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# THERMODYNAMIC PROPERTIES OF ORGANIC COMPOUNDS.

## NOTE V. ENTHALPY AND ENTROPY OF FUSION OF CAPRYLAMIDE AND STREARAMIDE

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Calorimetric and cryometric methods were employed to measure the enthalpy and entropy of fusion of caprylamide and stearamide.

Recently the thermodynamic properties of fusion of some aliphatic acids [1, 2] have been discussed and related [2, 3] to their structural properties. The results of similar research on two amides are reported in this note. We plan to study the influence of the substitution of OH by $NH_2$ on the melting properties.

## Experimental

The experimental methods employed are: cryoscopic and calorimetric. The freezing temperatures of the melted mixtures stirred by a vibro-mixer were determined with a chromel-alumel thermocouple, checked by comparison with an NBS-certified Pt resistance thermometer, and connected to a Leeds and Northrup K-5 potentiometer. The pyrex container of the melted mixtures was put in a furnace whose temperature was controlled by a second thermocouple, connected to a Leeds and Northrup CAT control unit. If certain measurements had to be repeated, an auxiliary heater was used for quick remelting. The details of this method have been described elsewhere [4, 5].

The calorimetric measurements were carried out with a differential scanning calorimeter (DSC-1B Perkin–Elmer), that records the differential energy to be supplied to keep the sample and the reference body continuously at the same temperature.

The details of the method and the calibrations have been described previously [4, 5].

The chemicals used are: Schuchardt caprylamide and stearamide, recrystallized from $C_2H_5OH$ and dried by warming in dynamic vacuum.

## Results and discussions

The melting enthalpies of the two amides were measured by employing both calorimetric and cryometric methods.

The DSC curves of caprylamide and stearamide are very diffuse, and that corresponding to caprylamide exhibits a "peak" preceding the fusion on the thermal curve (Fig. 1).

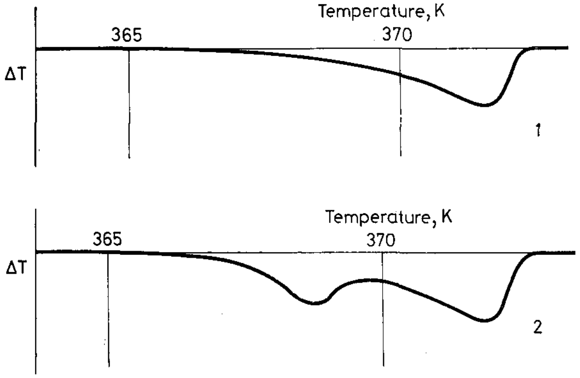

Fig. 1. DSC curves of 1, stearamide; 2, caprylamide

The $\Delta H_f$ values and the widths of the peaks are given in Table 1.

Table 1

| Substance | $T_f$, K | $(\Delta H_f)_{cal}$, Kcal/mole | $K_{cr}$, deg. molality$^{-1}$ | $(\Delta H_f)_{cr}$, Kcal/mole | $\Delta S_f$, Kcal/.mole | Width of DSC peak, K |
|---|---|---|---|---|---|---|
| Caprylamide | 374.9 | 5.8 | 7.1 | 5.7 | 15.2 | 7–8 |
| Stearamide | 373.7 | 10.9 | 6.8 | 11.6 | 31.0 | 10 |

The aliphatic acids [1, 2] and amides studied exhibit a remarkable premelting phenomenon, but in this case it is also considerable in the lower member, as shown in the DSC curves. However, the nature of the prefusion phenomenon is different in the two cases: diffuse for stearamide, "transition" type for caprylamide.

Furthermore, cryoscopic analysis of the two amides has been attempted, but in this case the melting temperatures are less reproducible, probably owing to a different manner of crystallization. In fact, the aliphatic acids crystallize in needle-shaped small crystals, whereas the amides crystallize as a solid mass; in this second case the agitation is less efficient.

The reliability of $K_{cr}$ and $\Delta H_f$ is lower ($\pm 3\%$) in this case.

The agreement between the cryoscopic and calorimetric values of $\Delta H_f$ is satisfactory (Table 1), but it is not possible to evaluate $\Delta H_{pref}$ owing to the low precision of the cryoscopic value of $\Delta H_f$. The melting entropies per C-number of the two amides are constant (1.9 and 1.7 e.u., respectively), and the value of 1.8 can represent with a good probability the mean value of $\bar{S}_f = \frac{\Delta S_f}{n_{\text{carbon atoms}}}$ for the even series.

In Table 2 $\bar{S}_f$, as defined previously [2], is reported for the paraffins, monocarboxylic acids and amides (even series); it is evident that the melting entropy per C-number decreases in the order paraffins, monocarboxylic acids, amides.

This fact shows that in the amides the entropy change in the fusion decreases, probably owing to a more rigid structure produced by the larger number of hydrogen bonds.

Also, $\bar{S}'_f \simeq \frac{(S_f)_{C_{18}} - (S_f)_{C_8}}{10}$ is lower than those found for the acids and the paraffins $\left(\text{where } \bar{S}'_f = \frac{dS_f}{dn_{\text{carbon atoms}}}\right)$ and the probable explanation is that: the larger number of hydrogen bonds (cis or trans type [6, 7]) stiffens more the amide group, and due to the inertia, also the methylene chain.

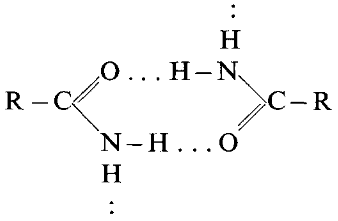

Table 2

| Substances | $\bar{S}_{f(\text{e.u.})}$ | $\bar{S}'_{f(\text{e.u.})}$ |
|---|---|---|
| Even amides | 1.8 | 1.6 |
| Even acids | 2.1 | 2.3 |
| Even alkanes | 2.8 | 2.6 |

Table 3

The ratio $\frac{\Delta t}{K_{cr}\, m}$ for stearamide (solute) in diphenyl (solvent)

| $\frac{\Delta t}{K_{cr} m} = 1 - \alpha \cdot \frac{n-1}{n}$ | $m_{\text{stearamide}}$ |
|---|---|
| 0.903 | 0.0417 |
| 0.871 | 0.0815 |
| 0.841 | 0.1229 |
| 0.810 | 0.1480 |
| 0.730 | 0.1782 |

However, these bonds are not so strong as in the aliphatic acids. In fact, by employing caprylamide and strearamide as cryoscopic solutes in polar or non-polar solvents the ratio $\frac{\Delta t}{K_{cr}m}$ is in any case close to unity at low concentrations (Table 3) $\left(\text{where } \frac{\Delta t}{K_{cr}m} = 1 - \alpha\frac{n-1}{n}\text{, for the equilibrium } n\ \mathrm{R-CONH_2} \leftrightarrow \leftrightarrow (\mathrm{R-CONH_2})_n, \alpha \text{ being the association degree}\right)$, indicating that the association degree is not important in dilute solution and does not increase much with increasing molality.

From the trends of $\bar{S}_r$, $\bar{S}_f$ and $\frac{\Delta t}{K_{cr}m}$, it can be concluded that the melting process is similar to that corresponding to the acids (i.e. feasibility of rotation of the molecule around its longitudinal axis increases on fusion), but the more branched hydrogen bonds stiffen more the amide groups and consequently the chains, even if they are weaker than in monocarboxylic acids.

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## References

1. G. Berchiesi, A. Cingolani and D. Leonesi, J. Thermal Anal., 6 (1973) 91.
2. G. Berchiesi, D. Leonesi and A. Cingolani, J. Thermal Anal., 7 (1975) 657.
3. G. Berchiesi, D. Leonesi and A. Cingolani, J. Chem. Eng. Data, Submitted, (1974).
4. M. Braghetti, G. Berchiesi and P. Franzosini, Ric. Sci., 39 (1969) 576.
5. M. A. Berchiesi, A. Cingolani and G. Berchiesi, J. Chem. Eng. Data, 17 (1972) 61.
6. L. J. Bellamy, The infrared spectra of complex molecules, Methuen & Co. Ltd., p. 203, foll.
7. J. Zabicky, The chemistry of the amides, Interscience Publishers, Series Editor S. Patai, 1970, p. 3, foll.

Résumé — On a déterminé les enthalpies de fusion du caprylamide et du stearamide par calorimétrie et cryométrie.

Zusammenfassung — Die Enthalpien des Schmelzens von Caprylamid und Stearamid wurden durch Anwendung kalorimetrischer und kryometrischer Methoden bestimmt.

Резюме — Были измерены, используя калориметрические и криометрические методы, энталпии плавления каприлового амида и стеариннового амида.