\left(\frac{T_m - T}{T}\right) + \frac{\Delta C_p}{2.3\,R}\left[\left(\frac{T_m - T}{T}\right) - \ln\left(\frac{T_m}{T}\right)\right] \tag{1}$$

Of all the physicochemical properties required to calculate the ideal solubility of a solid solute, heat capacity change on melting (ΔC_p) is the most difficult to measure experimentally. Very few data are available for this parameter in the literature.

In order to eliminate the ΔC_p term, Eq. (1) above has been simplified, using two assumptions.

Assumption 1. $\Delta C_p \simeq 0$, which results in Eq. (1) simplifying to

$$\log X = -\frac{\Delta S_f}{2.3\,R}\left(\frac{T_m - T}{T}\right) \tag{2}$$

Assumption 2. $\Delta C_p \simeq \Delta S_f$, which results in Eq. (1) simplifying to

$$\log X = -\frac{\Delta S_f}{2.3\,R}\ln\,(T_m/T) \tag{3}$$

Equation (2) has been used by several authors to calculate the ideal solubility of a solid solute (1–6). Equation (3) has been suggested to be a better approximation by some other workers (7–9). Mishra and Yalkowsky (10) have tested the suitability of both the assumptions and shown that Eq. (2) gives a better fit to the solubility data for a set of polycyclic aromatic hydrocarbons in benzene [data of McLaughlin and Zainal (11)]. Recently Neau and Flynn (12) measured some heat capacity data of *n*-alkyl *p*-aminobenzoates (Table I). From their data on the *p*-aminobenzoates and their compilation of other data from the literature, it is clear that the heat capacity change on melting is closer to the entropy of fusion than to zero for most of the molecules. This would justify the assumption of $\Delta C_p \simeq \Delta S_f$, which leads to Eq. (3) for ideal solubility.

This paper attempts to reconcile the apparent discrepancy and find a suitable ideal solubility equation. We have used the data compiled by Neau and Flynn (12) to calculate the ideal solubility at 25°C using the experimental entropy and heat capacity from Eqs. (1)–(3), respectively. Table II gives the calculated ideal solubilities from Eqs. (1)–(3) using measured values of entropy of fusion and heat capacity change on melting. The table also gives calculations using Walden's rule for entropy of fusion. Table III gives the average absolute errors involved in estimating ideal solubilities using different assumptions.

In spite of the data suggesting that $\Delta C_p \neq 0$, we found that the assumption that $\Delta C_p \simeq 0$ gives a lower average difference in ideal solubility [ideal solubility from Eq. (1) minus ideal solubility from the simplified Eq. (2) or (3)] than the assumption that $\Delta C_p \simeq \Delta S_f$.

This result is due to the fact that those compounds for which the differential heat capacity approaches the entropy of fusion are the ones with lower melting temperatures, such that the term $[(T_m - T)/T - \ln\,(T_m/T)]$ approaches zero. For higher-melting compounds, the differential heat capacity approaches or equals zero. In either case the effect of the heat capacity term is negligible, suggesting that even though it might appear that the second approximation is better, the

Table I. Physicochemical Properties of the Compounds Required to Calculate the Ideal Solubility

Compound	T_m (K)	ΔS_f (eu)[a]	ΔC_p (eu)[a]
Methyl *p*-aminobenzoate	385.2	13.99	11.65
Ethyl *p*-aminobenzoate	362.9	14.66	11.91
Propyl *p*-aminobenzoate	346.6	14.17	7.13
Butyl *p*-aminobenzoate	331.1	14.77	8.15
Pentyl *p*-aminobenzoate	325.5	17.57	12.34
Hexyl *p*-aminobenzoate	334.2	23.72	15.18
Nonyl *p*-aminobenzoate	343.4	30.84	12.84
Naphthalene	353.4	12.83	2.31
Anthracene	488.9	14.35	1.48
Acenaphthene	366.6	13.99	1.05
Phenanthrene	372.4	10.57	3.78
2-Methylnaphthalene	307.7	9.42	5.34
Biphenyl	342.2	12.99	9.43
Triphenylmethane	365.3	14.36	12.62
Dibenzothiophene	371.0	13.91	8.76
Fluorene	387.9	12.06	0.04

[a] Entrophy unit (eu), cal/deg · mol.

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Table II. Ideal Solubilities at 25 K Calculated from Different Assumptions

		log X			
		Eq. (2)	Eq. (3)	Eq. (2)	Eq. (3)
Compound	Full	ΔS = observed		ΔS = 13.5	
Methyl *p*-aminobenzoate	−0.806	−0.898	−0.787	−0.872	−0.760
Ethyl *p*-aminobenzoate	−0.646	−0.700	−0.633	−0.649	−0.583
Propyl *p*-aminobenzoate	−0.488	−0.507	−0.469	−0.486	−0.447
Butyl *p*-aminobenzoate	−0.350	−0.360	−0.341	−0.331	−0.312
Pentyl *p*-aminobenzoate	−0.345	−0.356	−0.340	−0.275	−0.261
Hexyl *p*-aminobenzoate	−0.609	−0.632	−0.596	−0.362	−0.339
Nonyl *p*-aminobenzoate	−1.001	−1.030	−0.959	−0.454	−0.420
Naphthalene	−0.515	−0.523	−0.480	−0.554	−0.505
Anthracene	−1.969	−2.016	−1.558	−1.909	−1.466
Acenaphthene	−0.701	−0.706	−0.636	−0.686	−0.613
Phenanthrene	−0.557	−0.579	−0.517	−0.744	−0.660
2-Methylnaphthalene	−0.067	−0.067	−0.066	−0.097	−0.095
Biphenyl	−0.402	−0.423	−0.394	−0.442	−0.410
Triphenylmethane	−0.650	−0.711	−0.641	−0.673	−0.603
Dibenzothiophene	−0.698	−0.747	−0.668	−0.730	−0.649
Fluorene	−0.798	−0.798	−0.697	−0.899	−0.781

first approximation gives numerically lower differences from the full Eq. (1).

The error involved is 0.03 log unit, which corresponds to a factor of 1.07 for ideal solubility calculated using Eq. (2). The average error for ideal solubility calculated from Eq. (3) is 0.048 log unit (factor of 1.117). It thus appears that unless there are compelling reasons to do otherwise, the choice among Eqs. (1), (2), or (3) should be based upon convenience and ease of use, rather than on the presumed theoretical superiority of a particular approximation.

Table III. Average Absolute Errors in Estimating Ideal Solubilities Using Different Assumptions

Model	Average absolute error	Factor[a]
$\log X(1) - \log X(2)$ ($\Delta C_p \simeq 0$)	0.030	1.072
$\log X(1) - \log X(3)$ ($\Delta C_p \simeq \Delta S_f$)	0.048	1.117
$\log X(1) - \log X(2)$ ($\Delta C_p \simeq 0$; $\Delta S_f = 13.5$ eu)[b]	0.092	1.236
$\log X(1) - \log X(3)$ ($\Delta C_p \simeq \Delta S_f$; $\Delta S_f = 13.5$ eu)[b]	0.130	1.349

[a] The factor represents the ratio of the ideal mole fractional solubility (calculated using measured differential heat capacity) and the ideal mole fractional solubility calculated using different assumptions.

[b] For long-chain compounds with a chain length greater than 5 carbons, the entropy of fusion is calculated using the following equation: $\Delta S_f = 13.5 + 2.5\,(n - 5)$, where n is the number of carbons in the long-chain compound.

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