THERMODYNAMIC PROPERTIES OF ORGANIC COMPOUNDS. NOTE III

CALORIMETRIC AND CRYOMETRIC ANALYSIS OF THE FUSION OF THE MONOCARBOXYLIC ACIDS FROM C_{10} TO C_{17}

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Calorimetric and cryometric methods are employed to measure the enthalpies of fusion and prefusion of some organic acids.

In a previous paper [1] results concerning cryoscopic and calorimetric measurements on stearic acid were reported. The present note deals with cryoscopy and calorimetry on the monocarboxylic acids from C_{10} to C_{17}.

Experimental

The apparatus and experimental methods are as reported in previous papers [1−5].

The chemicals employed were: Schuchardt margaric, myristic and pentadecanoic acids and diphenyl; Fluka palmitic, tridecanoic, lauric, undecanoic and capric acids; C. Erba R. P. benzhydrol and benzophenone; and B. D. H. azobenzene. They were recrystallized several times from C_2H_5OH and dried under vacuum.

Results

Calorimetric measurements

Calorimetric measurements were carried out on margaric, palmitic, pentadecanoic, myristic, tridecanoic and lauric acids. The curves are λ-shaped, as that of stearic acid [1], but the curves of margaric and pentadecanoic acids exhibit a small peak preceding the fusion and arising on the tail (Fig. 1). This fact has also been pointed out for some n-odd dicarboxylic acids [6]. The melting enthalpies are reported in Table 1. The agreement between our values and those of Garner et al. is satisfactory.

Cryoscopic measurements

From experience on stearic acid, it can be assumed as very probable that azobenzene, diphenyl, benzophenone and benzhydrol, employed as cryoscopic solutes, do not give mixed crystals with the solvent. The same substances are therefore

employed as cryoscopic solutes for the following solvents: margaric, palmitic, pentadecanoic, myristic, tridecanoic, lauric, undecanoic and capric acids. As shown in Fig. 2, the experimental points fall into an ideal curve, and this fact supports our hypothesis. Figure 3 presents $\dfrac{1}{K_{cr}} \cdot \dfrac{\Delta t}{m}$ versus m for the example of margaric acid as solute in diphenyl or benzhydrol. The thermodynamic data obtained by cryoscopy are given in Table 2.
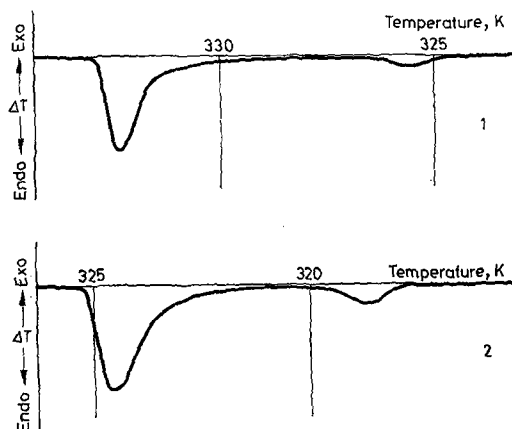

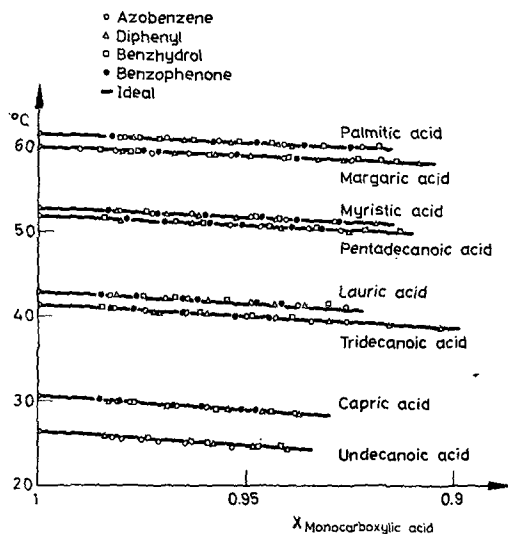Fig. 1. DTA curves of: 1) margaric, 2) pentadecanoic acids

Fig. 2. T versus x curves for the monocarboxylic acids C_{10} to C_{17}
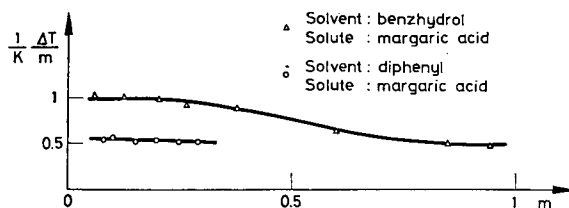
Fig. 3. Curves of $\dfrac{1}{K}\dfrac{\Delta t}{m} = 1 - \dfrac{\alpha}{2}$ (α = association degree) for the systems margaric acid (solute) and benzhydrol or diphenyl (solvents)

Table 1[a]

Calorimetric data of fusion of C_{12} to C_{17} acids

Acid	ΔH ($\pm 1\%$) (kcal/mole)	ΔH [b] (kcal/mole)	Diffusion of the curve, K
margaric	12.4	12.2	10—11
palmitic	12.3	12.98	7—8
pentadecanoic	11.0	10.30	7—8
myristic	10.1	10.74	7
tridecanoic	7.9	8.02	4—5
lauric	8.2	8.75	5

[a] Throughout this paper, $cal_{th} = 4.184$ J
[b] W. M. E. Garner, A. M. King. — J. Chem. Soc. (1929), 1849.

Table 2

Cryoscopic data of C_{10} to C_{17} acids

Acid	K_{Cr} ($\pm 2\%$) (deg/mole)	T_f° (± 0.3 K)	T_f° (°C)	ΔH ($\pm 2\%$) (kcal/mole)	ΔS ($\pm 2\%$) (cal/deg mole)
margaric	5.4	333.0		11.1	33.2
palmitic	5.2	334.6	62.6-[a] 62.30[b]	11.0	32.9
pentadecanoic	5.3	324.9		9.6	29.5
myristic	5.1	325.9	53.8[a]; 53.85[b]	9.5	29.0
tridecanoic	5.6	314.5		7.5	23.9
lauric	5.1	316 0	43.6[a]; 43.24[b]	7.8	24.6
undecanoic	6.1	299.5		5.4	18.1
capric	5.6	303.7	31.3 ;	5.6	18.5

[a] A. Eisenstein-Öl-u. Fett. Ind. nos. 19—22 (1920).
[b] R. Perron, A. Mathieu. C. Paquot, Bull. Soc. Chim. France, 1962, 2085.

Discussion

Figure 3 shows the phenomenon of dimerization, as pointed out previously [1, 7, 8]. Column IV of Table 1 gives the diffusion of the melting process; the calorimetric and cryometric measurements are useful for division of the energy of the processes:

1. monocarboxylic acid solid → monocarboxylic acid liquid
   (with very disordered lattice)
2. monocarboxylic acid solid → monocarboxylic acid solid
   (with ordered lattice)   (with very disordered lattice)

The first process occurs at the melting temperature, and the corresponding enthalpy and entropy are given in Table 2. The second process occurs in the temperature range shown in column IV of Table 1, and the corresponding enthalpy can be appraised from the difference between the enthalpy of Table 1 and the corresponding enthalpy of Table 2 (Fig. 4).
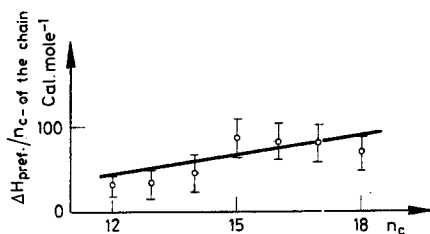

Fig. 4. Prefusion enthalpy per CH_2 group versus carbon atom number

As noted by Barr et al. [9], the importance of process 2 vanishes as the chain-length decreases. This prefusion phenomenon was explained [9] as a rocking motion of the CH_2 groups in the solid state. However, the dicarboxylic ring is probably more hindered in the solid state and induces some inertia to the near-er CH_2 groups. This is the probable reason for the decrease of the prefusion (Fig. 4).

The following equations fit the values of the entropy change corresponding to process 1:

3. $\begin{cases} \Delta S_f, \text{ even} = 2.29n - 3.59 \\ \Delta S_f, \text{ odd} = 2.56n - 9.64 \end{cases}$

According to Aranov et al. [10], the angular coefficient in similar equations for alkanes is $R \ln 3$ ($\simeq 2.18$ cal/deg.mole), i.e. very close to the angular coefficients

of Eqs 3. For comparison of the results of this paper with the corresponding values for similar organic compounds (alkanes), the quantities $\bar{S}_f = \dfrac{\varDelta S_f}{n_c}$ and $\bar{S}_f' = \dfrac{\mathrm{d}\varDelta S_f}{\mathrm{d}n}$ are analyzed. As shown in Table 3, $\bar{S}_f$ is fairly constant along the sequence of monocarboxylic acids.

Table 3

n_c	$\bar{S}_f$ (e.u.)	n_c	$\bar{S}_f$ (e.u.)
18	2.1	17	2.0
16	2.1	15	2.0
14	2.1*	13	1.8**
12	2.1	11	1.6
10	1.9		

 * mean value = 2.1 e.u.
** mean value = 1.85 e.u.

Thus the mean value can be compared with those corresponding to other similar compounds [6, 11, 12], in a similar range of chain-length.

$\bar{S}_f'$ represents the change of the melting entropy when one CH_2 group is added to the chain, i.e. it is the contribution to the $\varDelta S_f$ of one CH_2 group.
In contrast, $\bar{S}_f$ is the mean value

$$\frac{\varDelta S_f}{n_{CH_2} + n_{CH_3} + n_{COOH}} \cdot$$

If the even series is analyzed the following remarks arise: $\bar{S}_f$ falls from 2.8 e.u. to 2.1 e.u. when a CH_3 group is substituted by a COOH group. $\bar{S}_f'$ also falls, from 2.6 e.u. to 2.3 e.u. A COOH group (or its dimer) is sterically hindered more than is a CH_3 group. This fact reduces the entropy of fusion, i.e. $\bar{S}_f$. The melting entropy of the CH_2 group, $\bar{S}_f'$, diminishes from 2.6 to 2.3 e.u., probably due to an inertia effect induced by the COOH group.

Table 4

Compounds	Series	$\bar{S}_f$	$\bar{S}_f'$
		(e.u.)	
alkanes	even	2.8	2.6
	odd	2.0	2.1
monocarboxylic acids	even	2.1	2.3
	odd	1.9	2.6

For the even alkanes $\bar{S}_f > \bar{S}'_f$, and for the even monocarboxylic acids $\bar{S}_f \ll \bar{S}'_f$. The first case is probably attributable to the larger possibility of rotation of the CH_3 group (at the end of the chain) than that of the CH_2 group in the chain. The second case is attributable to the fact that the dicarboxylic ring is more hindered than a CH_2 group.

An equation connecting the melting entropy of the alkanes and monocarboxylic acids is as follows:

$$\text{alkane } \Delta S = \text{acid } \Delta S + A \quad (A = \text{correction term})$$

A = entropy loss imputable to the COOH group + entropy loss imputable to the inertia induced by the COOH group + entropy loss imputable to the difference between the CH_3 and the CH_2 groups.

$$A = (2.3 - 2.1)n + (2.6 - 2.3)n + (2.8 - 2.6)n$$

$$\text{alkane } \Delta S = \text{acid } \Delta S + 0.70n$$

The calculated values are roughly in agreement with the experimental values, as shown in Table 5.

Table 5

n	ΔS_f calculated (e.u.)	ΔS_f experimental (e.u.)
10	26	28.2
12	33	33.4
14	39	38.6
16	44	43.8
18	50	47.8

In contrast, comparison in the odd series is very complicated and imputable not only to the molecular structure. In fact $\bar{S}_f \simeq \bar{S}'_f$ for the alkanes, $\bar{S}_f$ (alkane) $> \bar{S}_f$ (acid) but $\bar{S}'_f$ (alkane) $< \bar{S}'_f$ (acid). The entropy change of the CH_2 group (in the fusion) seems be larger in the acids than in the alkanes (this fact probably arises for crystallographic reasons). The melting entropy of the dicarboxylic acids is not a regular function of the chain-length but is the sum of the melting and transition entropies [6]. For this reason comparison with the monocarboxylic acids is not possible. However, the fact that the angular coefficients in the equations

$$\Delta S_{fus} + \Delta S_{tr} = a + b \cdot n \quad (1.16 \text{ even}; 1.60 \text{ odd})$$

are smaller than those corresponding to the monocarboxylic acids, is attributable to a more rigid structure in the dicarboxylic acids.

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RÉSUMÉ — On a déterminé les enthalpies de fusion et de préfusion de quelques acides organiques par calorimétrie et cryométrie.

ZUSAMMENFASSUNG — Die Enthalpien des Schmelzens und des Vorschmelzens einiger organischer Säuren wurden durch Anwendung kalorimetrischer und kryometrischer Methoden bestimmt.

Резюме — Были измерены, используя калориметрические и криометрические методы, энтальпии предплавления и плавления некоторых органических кислот.