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THERMODYNAMIC PROPERTIES OF ORGANIC COMPOUNDS

NOTE I. A DSC STUDY OF PHASE TRANSITIONS IN ALIPHATIC DICARBOXYLIC ACIDS

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DSC measurements were used to calculate T_t, ΔH_t, ΔS_t, T_f, ΔH_f and ΔS_f for ten aliphatic dicarboxylic acids, azobenzene and benzhydrol. $\Delta S_{t,f}$ follows a regular function of the C-atom number of the aliphatic chain.

To understand properly the phase diagrams involving the dicarboxylic aliphatic acids, azobenzene and benzhydrol, the molar heat effects accompanying the solid–solid (ΔH_t) and solid–liquid (ΔH_f) transitions in these compounds were needed. The cryometric technique employed previously [1–3] was able to give an accurate ΔH_f, but it was not possible to adopt it in this case because the technique requires a longer time for the execution of the measurements.

Experimental

Materials

Succinic, glutaric and adipic acids (C. Erba), whose purities were not less than 99.5%, were recrystallized from ethanol. Pimelic, suberic, dodecanedioic and tridecanedioic acids (Schuchardt), of purities of approximetely 99.0%, were recrystallized from ethanol. Azelaic acid (Fluka, purum) was recrystallized many times from ethanol and ether, and undecanedioic acid (Fluka, purissimum, purity $\geqslant$99%) from ethanol. Azobenzene (BDH) and benzhydrol (C. Erba RP) were recrystallized from ethanol.

The melting temperatures (T_f) for the above compounds are reported in Table 1.

Apparatus and technique

The heats of fusion and solid–solid transition enthalpies were investigated with a Perkin–Elmer Differential Scanning Calorimeter (type DSC-1B). The samples were generally cycled three or four times through fusion and freezing at a heating rate of 2°/min and a cooling rate of 4°/min until room temperature. After any freezing the samples were shocked with liquid air. For all compounds the temperature range studied was from room temperature up to few degrees above the melting points.

Table 1

Calorimetric data

	T_t, °K	ΔH_t, kcal · ·mole^{-1}	ΔS_t eu	T_f, °K	ΔH_f, kcal · ·mole^{-1}	ΔS_f eu	ΔH_{tot} kcal · ·mole^{-1}	ΔS_{tot} eu
Acid:								
Succinic	—	—	—	457.0	7.874	17.23	7.874	17.23
Glutaric	348.5	0.589	1.69	371.0	4.995	13.46	5.584	15.15
Adipic	—	—	—	425.5	8.330	19.58	8.330	19.58
Pimelic	369.0	0.316	0.86	377.5	6.602	17.49	6.918	18.35
Suberic	407.0	2.159	5.31	415.5	6.970	16.78	9.129	22.09
Azelaic	—	—	—	380.0	7.810	20.55	7.810	20.55
Sebacic	—	—	—	404.0	9.753	24.14	9.753	24.14
Undecanedioic	—	—	—	385.0	9.477	24.62	9.477	24.62
Dodecanedioic	—	—	—	402.5	12.085	30.02	12.085	30.02
Tridecanedioic	—	—	—	387.5	10.826	27.94	10.826	27.94
Azobenzene	—	—	—	340.5	5.346	15.70	5.346	15.70
Benzhydrol	—	—	—	338.5	5.496	16.24	5.496	16.24

The experimental details for the calibration were reported previously [4].

The melting temperatures and solid-solid transition temperatures were taken from the peak maxima with an accuracy of ±0.5°. Enthalpy changes were calculated from peak areas with an accuracy of ±1%.

Results and discussion

Transition temperatures (T_t), melting temperatures T_f, and ΔH_t, ΔH_f, ΔS_t and ΔS_f values are reported in Table 1.

The azobenzene and benzhydrol exhibit very sharp fusion peaks while all the dicarboxylic acids present a diffuse phenomenon of fusion more evident with the chain lengthening: this is shown by the λ-shaped thermal curves. This fact is not to be attributed only to the sample purity, but to the different mechanisms of fusion. For the odd series of dicarboxylic acids it is possible to distinguish a small peak preceding the fusion. The ΔH_t values of these transitions diminish from glutaric acid to pimelic acid. Azelaic acid gives a very small peak prior to the fusion and it is not possible to evaluate the transition enthalpy. In contrast, undecanedioic and tridecanedioic acids exhibit fusion thermal curves with two very close peaks and it is not possible to separate them. Consequently, the ΔH_f value assigned is calculated from the total area of the thermal curve.

In the even series of dicarboxylic acids, only in the thermal curve for suberic acid is there a large peak adjacent to that for the fusion, but in this case it is possible to calculate the areas of the two peaks.

It is very interesting to examine the changes of the total entropy vs. the C-atom number of the dicarboxylic acid chain. Fig. 1 shows the two straight lines for the even and the odd series of dicarboxylic acids. In the dicarboxylic aliphatic acids the difference of ΔS_{tot} between the odd and the even series diminishes with the increase of the number of CH_2 groups in the chain.

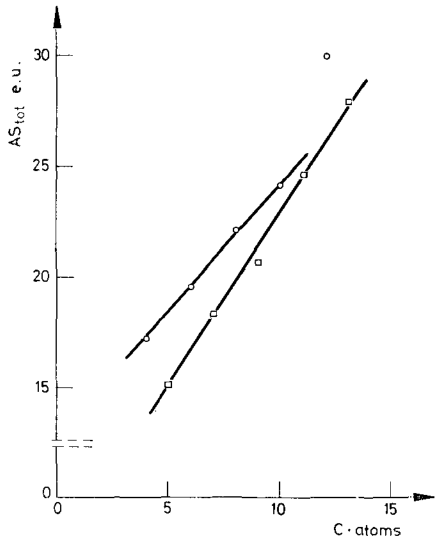

Fig. 1. ΔS_{tot} change for the even and odd series of aliphatic dicarboxylic acids

Only for dodecanedioic acid is the ΔS_{tot} value greater than that expected. This can be attributed to the beginning of a sequence at higher entropy change. The entropy of fusion of long-chain hydrocarbons increases by a factor very close to $R\ln3$ for each additional CH_2 group added to the chain [5]. It is not possible to verify this rule in the dicarboxylic acids. In fact the presence of two carboxylic groups in the chain stiffens the hydrogen-bond structure between the close carboxylic groups compared to the paraffins.

However, it is noteworthy that ΔS_{tot} is a regular function of the chain length rather than only ΔS_f. In a previous work [6] a similar relation between ΔS_{tot} and the ionic size was observed in some families of low-melting ionic melts.

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RÉSUMÉ — Mesure des grandeurs $T_t, \Delta H_t, \Delta S_t, T_f, \Delta H_f, \Delta S_f$ pour dix acides aliphatiques dicarboxyliques de l'azobenzène et du benzhydrol, par voie calorimétrique. Mise en évidence d'une relation entre ΔS_{tot} et le nombre d'atomes de carbone de la chaîne aliphatique.

ZUSAMMENFASSUNG — Die $T_t, \Delta H_t, \Delta S_t, T_f, \Delta H_f$ und ΔS_f Werte von zehn aliphatischen Dicarboxylsäuren des Azobenzols und Benzhydrols wurden kalorimetrisch bestimmt. Es wurde eine Beziehung zwischen ΔS_{tot} und der Kohlenstoffzahl der aliphatischen Kette ermittelt.

Резюме — Путем измерений на приборе ДСК рассчитаны $T_t, \Delta H_t, \Delta S_t, T_f, \Delta H_f, \Delta S_f$ для 10 албфатических дикарбоновых кислот, азобензола, бензгидрала. ΔS_{tot} является функцией числа С-атомов алифатической цепи.