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A LINEAR ENTROPY RELATIONSHIP FOR FUSION OF *n*-ALKYL CHAINS *

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ABSTRACT

This paper presents a new plotting technique (the *SnT* plot) which allows one to estimate the entropy of fusion or transition of homologous long-chain *n*-alkyl derivatives given the temperature of fusion or solid–solid phase transition.

INTRODUCTION

A number of the physical properties of homologous series of *n*-alkyl derivatives exhibit a linear relationship with respect to the length of the hydrocarbon chain [1–3]. The generation of empirical equations to describe and estimate thermodynamic quantities of homologous series of hydrocarbon derivatives is a common practice. A number of plotting techniques are used but the most popular method is to plot the thermodynamic quantity (or its reciprocal) against the number of carbons in the chain. An incremental quantity per methylene group results, providing a method of estimating values for longer-chain derivatives and values for theoretical calculations.

Because of its direct correlation with microscopic disorder, there is considerable interest in the direct calculation of entropies of phase transitions. Correlations between the entropies of fusion and crystal structures of many materials have been reviewed [1,4]. In this paper a new method of plotting data is given; this allows one to estimate the entropy (and hence enthalpy) of fusion of a homologous series containing *n*-alkyl chains, given their melting points and thermodynamic data for two representative long-chain derivatives.

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A LINEAR ENTROPY RELATIONSHIP (*SnT* PLOT)

The experimental values of the thermodynamics of fusion and solid–solid phase transitions of the *n*-alkanes from methane (C1) to eicosane (C20) are given in Table 1. In addition, Table 1 also gives the entropy change divided by the number of carbons in the chain, $\Delta S/n$. The values of $\Delta S_{fus}/n$ are plotted against the temperature of fusion (henceforth referred to as an *SnT* plot) in Fig. 1 for the *n*-alkanes from C1 to C20. For chain lengths in excess of about six carbons, there appear to be two general trends, typical of the odd–even effect often observed [1] in alkyl chain series. The upper curve is that for the *n*-alkanes containing an even number of carbons, which shows a

TABLE 1

Thermodynamic data for *n*-alkanes

Compound	*n*	Type of process [a]	Temp. (K)	ΔS (J K^{-1} mol^{-1})	$\Delta S/n$ [b] (J K^{-1} mol^{-1})	Ref.
Methane	1	T	20.50	3.81	3.81	5
		F	90.676	10.38	10.38	5
Ethane	2	F	89.89	31.81	15.90	5
Propane	3	F	85.47	41.23	13.74	5
Butane	4	T	107.56	19.2	4.80	5
		F	134.86	34.56	8.640	5
Pentane	5	F	143.47	56.56	11.71	5
Hexane	6	F	177.802	73.55	12.26	5
Heptane	7	F	182.540	76.99	11.00	5
Octane	8	F	216.37	95.85	11.98	6
Nonane	9	T	217.18	28.92	3.213	6
		F	219.65	70.42	7.825	6
Decane	10	F	243.50	117.9	11.79	6
Undecane	11	T	236.60	28.98	2.635	6
		F	247.58	89.58	8.144	6
Dodecane	12	F	263.58	139.8	11.65	6
Tridecane	13	T	255.00	30.04	2.311	6
		F	267.78	106.4	8.187	6
Tetradecane	14	F	279.02	161.53	11.538	6
Pentadecane	15	T	270.90	63.84	2.256	6
		F	283.1	122.2	8.146	6
Hexadecane	16	F	291.33	183.15	11.447	6
Heptadecane	17	T	284.22	38.51	2.265	6
		F	295.14	136.1	8.005	6
Octadecane	18	F	301.33	204.78	11.377	6
Nonadecane	19	T	295.9	46.66	2.455	6a
		F	305.1	150.2	7.903	6a
Eicosane	20	T	309.4			6a
		F	309.7	255.6	11.281	6a

[a] F = fusion, T = solid–solid phase transition.

[b] $\Delta S/n$ = entropy change/number of carbons.

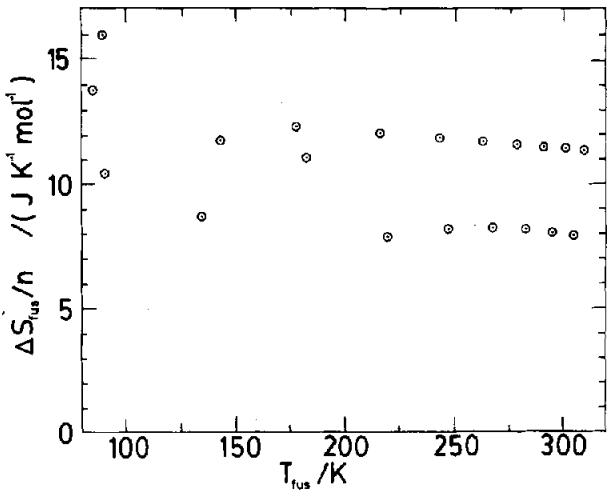

Fig. 1. The entropy of fusion per carbon, $\Delta S_{fus}/n$, for the unbranched alkanes, C_nH_{2n+2}, from $n = 1$ to 20, as a function of their melting melting points, T_{fus}.

much higher entropy change on fusion than that for the odd *n*-alkanes. The difference between the two series can be attributed to their differing crystal structures and the fact that a number of the odd-numbered *n*-alkanes undergo solid–solid phase transitions prior to fusion.

Figure 2 is an *SnT* plot of the isostructural [7], even-numbered *n*-alkanes from C6 to C20. This plot shows a remarkably linear relationship between the entropy of fusion per carbon and temperature of fusion over a wide temperature range. It appears that there are two conditions for this linear relationship: the compounds considered must be isostructural and cannot

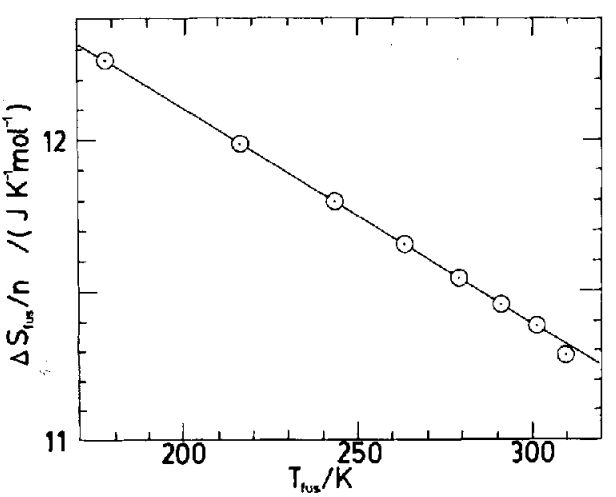

Fig. 2. The entropy of fusion per carbon, $\Delta S_{fus}/n$, for unbranched alkanes, C_nH_{2n+2}, for even n from $n = 6$ to 20, as a function of their melting points, T_{fus}.

undergo any solid–solid phase transitions prior to fusion. While the even *n*-alkanes from C6 to C18 meet both these criteria, C20 undergoes a solid–solid phase transition prior to fusion, which would explain why it falls below the line.

The equation of the line for the C6 to C18 even-numbered *n*-alkanes, as determined by linear least squares, is

$$\Delta S_{\text{fus}} = n\left(13.53 - 7.129 \times 10^{-3} T_{\text{fus}}\right) \text{J K}^{-1} \text{ mol}^{-1} \quad (1)$$

where ΔS_{fus} is the entropy of fusion, n is the number of carbons in the alkyl chains, and T_{fus} is the temperature of fusion (in K).

DISCUSSION

Although the exact meanings of the slope and the intercept of the *SnT* plot are not fully understood, some rationale for their physical bases can be put forward.

The slightly negative slope in the C6 to C18 *SnT* plot (Fig. 2) indicates that the entropy of fusion per carbon decreases as the length of the chain increases. This is not an entirely surprising result because as the chains get longer and heavier a decrease in the translational entropy per carbon could be expected to occur. The slope might also give an indication of the effect of pressure on the entropy of fusion. If the pressure on the *n*-alkane is increased, an increase in the melting point occurs, and this results in a decrease in the entropy of fusion as reflected in the *SnT*. No high-pressure calorimetric results for these compounds are known at the present time to test this hypothesis.

A clue to the interpretation of the intercept comes from an *SnT* plot for another system of compounds containing *n*-alkyl chains, the layered perovskites (LP). These compounds are of the general formula $(C_nH_{2n+1}NH_3)_2MCl_4$, where M = Cr, Fe, Cu, Mn, Cd, abbreviated to C*n*M. These compounds have been the subject of many investigations since they show a variety of structural and magnetic phase transitions. Their structure consists of layers of corner-sharing MCl_6 octahedra separated by alkylammonium groups (see ref. 8 and references cited therein). The ammonium headgroup points at the layer and is situated in a cavity of the layer, and the alkyl chains of neighbouring layers do not interdigitate but have structures similar to phospholipid bilayers. The alkyl chains can undergo solid–solid phase transitions due to chain "melting" while the layer remains solid, and this is essentially the two-dimensional melting of alkyl chains. Most of these compounds undergo one or more solid–solid phase transitions.

Using the best thermodynamic data available on the C12Mn and C14Mn [8] derivatives, an *SnT* plot was generated. Since both of these compounds

have two solid–solid phase transitions due to the stepwise melting of the alkyl chains, the entropy represents the sum of the two transitions and the temperature is that of the upper transition. The equation of the line is

$$\Delta S_{tr} = n(18.23 - 1.243 \times 10^{-2}\, T_{tr})\ \text{J K}^{-1}\ \text{mol}^{-1} \quad (2)$$

where ΔS_{tr} is the sum of the entropies of transitions, n is the number of carbons in the alkyl chain and T_{tr} is the temperature of the upper transition (in K).

A comparison between the summed experimental entropies and the entropies calculated by using eqn. (2) for other compounds of the general formula $(C_nH_{2n+1}NH_3)_2MnCl_4$ is given in Table 2. The agreement between the values derived from eqn. (2) and the experimental values are within the experimental error.

The layered pervoskite data can shed some light on the meaning of the intercept of the *SnT* plot by comparison of the intercepts for the layered pervoskite and *n*-alkanes per mole of alkyl chain. (Since there are two moles of alkyl chains per mole of LP, division of the intercept of eqn. (2) by 2 will give the intercept per mole of LP alkyl chain, 9.12 J K^{-1} mol^{-1}.) The ratio of the intercepts for the *n*-alkanes to LP is then 13.53: 9.12, or 1.48 : 1. This value is very close to 3 : 2, the ratio of the dimensionalities of the melting of the *n*-alkanes and layered pervoskites. Further theoretical support for the correlation of melting dimensionality with the intercept is illustrated by the similarity between the layered pervoskite intercept per mole of alkyl chain (9.12 J K^{-1} mol^{-1}) and the entropy of 2-dimensional fusion of alkyl chains per methylene group ($0.25R \ln 3^4 = 9.13$ J K^{-1} mol^{-1}), derived by Pechhold et al. [11] from kink-block theory.

TABLE 2

Empirical and experimental transition entropies of compounds of the general formula $(C_nH_{2n+1}NH_3)_2MnCl_4$

n [a]	T_{tr} [b] (K)	ΔS(calc) [c] (J K^{-1} mol^{-1})	ΔS(exp) (J K^{-1} mol^{-1})	Ref.
7	313.8	100.3	100.7	9
11	316	157.3	146.5	10
12	336	168.7	168.7	8
13	343	181.6	179.6	10
14	357	193.1	193.1	8
15	362	206	212.5	10
16	364	219.3	204.4	10
17	373	231.1	249.9	10

[a] n = number of carbons in alkylammonium group.

[b] T_{tr} = temperature of the upper transition.

[c] calculated using eqn. (2).

CONCLUSIONS

A linear relationship between the entropy of fusion per carbon of *n*-alkyl chains and the temperature of fusion has been illustrated for isostructural *n*-alkanes that do not exhibit solid–solid phase transitions prior to melting.

A similar relationship for layered pervoskite compounds of the general formula $(C_nH_{2n+1}NH_3)_2MnCl_4$ has been derived. Given the upper solid–solid phase transition temperature, the total entropy change of the solid–solid phase transitions in these compounds can be predicted accurately.

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