CONFORMATIONAL DISORDER IN FUSION ENTROPY OF n-PARAFFINS

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Abstract Particular disorder and volume contributions to fusion entropy of even n-paraffins are evaluated from available experimental data. Their dependences on the number of effective C-C bonds are defined. Conformational and basic disorder contributions are compared with theory and discussed.

1. Introduction

A certain uniformity of the fusion process for two groups of simple liquids with spherical and linear molecules has recently been pointed out[1]. The linear correlation between relative volume change $\Delta V/V_s$ and associated fusion entropy S_f has been verified. Thus the basic disorder contribution S_{do} (which would be equal to fusion entropy at no volume change) arises as a term common to either group, as well as a constant of proportionality b between volume change and its contribution to fusion entropy S_v. The first entropy term rises with the increasing number of translational and rotational molecular degrees of freedom which may be activated at melting. The second term is necessarily associated with the first one, because an appropriate larger volume is required to accomodate each new type of molecular motions in liquid compared to those in solid.

In non-simple liquids with general molecules, intra- and inter-molecular changes may also be activated. Then additional disorder components ΣS_{di}, resulting also in an increase of volume contributions ΣS_{vi}, should be taken into account. Thus generally fusion entropy

$$S_f = S_{do} + \Sigma S_{di} + S_{vo} + \Sigma S_{vi} = S_{do} + \Sigma S_{di} + b\Delta V/V_s \qquad (1)$$

contains more terms, which complicate analysis. Even for substances with rigid general molecules, b is no longer a common constant; fusion data under high pressure were necessary for determining the single disorder term S_{do} for this third group[2]. One may expect this basic disorder term to remain the same also for substances with non-rigid molecules, where intramolecular changes introduce new entropy terms.

Liquids of n-paraffins (C_nH_{2n+2}), with possible molecular

translations and rotations, but also intra-molecular conformations, are suitable to confirm this statement, as well as the assumption that a particular volume contribution to fusion entropy is associated to each type of motions, which disappear at fusion. Therefore only paraffins without solid-to-solid (s-s) transitions will be considered. In such a homologous series, conformational changes, due to the onset of internal hindered rotations around C-C bonds of a molecule, should depend on the number n of C atoms. Therefore their entropy contributions should depend on n as well. Thus the individual terms of fusion entropy in eq.(1) could be successively resolved and compared with theoretically expected values and with those obtained experimentally for other substances with rigid general molecules[2,3], giving a new insight into the fusion process of non-simple liquids.

2. Experimental data

Necessary fusion data for n-paraffins are not abundant and sometimes even controversial[3,4,5]. Especially scanty are data for fusion under high pressures[5] which are necessary for determining the constant b and the total volume contribution S_v in eq.(1), according to[1]

$$S_v \simeq (\partial S/\partial V)_{T_f,P_f} \Delta V = \gamma_f \Delta V = b\Delta V/V_s. \qquad (2)$$

Therefore gradients of measured P-T (pressure-to-temperature) isochores, extrapolated to fusion temperature are also used, due to the equality: $(\partial S/\partial V)_T = (\partial P/\partial T)_V = \gamma$[1,6].

Among the even paraffins without s-s transitions, available data under increased pressure were found only for dodecane (C_{12}) and octadecane (C_{18}). They are presented in Fig.1 as curves of $\Delta V/V_s$ on S_f dependence. At relatively lower pressures, the curves can be approximated by straight lines of definite slopes, resulting in b equal to about 29R and 33R for C_{12} and C_{18}, respectively. These values are considerably higher than those obtained for substances with spherical and linear molecules of about 7R and 11R, respectively; R being the gas constant. The gradients of isochores have been determined for liquid paraffins of n equal to 6, 8, 14, 16 and 20, but not at fusion temperatures[7,8]. Using Flory's least-square (l-s) equations for lines drawn through the data points, extra- and inter-polated values of γ_f are obtained which are in reasonable agreement with

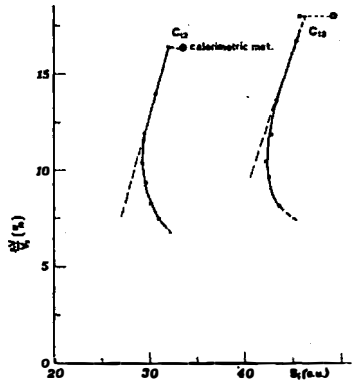

Fig.1 Dependence of the relative volume change $\Delta V/V_s$ on the fusion entropy S_f for dodecane $C_{12}H_{26}$ and octadecane $C_{18}H_{38}$ at normal and high pressures.

other authors[6,7,8]. For lower n, the temperature extrapolations were too high (about 100K), introducing greater uncertainties which must be taken into account. This is the reason why butane was excluded from consideration.

Moreover, volume changes at fusion at normal pressure are not available for some of the considered paraffins. Thus ΔV values for them are also inter- and extra-polated from available data of n equal to 6, 12 and 18, according to certain regularities of V_l, $\Delta V/V_s$ and the total relative volume change (including s-s transitions) for even and odd paraffins[3,5,6], which will be published elsewhere.

3. Volume and disorder entropy contributions

Approximate values for S_v are then calculated using eq.(2). Within experimental errors, S_v depends nearly linearly on n, as can be seen in Fig.2a. Thus an approximately constant increase S'_{vc} per additional C-C bond appears. As is well known, only (n-3) bonds can be effective in increasing the number of conformations[6]. Therefore the straight line in Fig.2a may be expressed by

$$S_v = S_{vo} + (n-3)S'_{vc} \qquad (3)$$

with S_{vo} about 3.8 e.u., and S'_{vc} about 0.55 e.u.

From experimentally evaluated S_v, the associated values of the constants b, according to eq.(2), are also calculated. Again a nearly linear rise with n is obtained, i.e. $b=b_o+(n-3)b'$, as presented in Fig.2b. The l-s method gives $b_o=16.25R$ and $b'=1.17R$. The values of b evaluated from $\Delta V/V_s$-S_f diagrams in Fig.1 are in good agreement with those obtained from the

thermal pressure coefficient γ_f at fusion (Fig.2b), bearing in mind the respective approximations.

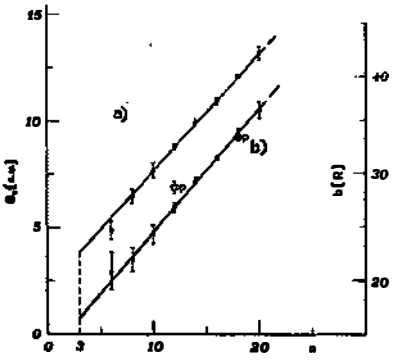

Fig.2 a) dependence of volume contribution S_v to fusion entropy and b) dependence of the constant b on the number of C atoms n of even n-paraffins from C_6H_{14} to $C_{20}H_{42}$.

Once the volume contribution to fusion entropy is determined, the remaining difference $S_f - S_v$ should be pure disorder contribution S_d. Linearity of its dependence on n shown in Fig.3a, leads to the correlation

$$S_d = S_{do} + (n-3)\, S'_{dc} \qquad (4)$$

with constant disorder contribution S'_{dc} per additional C-C bond.

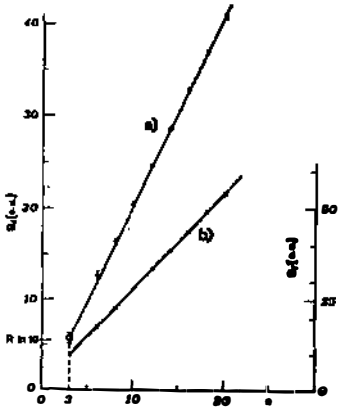

Fig.3 a) dependence of disorder entropy contribution S_d, and b) dependence of total fusion entropy S_f on the number of C atoms n of even n-paraffins from C_6H_{14} to $C_{20}H_{42}$.

As γ_f and ΔV are directly evaluated for C_{16}, and as b values from both sources (Figs.1 and 2a) agree well for C_{18},

S_d for these two compounds may be expected to be the most accurate. From them follows the difference $S_d = S_d(18) - S_d(16) = S'_{dc} \simeq 2.1$ e.u. which, introduced in eq.(4), gives $S_{do} \simeq 5.7$ e.u. with ± 0.1 e.u. and ± 0.6 e.u. rms and maximum error, repectively. The 1-s method for data of eq.(4) from C_{10} to C_{18} gives $S_{do} \simeq 5.99$ e.u. and $S'_{dc} \simeq 2.07$ e.u. With both pairs of values, the fusion data are fitted within an error less than 1% by means of relation which is analogous to eq.(1) and follows from eqs.(3) and (4), i.e.

$$S_f = S_{do} + S_{vo} + (n-3)S'_{dc} + (n-3)S'_{vc} \qquad (5)$$

as presented in Fig.3b.

4. Conclusion and discussion

The basic disorder entropy S_{do} has been explained by means of molecular degrees of freedom[1,2], and thus, S_{do} should be equal to $R\ln 16 \simeq 5.5$ e.u., as was experimentally evaluated for substances with rigid general molecules[2]. Here, this value is confirmed, within estimated deviations, for n-paraffins as well, i.e. for non-rigid molecules. This presents an additional support to our assumption that basic disorder entropy S_{do} is determined only by the general effective shape of molecules. Consequently, the associated dimensionality of translational and rotational motions defines the number of new distinguishable states in the liquid near fusion[2]. Thus non-rigidity of molecules has no influence on the value of S_{do}.

On the other hand, the flexibility of molecules directly determines S_c, resulting in its indefinite growth with increasing chain length of n-paraffins. The importance of volume contributions to fusion entropy has been emphasized before[3], expecting volume contributions to be even dominant. This is evidently not true, according to the quantitatively resolved terms of the final eq.(5). It follows (see Sec.3) that S_{dc} is about four times greater than S_{vc} at normal pressure. Under increased pressure, this ratio will still be more pronounced (see Fig.1).

The theoretical evaluation of S_{dc} has been based on more or less simplified models[6,9,10]. If the C-C bond had three discrete conformations, one trans and two gauche, then S_{dc} could be calculated by means of standard equations of statistical thermodynamics[10], using the energy difference U between

the trans and the gauche forms. However, various modifications of such a calculation lead to too small values of S_{dc}, even for all possible $3^{(n-3)}$ configurations[9] with the smallest experimentally evaluated energy U=450 cal/mole[11]. Only for the simplest, but unreal model[9,10], with U=0, $S'_{dc}=R\ln 3\simeq 2.18$ e.u. reaches a higher value than is the experimentally evaluated one (in Sec.3). Detailed discussion of these problems would exceed the scope of this work. Here it may be emphasized that our simple calculations, in very good agreement with experimental value of S'_{dc}, indicate that more than two effective gauche conformations should exist, which is theoretically possible[11,12]. It follows also, that some conformations should be forbidden due to the intramolecular excluded volume effect[10]. Contrary to that is the solvent effect which favorizes gauche conformations in liquid compared to those of non-interacting chains[13]. Thus, the traditional model of only three states for each C-C bond[9,10] is evidently an oversimplification of the rotational isomeric states of n-paraffins[11,12]. An exact calculation of S_{dc} is an enormously difficult problem still to be solved. For a better approach to the fusion process, members with s-s transitions of n-paraffins will be analyzed for a further improvement of the theory.

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