

Lattice and phase transition thermodynamics of ionic liquids

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Received 23 February 2004; received in revised form 24 March 2004; accepted 27 March 2004

Available online 20 May 2004

Abstract

The thermodynamic systematics of the formation and phase changes of a range of materials which form ionic liquids is examined, based upon experimental values of densities and calorimetric quantities. Certain results are shown to be consistent across groups of these materials, namely: the lattice potential energies decrease with increasing alkyl chain length; the molecular volumes and ‘total phase change’ entropies (from crystal through liquid crystalline phases to melt) increase linearly with alkyl group chain length for pyridinium cations. However, the total phase change transition entropies for the two 1-alkyl-3-methylimidazolium cation systems examined are anomalous, having dome-shaped graphs with a dip in value around C₁₄.

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Keywords: Phase transitions; Lattice energies; Ionic liquids; Thermodynamics

1. Introduction

Thermodynamic considerations are important in understanding the stability and behaviour of solid, liquid crystalline and molten materials. An important quantity in assessing the stability of an ionic material is its lattice energy (that is, the energy required to remove the ions from their positions in the crystal structure to infinite separation). The lattice energy, in a Born–Haber–Fajans cycle, often determines whether the material can be synthesised or not; indeed, Bartlett [1] used just such a quantity in predicting the stability of the first known noble gas complex, XePtF₆.

Furthermore, as temperature rises and energy is gained, crystalline solids lose their long-range order correlation [2] which becomes reduced to disorder, whether through a ‘continuous’ (lambda) transition from one solid phase to another, or at a single fusion temperature (where the solid becomes a liquid melt), or through a sequence of transitions in the solid and/or liquid, to a final ‘clearing’ temperature. In the last case, the liquid may pass through one or more liquid crystalline states of considerable technological concern. These increases in disorder are observed as changes in the structures of the material concerned, accompanied by

enthalpy increases resulting from the altered interactions, and are described by increases in entropy. Although the enthalpy and entropy increases for any transition (tr) are closely connected, by the equilibrium relation:

$$\Delta_{\text{tr}}S = \frac{\Delta_{\text{tr}}H}{T_{\text{tr}}} \quad (1)$$

the entropy increases generally over less than an order of magnitude for most substances and is largely temperature-independent, whereas enthalpy increases may vary over several orders of magnitude [3] and are somewhat temperature-dependent, so that the systematics of entropy change are more readily dealt with.

‘Ionic liquids’ are materials of increasing importance, providing new, low vapour pressure, non-flammable solvents for replacement of volatile organic compounds in chemical and electrochemical processing [4].¹ However, little has yet been done in establishing correlations of their thermodynamic properties. It is the purpose of this paper to contribute to such analyses by (a) implementing a recently published method for estimating ‘lattice’ potential energies of ionic liquids, in order to provide information on their relative stabilities; (b) establishing some thermodynamic regularities; and (c) comparing entropies and entropy changes

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¹ This is the lead paper in issue 57(2) of this journal, resulting from an Ionic Liquid Workshop, Melbourne, May 2003.

encountered in a number of homologous series undergoing liquid crystal transitions, in order to better understand the processes involved and to point out some unexpected anomalies that are observed. Although studies of transition entropies are well-established in the general case [2,3,5] they seem to have been neglected or remain largely uninterpreted for ionic liquids even though the relevant experimental data may be available (even if seldom published), often through modern differential-scanning calorimetry (DSC) experiments which yield both $\Delta_{tr}H$ and T_{tr} and, so, $\Delta_{tr}S$.

2. ‘Lattice’ potential energies

We have recently developed procedures for the evaluation of the lattice potential energies of ionic solids of essentially any ionic complexity [6–9]. Our procedures rely only on the chemical formula, ionic charges and molecular volume (or density) of the materials involved, and neither require nor depend upon any other structural information. For this reason, we believe that the equations apply equally well to amorphous solids and to ionic liquids as to their well-tested application for ionic solids since these procedures rely on coulombic interactions being principal contributors to the lattice energy.

For relatively simple salts, such as of type MX, lattice energies are smaller than 5000 kJ mol^{-1} and are given [7] by

$$U_{\text{POT}} = 2I \left[\frac{\alpha}{V_{\text{m}}^{1/3}} + \beta \right] \quad (2)$$

where α and β are appropriate fitted coefficients chosen according to the stoichiometry of the salt, V_{m} the molecular volume, and I an ionic strength factor of the chemical formula unit (I can be simply calculated as $I = (1/2) \sum n_i z_i^2$, where n_i is the number of ions of type i in the formula unit having integer charge, z_i , and the summation extends over all ions in the formula unit). For the present case of salts of formula MX with charge ratio (1:1), $I = 1$, $\alpha = 117.3 \text{ kJ mol}^{-1} \text{ nm}$, and $\beta = 51.9 \text{ kJ mol}^{-1}$ with V_{m} in units of nm^3 (which is most convenient in reference to crystal structures), where $V_{\text{m}} = V_{\text{cell}}/z$ with z being the number of molecules in the unit cell.

The lattice energy can equivalently be expressed in terms of the density, ρ (g cm^{-3}), and formula (molar) mass, M_{m} (g mol^{-1}), of the material, since:

$$V_{\text{m}} (\text{nm}^3) = \frac{M_{\text{m}}}{\rho N_{\text{A}}} = 1.66 \times 10^{-3} \frac{M_{\text{m}}}{\rho} \quad (3)$$

where N_{A} is the Avogadro’s constant, 6.02245×10^{23} molecule mol^{-1} . Thus [9]:

$$U_{\text{POT}} = \gamma \left(\frac{\rho}{M_{\text{m}}} \right)^{1/3} + \delta \quad (4)$$

where the constants for MX (1:1) have the values: $\gamma = 1981.2 \text{ kJ mol}^{-1} \text{ cm}$ and $\delta = 103.8 \text{ kJ mol}^{-1}$.

Table 1

Lattice potential energy and entropy from density for $[\text{C}_n\text{-mim}][\text{BF}_4]$ at 20°C

n	M_{m}	ρ (g cm^{-3})	U_{POT} (kJ mol^{-1})	S_{293} ($\text{JK}^{-1} \text{mol}^{-1}$)
2	197.8	1.2479	470	358
4	225.8	1.2077	450	417
6	253.8	1.1531	432	485
8	281.8	1.1095	417	555
10	309.8	1.0723	404	627

The densities of the condensed melt and solid phases are very similar, and so the calculated lattice potential energies may well be applied to either phase of the material, with the difference between the values so generated resulting from the change in density and corresponding to the energy (and quite closely approximating the enthalpy) of the phase transition. However, the small differences involved render wholly unreliable any evaluation of transition enthalpies by this method, which is therefore not recommended.

Seddon and co-workers [10–13] have recently reported the densities of a number of homologous series of ionic liquid salts, each having a 1-alkyl-3-methylimidazolium cation (abbreviated as $[\text{C}_n\text{-mim}]$) with a number of different anions, and alkyl groups $n = 1$ –18. (Structures of these and other molecular systems mentioned in this paper may be found in Ref. [4].) From these densities, lattice potential energies are readily calculated using Eq. (4) (see Tables 1 and 2).

Fig. 1 shows that there is a smooth, monotonic decrease in lattice potential energy with increasing alkyl chain length (consonant with the smooth changes in density).

The data for each homologous series fit quadratic relations very well, with slightly differing constants; such lattice energies may be helpful in assessing the relative stabilities of various ionic liquids. From prior experience with crystalline solids, these methods for calculation of the lattice potential energies of simple salts yield values which are generally within 5% of the values generated by more elaborate methods. While we have no reference values against which to judge the present calculated values for melts, we may reasonably anticipate that the trends shown are reliable and, thus, useful. This perception is reinforced by recent ab initio quantum mechanical calculations [14] which demonstrate a decrease in interaction energy with increasing alkyl chain

Table 2

Lattice potential energy and entropy from density for $[\text{C}_n\text{-mim}][\text{NTf}_2]^{\text{a}}$ at 20°C

n	M_{m}	ρ (g cm^{-3})	U_{POT} (kJ mol^{-1})	S_{293} ($\text{JK}^{-1} \text{mol}^{-1}$)
1	377.2	1.574	423	526
2	391.2	1.5154	415	564
4	419.2	1.4378	403	633
6	447.2	1.3926	393	694
8	475.2	1.3189	382	775
10	503.2	1.2792	374	844
12	531.2	1.246	367	912

^a $[\text{NTf}_2]$: bistriflamide: bis(trifluoromethanesulphonyl)imide.

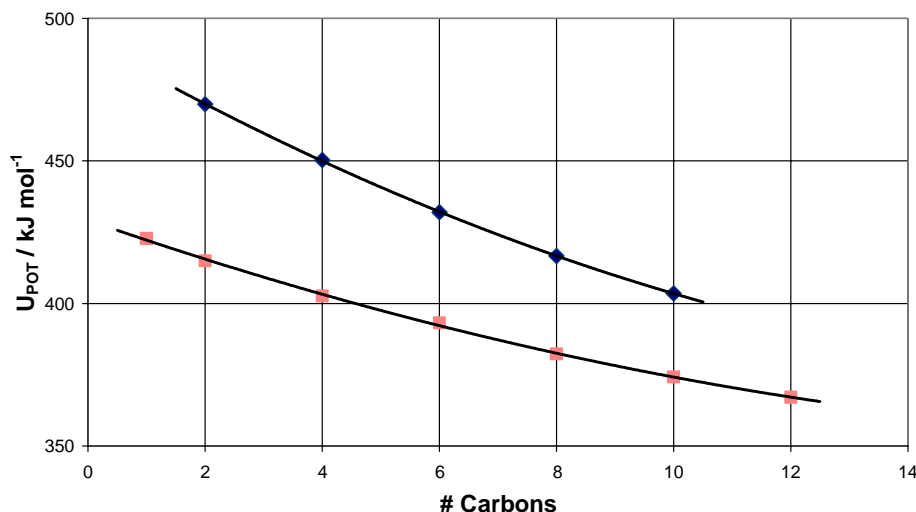


Fig. 1. Lattice potential energy, U_{POT} (kJ mol^{-1}), vs. number (n) of carbons in the alkyl chains of the ionic liquids $[\text{C}_n\text{-mim}][\text{BF}_4]$ (◆) and $[\text{C}_n\text{-mim}][\text{NTf}_2]$ (■), as calculated from their densities and molecular formulae ($[\text{NTf}_2]$ = bistriflamide = bis(trifluoromethanesulphonyl)imide). The least-squares fitted equations are: $U_{\text{POT}} (\text{kJ mol}^{-1}) = 0.285n^2 - 11.741n + 492.4$ for $[\text{C}_n\text{-mim}][\text{BF}_4]$, and $U_{\text{POT}} (\text{kJ mol}^{-1}) = 0.165n^2 - 7.157n + 429.2$ for $[\text{C}_n\text{-mim}][\text{NTf}_2]$.

length (for the shorter $\text{C}_1\text{--C}_4$ alkyl chains investigated) at the Hartree–Fock level.

The experimental density data also yield the molecular volumes of the materials, which behave in a regular manner, as shown in Fig. 2, with a mean contribution of 0.0275 nm^3 per methylene ($-\text{CH}_2-$) group.

This agrees well with methylene contributions of 0.0280 nm^3 from n -alcohols, 0.0272 nm^3 from n -amines, and 0.0267 nm^3 from n -paraffins (from our own calcula-

tions using data from Ref. [15]). These are slightly larger than the value 0.024173 nm^3 recently established [16] for methylene groups (also not in rings) in crystalline materials. The increased values for liquid state relative to crystalline materials is perhaps not unexpected.

In a corresponding vein, we have recently established good linear relations between standard entropies molecular volumes of both ionic solids [17] and organic liquids [18]. Since the materials under present consideration are ionic

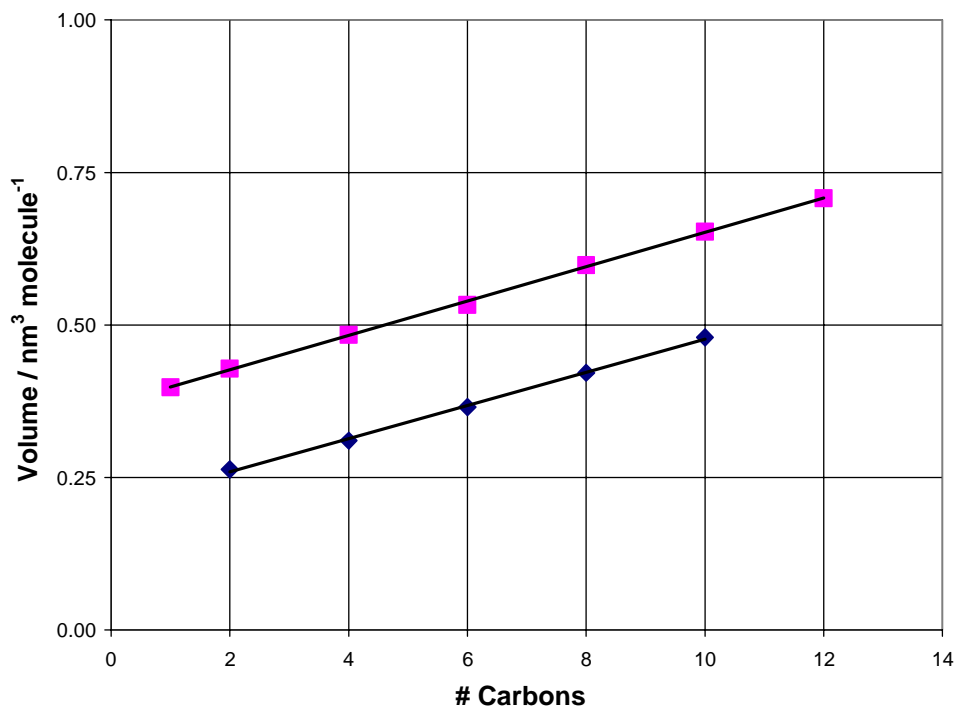


Fig. 2. Molecular volume vs. n for the ionic liquids $[\text{C}_n\text{-mim}][\text{BF}_4]$ (◆) and $[\text{C}_n\text{-mim}][\text{NTf}_2]$ (■). The least-squares fitted equations are: $V_m (\text{nm}^3) = 0.0272n + 0.205$ for $[\text{C}_n\text{-mim}][\text{BF}_4]$, and $V_m (\text{nm}^3) = 0.0282n + 0.370$ for $[\text{C}_n\text{-mim}][\text{NTf}_2]$.

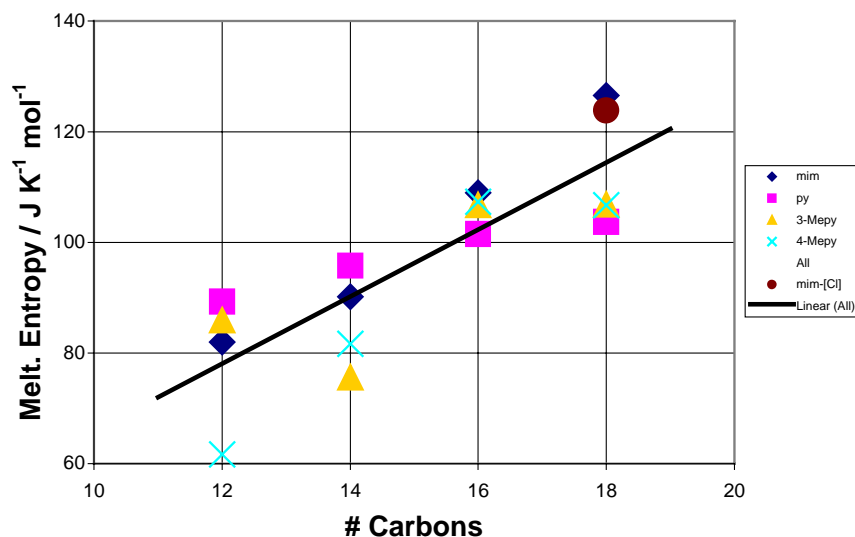


Fig. 3. Total phase change entropy, $\Delta_{\text{tpce}}S$ ($\text{J K}^{-1} \text{mol}^{-1}$), from crystal to clear melt, of $[\text{C}_n\text{-mim}][\text{PF}_6]$. $\Delta_{\text{fus}}S$ ($\text{J K}^{-1} \text{mol}^{-1}$) = $6.06n + 5.31$.

liquids with large organic cations, we use average values of the linear correlation constants, in the absence of more directly obtained parameters, to obtain the absolute entropies at ambient conditions, thus:

$$S (\text{J K}^{-1} \text{mol}^{-1}) = 1246.5(V_m, \text{nm}^3) + 29.5 \quad (5)$$

This implies entropy contributions per methylene group to the entropy for $[\text{C}_n\text{-mim}][\text{BF}_4]$ of $33.9 \text{ J K}^{-1} \text{mol}^{-1}$, and for $[\text{C}_n\text{-mim}][\text{NTf}_2]$ of $35.1 \text{ J K}^{-1} \text{mol}^{-1}$. These values are in excellent agreement with the value of $32.2 \text{ J K}^{-1} \text{mol}^{-1}$ from the earlier literature for an extended group of organic materials [5].

3. Structural similarity and transition entropies

The well-established, empirical method of structural similarity [5] suggests that there is a regularity of properties among homologous series of compounds. Chickos et al. [19] have shown that there are strong regularities in solid–liquid total phase change enthalpies and entropies, leading to the establishment of reliable group additivity procedures for the total phase change property, that is, the change in the property “in going from a rigid solid at 0 K to an isotropic liquid at the melting point”. We test this for the total phase change entropy of a series of hexafluorophosphate ionic liquid crystal salts [10] in Fig. 3 (data in Table 3).

Table 3
Transition and total phase change ($\Delta_{\text{tpce}}S$) entropies ($\text{J K}^{-1} \text{mol}^{-1}$) for $[\text{C}_n\text{-Y}][\text{PF}_6]^{\text{a}}$

Cation ^b	<i>n</i> (C)	C → I	C → SA	C1 → SA	SA → I	C → C1	C1 → C2	C2 → C3	C3 → I	?	$\Delta_{\text{tpce}}S$
[C _n -mim]	12	82									82
	14		89		1						90
	16		108		1						109
	18		124		3						127
[C _n -py]	12					19	11	30	30		90
	14					18	11	43	24		96
	16			21	2	65				14	102
	18			19	3	72				10	104
[C _n -3-Mepy]	12	86									86
	14	76									76
	16		108		2						110
	18		106		1						107
[C _n -4-Mepy]	12	62									62
	14	82									82
	16		106		3						109
	18		119		1						120

^a Phase symbols: C_n, crystal; SA, smectic A; I, isotropic liquid; ?, unidentified transition.

^b Alkyl-substituted cations: mim, methylimidazolium; py, pyridinium; 3-Mepy, 3-methylpyridinium; 4-Mepy, 4-methylpyridinium.

Table 4
Transition and total phase change ($\Delta_{\text{tpe}}S$) entropies ($\text{J K}^{-1} \text{mol}^{-1}$) for $(C_n)_2\text{-Bim-X}$ and $(C_n)_2\text{-Im-X}^a$

Formula ^b	Crystal	Fusion				$\Delta_{\text{tpe}}S$
	K1 \rightarrow K2	K2 \rightarrow L α	L α \rightarrow L β	L β \rightarrow I	Total fusion	
$(C_{12})_2\text{-Bim-Cl}$	16	163	59	14	236	252
$(C_{14})_2\text{-Bim-Cl}$	108	151	67	17	235	343
$(C_{16})_2\text{-Bim-Cl}$	73	125	46	11	182	255
$(C_{18})_2\text{-Bim-Cl}$	98	184	54	12	250	348
$(C_{14})_2\text{-Bim-Br}$	13	110		7	117	130
$(C_{16})_2\text{-Im-Cl}$		85		6	91	91
$(C_{16})_2\text{-Im-Br}$		98		5	103	103
$(C_{16})_2\text{-Im-PF}_6$		138		5	143	143

^a Phase symbols: Kn, crystal; L, lamellar; I, isotropic liquid.

^b Bim: benzimidazolium; Im: imidazolium.

The figure shows that there is a roughly linear increase in the total phase change entropy (from solid to clear liquid) averaging about 6 J K^{-1} per mole of added methylene group for the series $(C_{12}\text{--}C_{18})$ of salts of alkyl-substituted methylimidazolium, pyridinium, 3- and 4-methylpyridinium cations. This value for the added entropy of transition per mole of added methylene group is thus not very different from the value of $8 \text{ J K}^{-1} \text{mol}^{-1}$ earlier established (Eq. (5)) from principles of structural similarity for insertion of a methylene group into an organic material—being the difference between the mean entropy added by a methylene group to a liquid of $32.2 \text{ J K}^{-1} \text{mol}^{-1}$ and to a solid of $24.3 \text{ J K}^{-1} \text{mol}^{-1}$ (but quite smaller than the recent value [19] of $17.3 \text{ J K}^{-1} \text{mol}^{-1}$ for the total phase change entropy contribution of a methylene group in an extensive general set of organic materials).

Seddon and co-workers [10] have measured the transition thermodynamics of hexafluorophosphate salts, and Lee et al. [20]² have made similar measurements on 1,3-dialkylimidazolium salts (Im) and 1,3-dialkylbenzimidazolium salts (Bim); their total phase change entropies (Tables 3 and 4) may thus be compared.

The comparison is necessarily rather rough, however, because we are examining simultaneous changes in both cation and anion. As an example, consider $[\text{C}_{16}\text{-mim}][\text{PF}_6]$ (mim = 1-alkyl-3-methylimidazolium), which has an overall phase change entropy of $109 \text{ J K}^{-1} \text{mol}^{-1}$, while the value for $[(\text{C}_{16})_2\text{-Bim}][\text{Cl}]$ is $255 \text{ J K}^{-1} \text{mol}^{-1}$. In the Bim cation, 15 methylene groups have been added to the methyl substituent, contributing an extra $15 \times 6 = 90 \text{ J K}^{-1} \text{mol}^{-1}$ to the transition entropy. To this should be added the (unknown) contribution from the fused benzene ring, and the (unknown) difference between the contributions of the $[\text{Cl}]^-$ and $[\text{PF}_6]^-$ anions. It is thus perhaps appropriate that the transition entropy of the Bim salt, at $255 \text{ J K}^{-1} \text{mol}^{-1}$, is larger than $109 + 90 = 199 \text{ J K}^{-1} \text{mol}^{-1}$.

² The formulae and molecular weights given in the footnote for the two crystal structures reported are incorrect, each containing a redundant oxygen atom. Thus, $[(\text{C}_{12})_2\text{-Bim}]\text{Cl}$ has formula $\text{C}_{31}\text{H}_{57}\text{N}_2\text{Cl}$ and MW = 493.3, while $[(\text{C}_{12})_2\text{-Bim}]\text{Br}$ has formula $\text{C}_{31}\text{H}_{57}\text{N}_2\text{Br}$ and MW = 537.7.

Holbrey and Seddon [11] have provided an extensive data-set for the tetrafluoroborate salts of mim ionic liquid crystals ($C_0\text{--}C_{18}$), from which the total phase change entropies may be calculated (Fig. 4).

In this case, the behaviour is anomalous, with the entropy changes generally following a dome-shaped curve in the liquid crystal range ($C_{12}\text{--}C_{18}$). However, there is a sharp dip in the curve at C_{14} (where the fact that the data for C_{12} and C_{16} are slightly below their expected values—if one follows the dome—suggests that the C_{14} value is not a single aberration). Indeed, in Fig. 5 (for mim salts of bis(trifluoromethanesulphonyl) imide = $[\text{NTf}_2]$) [13], we see a similar dip for the C_{14} salt (which, however, melts directly to a clear liquid without any intervening mesophases).

It may be that a solid-state transition at lower temperatures has occurred in each of these homologous series which

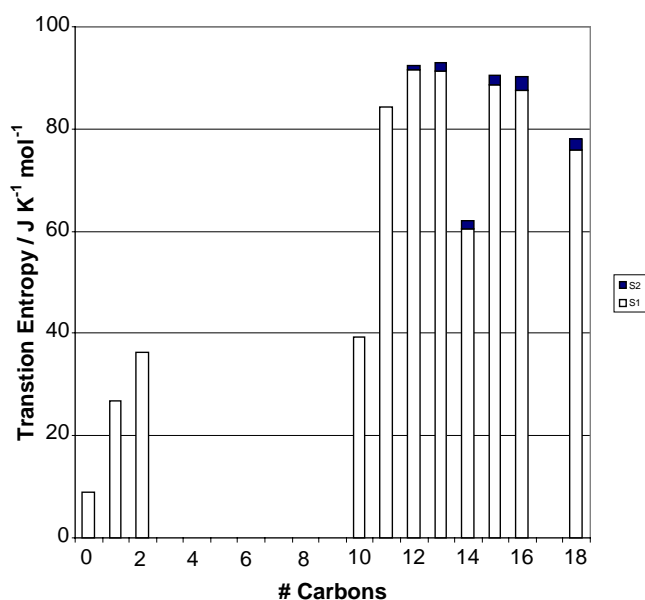


Fig. 4. Total phase change entropy, $\Delta_{\text{tpe}}S$ ($\text{J K}^{-1} \text{mol}^{-1}$), from crystal to clear melt, of $[\text{C}_n\text{-mim}][\text{BF}_4]$. The lower part of each bar corresponds to the contribution from crystalline solid to smectic A mesophase (or directly to clear melt, if there is no intervening mesophase), while the small upper portion corresponds to the transition from the mesophase to a clear liquid.

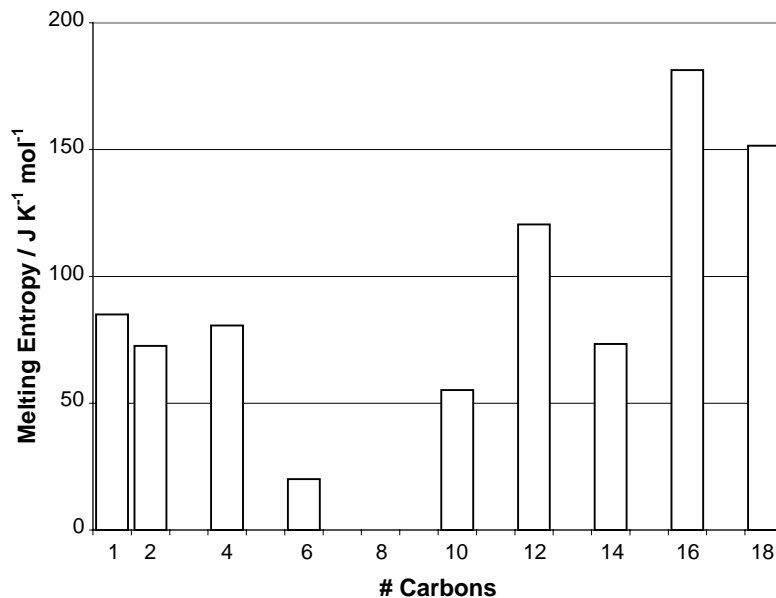


Fig. 5. Melting transition entropy, $\Delta_{\text{mpe}}S$ ($\text{J K}^{-1} \text{mol}^{-1}$), from crystal to clear melt, of $[\text{C}_n\text{-mim}][\text{NTf}_2]$ (no liquid crystalline phases were observed).

has perhaps been missed for both materials, and its contribution to the transition entropy thus omitted, or that this is a real phenomenon—in either case, this observation calls for further investigation.

An interesting observation (Table 3 and Fig. 4) is that, at least for $[\text{C}_n\text{-mim}][\text{BF}_4]$, the transition entropy of the mesophase to the total phase change entropy (to clearing) is very small. This contradicts earlier assertions [2] that the

mesophase entropy contributions for ionic liquids are large, whereas those for molecular liquids are dominated by the first melting transition. On the other hand, this generalisation does hold for $[\text{C}_n\text{-py}][\text{PF}_6]$ (Table 3 and Fig. 6). Fig. 6 also demonstrates that it is the total phase change entropy which is of importance in studying the thermodynamics of materials with multiple phase changes, as already asserted by Chickos et al. [19].

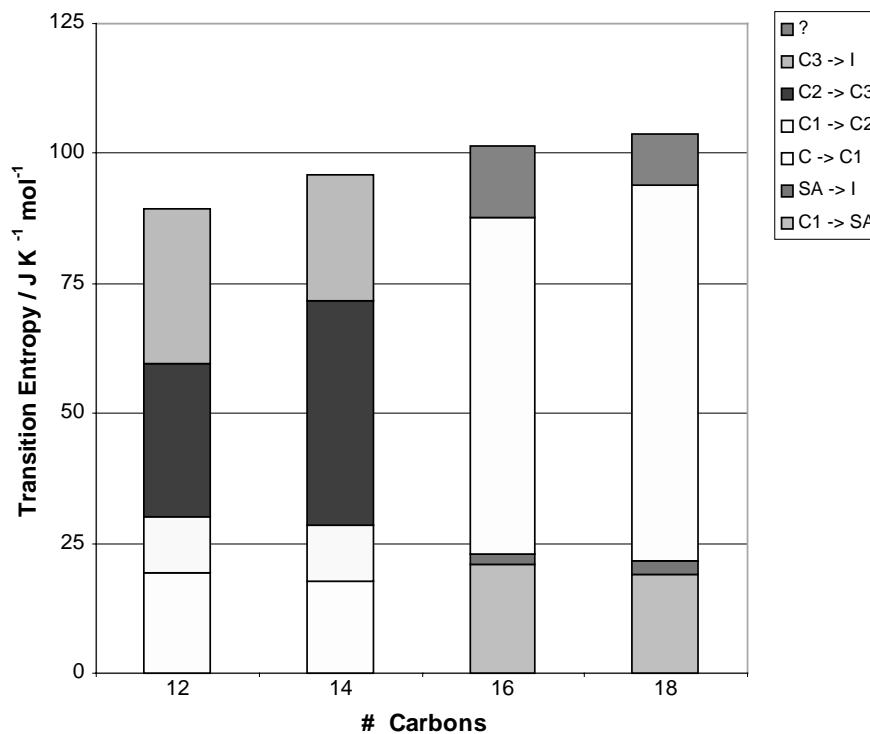


Fig. 6. Total phase change entropy, $\Delta_{\text{tpe}}S$ ($\text{J K}^{-1} \text{mol}^{-1}$), from crystal to clear melt, of $[\text{C}_n\text{-py}][\text{PF}_6]$. The successive parts of each bar correspond to successive transitions from crystalline solid to clear liquid.

Acknowledgements

My attention to much of the data used in this paper was kindly provided by Prof. K.R. Seddon, Queen's University of Belfast, Northern Ireland, whose interest is gratefully acknowledged.

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