Journal of Thermal Analysis, Vol. 6 (1974) 91—99

THERMODYNAMIC PROPERTIES OF ORGANIC COMPOUNDS

NOTE II. CALORIMETRIC AND CRYOMETRIC ANALYSIS OF STEARIC ACID FUSION

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(Received July 12, 1972)

By employing calorimetric and cryometric methods, the melting total and the pre-melting enthalpies of stearic acid were measured and the phase diagrams of the solid-liquid equilibria stearic acid + A (where A is an aromatic compound or a dicarboxylic acid or I_2) were determined.

In this paper the results of calorimetric and cryometric studies on stearic acid are reported.

Experimental

The calorimetric measurements were performed with a Perkin – Elmer Differential Scanning Calorimeter (DSC-1B). The details of the calibration were given in previous papers [1, 2]. The description of the cryometric measurements method is reported in the notes [3, 4]; the crystallization temperatures of the melts were

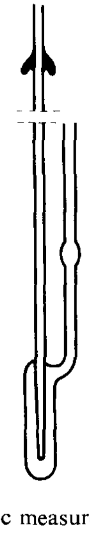


Fig. 1. Cell for the cryometric measurements of volatile substances

measured with a Chromel-Alumel thermocouple, checked by comparison with an NBS-certified Pt resistance thermometer, and connected with a Leeds and Northrup type K5 potentiometer. For the systems employing a component with high vapor pressure, the measurements were carried out in the closed cell shown in Fig. 1.

The chemicals employed: stearic, suberic, sebacic and pimelic acids, diphenyl, *o,m,p*-terphenyl (Schuchardt); malonic, succinic, glutaric, adipic and benzoic acids, benzohydrol, benzophenone, iodine (C. Erba R. P.); azealic acid (K. & K); azobenzene (BDH); were recrystallized from C_2H_5OH and dried under vacuum.

Results

Calorimetric measurements

The DTA curve of stearic acid from 0°C until the melting temperature exhibits a continuous phenomenon that starts 50°C below the melting temperature, as shown in Fig. 2. It is not possible to separate this "diffuse" phenomenon graphically into two components (fusion and prefusion), because the curve does not, as in other cases [1, 5, 6], show any discontinuity.

The enthalpy of the total diffuse phenomenon (ΔH_f) is 13.8 kcal/mole (accuracy $\pm 1\%$) and the melting temperature T_f is 342°K.

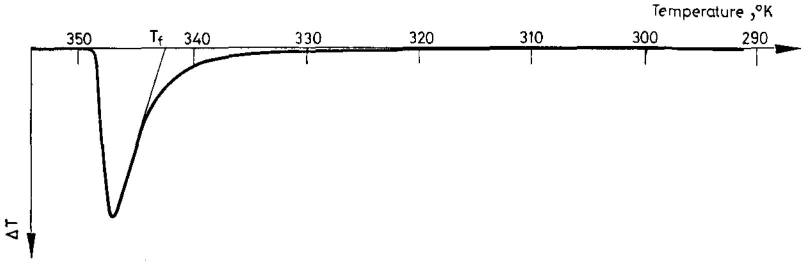


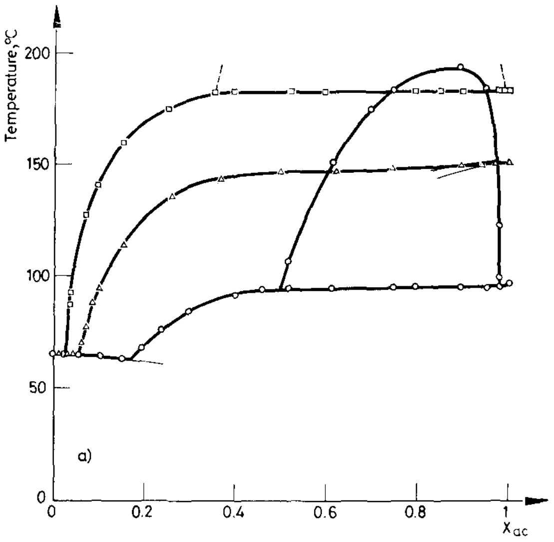
Fig. 2. DTA curve of a sample of stearic acid at a heating rate of 1°K/min

Table 1

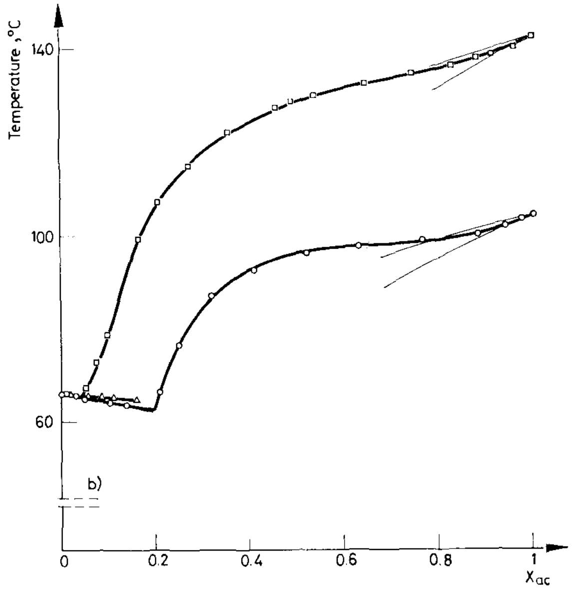
Solute	K°_{cr}, deg.molality^{-1}	$\overline{K^\circ}$	ΔH_f (kcal/mole)	T_f, °K	ΔS_f, cal/°K mole
$COOH(CH_2)_3-COOH$	5.30	5.15	12.6	339.3	37.14
$C_6H_5-C_6H_5$	5.00				
$C_6H_5-N=N-C_6H_5$	4.81				

Cryometric measurements

Some measurements of the cryoscopic constant (K_{cr}) were carried out to evaluate ΔH_f. The phase diagrams of the solid–liquid equilibria $C_{17}H_{35}COOH$ + A

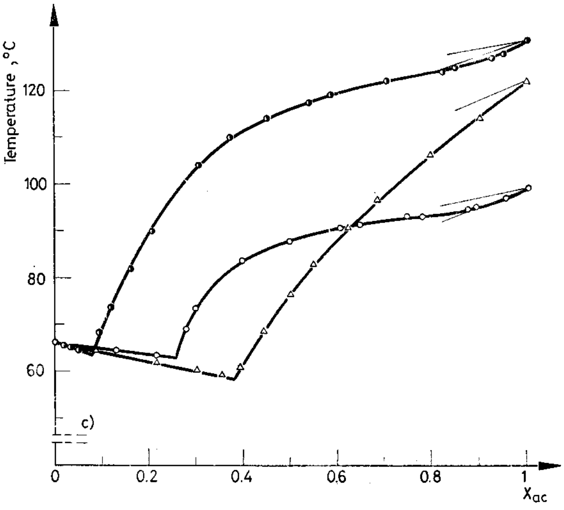


a)

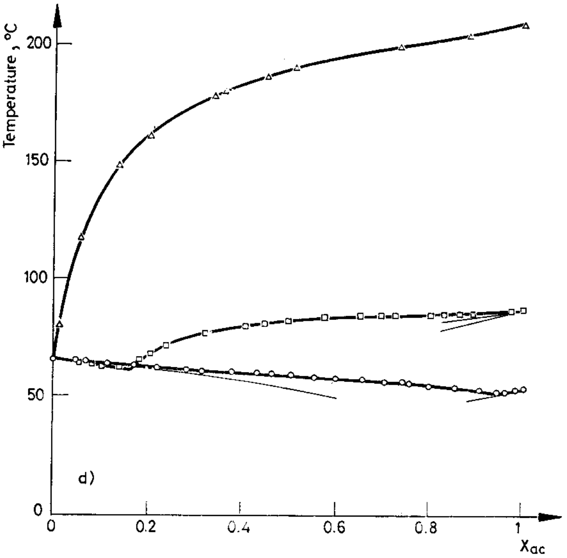


b)

(where A is an aromatic compound or a dicarboxylic acid or I_2) were determined (Fig. 3). Only the systems showing a high slope of the branch richer in stearic acid were chosen for the cryoscopic constant measurements. The non-linear depend-



c)



d)

e)

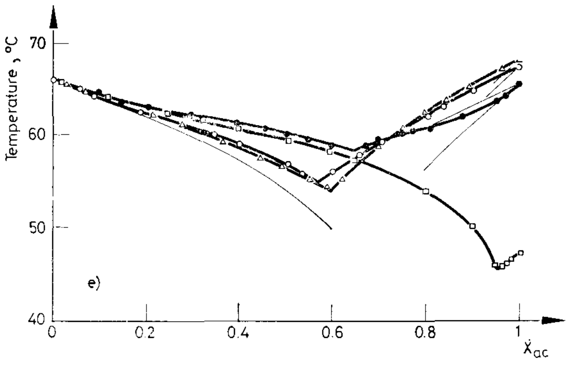


Fig. 3. Liquid-solid equilibria in the binary systems composed by stearic acid and: a) □ succinic acid, △ adipic acid, ○ glutaric acid; b) □ suberic acid, ○ pimelic acid, △ I_2; c) ◑ sebacic acid, ○ azelaic acid, △ benzoic acid; d) ○ ortho-terphenyl, □ meta-terphenyl, △ para-terphenyl; e) ● benzohydrol, △ diphenyl, □ benzophenone, ○ azobenzene

ence between the molality (m) and the K_{cr} is shown in Fig. 4. To extrapolate to $m = 0$ $\log \Delta T/m$ was plotted vs. m. The values of K_{cr} for the different solutes, T_f, ΔH_f (accuracy $\pm 2\%$) and ΔS_f calculated are reported in Table 1.

Discussion

Some works on the fusion of stearic acid exist in the literature [7–9]. Perron et al. found a melting temperature of 69.9°C (measured by DTA methods); Mod et al. evaluated the melting enthalpy from the slope of some crystallization curves and proposed the value of 16.8 kcal/mole; by NMR and IR methods Barr et al. found a small fraction of disordered lattice until 50°C below T_f.

The melting temperature determined by the DSC method agrees with the value of Perron, but is 3°C higher than that obtained by the cryoscopic measurements. We think that this difference is to be attributed to the dynamism of the DSC or DTA methods and we propose the cryoscopic value $T_f = 339.3$°K.

The $\Delta H_f = 16.8$ kcal/mole proposed by Mod is very much higher than the 13.8 kcal/mole proposed by us for the total phenomenon. Mod's value was probably calculated for the high concentration range where the non-ideal behaviour of the solutions can affect the calculations.

The results of Barr et al. agree with the feature of the fusion curve extended for 50°C.

Table 2 gives the coordinates of the characteristic points of the binary systems. From Fig. 3 it can be deduced that the aromatic compounds are more soluble in stearic acid than the dicarboxylic acids. Succinic and glutaric acids present a miscibility gap in the liquid state.

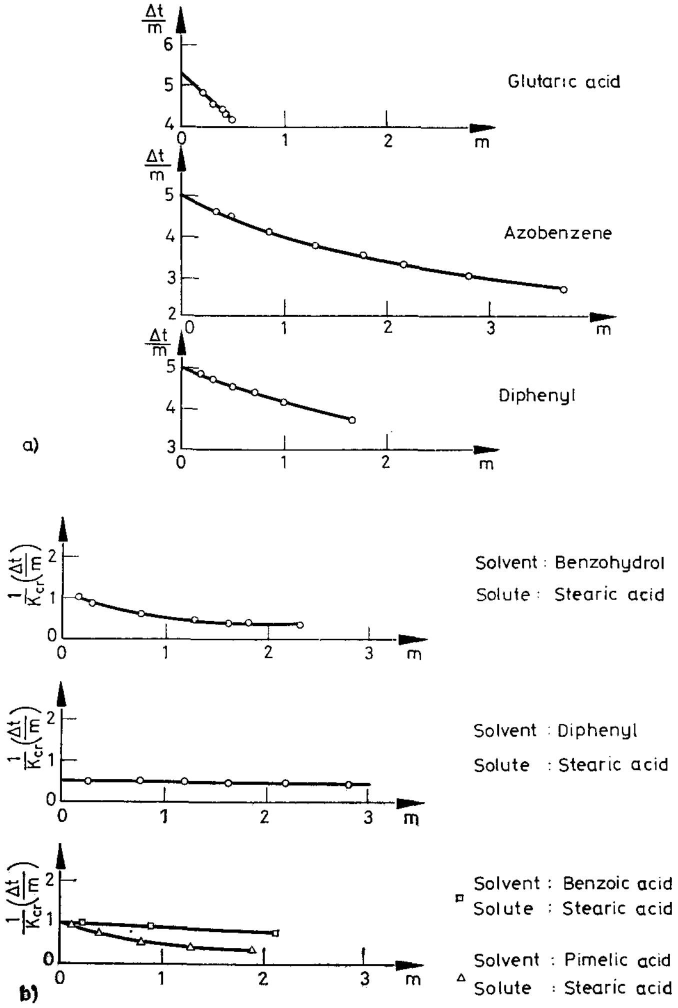


Fig. 4. Upper curve: cryoscopies in molten stearic acid. Lower curve: association of monomeric to dimeric stearic acid in different solvents

The long CH_2-chain in the molecule of $C_{17}J_{35}COOH$ seems to be the principal factor determining the solubility behaviour. In fact, the aromatic compounds are very soluble; the dicarboxylic acids with a long chain are soluble but the first members (that have high ratio "number of polar group/number of CH_2") exhibit the demixing phenomenon.

The crystallization curve of substance *A* involves a slope change when a polar group is present in the molecule of substance *A*. The results of the calorimetric (DSC) measurements have been reported in a preliminary note [10]. By employing

Table 2

Solute (A)	Eutectic		Miscibility gap			
	$^{*}x_{ac}$	T, °C	$^{*}x_{ac}^{l}$	$^{*}x_{ac}^{r}$	T_1	T_2
Benzoic acid	0.3820	58.7				
Succinic acid	0.0340	65.5	0.3500	≃0.9970	180.5	—
Glutaric acid	0.1640	63.4	0.5040	0.9800	95.5	193.0
Adipic acid	0.0500	65.0				
Pimelic acid	0.1950	62.5				
Suberic acid	0.0300	65.0				
Sebacic acid	0.0800	63.8				
Azelaic acid	0.2640	63.0				
o-terphenyl	0.9550	53.0				
m-terphenyl	0.1660	63.0				
p-terphenyl	—	—				
Diphenyl	0.5970	54.0				
Benzophenone	0.9520	45.3				
Benzohydrol	0.6600	58.5				
Azobenzene	0.5670	59.5				
I_2	0.1619	64.8				

x_{ac} = molar fraction of added component, calculated considering the molecular weight of stearic acid monomer.

x_{ac}^{l}, x_{ac}^{r} = molar fraction of added component in the left and right hand of the miscibility gap.

T_1 = monotectic temperature.

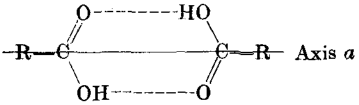
T_2 = consolute temperature.

* The molar fraction is calculated with the molecular weight of monomeric stearic acid.

Table 3

Substance	ΔH_f, cal/mole	T_f, °K	K°_{cr}	Ref.
Benzohydrol	5496.2	338.6	7.63	[10]
Diphenyl	4444.6	341.5	8.03	[13]
o-terphenyl	4568.6	327.6	10.75	[13]
m-terphenyl	6054.8	359.1	—	[13]
Benzophenone	4061.0	320.5	9.15	[11]
Benzoic acid	4140.0	395.4	9.13	[12]
Azobenzene	5346.3	340.6	7.85	[10]
Succinic acid	7874.0	457.0	—	[10]
Glutaric acid	4995.0	371.0	—	[10]
Adipic acid	8330.0	425.5	6.31	[10]
Pimelic acid	6602.0	377.5	6.87	[10]
Suberic acid	6970.0	415.5	8.56	[10]
Azelaic acid	7710.0	372.5	6.72	[10]
Sebacic acid	9753.0	404.0	6.73	[10]

these ΔH_f values the ideal crystallization curves of the substances A are calculated considering the stearic acid molecule as dimeric (upper curve) or monomeric (lower curve). From Fig. 3 it may be deduced that in the dicarboxylic acids or benzhydrol the stearic acid is monomeric at low concentration and dimeric at high concentration. It is monomeric at high concentration in benzoic acid, and dimeric in diphenyl, azobenzene or other non-polar solvents. In some solvents the behaviour is not clear (benzophenone, *m,o*-terphenyl), probably because of the solubility in the solid state. The cryoscopic constant of A is calculated from the melting enthalpy (Tab. 3) and $\Delta T/mK_{cr}$ is plotted vs. m (Fig. 4). The ratio $\Delta T/mK_{cr} = 1 - a/2$ (where a = association degree) changes from 1 to $\simeq 0.5$ for polar solvents, and is 0.5 for non-polar solvents. For this reason the stearic acid is assumed dimeric in the liquid state:



and also in the solid state.

The change solid → liquid is not sharp and the two phenomena (prefusion and fusion) are not distinguishable calorimetrically as in HCOOTl or HCOOK [1, 5] where the prefusion is a solid–solid transition near to the fusion. The thermal curve of stearic acid shows a "diffuse phenomenon of melting", because the creation of disordered centers occurs in a large range of temperature [9]. By means of the cryoscopic measurements it was possible to evaluate the melting enthalpy close to T_f (12.6 kcal/mole), that corresponds to the process:

$$\text{stearic acid, solid (with very disordered lattice)} \rightarrow \text{stearic acid, liquid} \qquad (1)$$

The remaining 1.2 kcal/mole (10% of total ΔH_f) corresponds to the creation of disorder in the stearic acid lattice, and in accordance with Barr's measurements is employed in the vibration of the methylene groups of the long chain. The high values of the enthalpy and entropy of process (1) cannot be ascribed to the breaking of the hydrogen bonds, because they exist also in the liquid state, but probably to an increase of the feasibility of rotation of the dicarboxylic ring or the methylene groups around axis *a*.

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Résumé — Mesure de l'enthalpie totale de fusion de l'acide stéarique, ainsi que de celle de pré-fusion, par calorimétrie et cryométrie. Etablissement des diagrammes de phases pour les équilibres solide-liquide du système acide stéarique + A; A désignant un composé aromatique ou un acide dicarboxylique ou I_2.

Zusammenfassung — Die Gesamt-Schmelz-Enthalpie und die Vor-Schmelz-Enthalpie der Stearinsäure werden unter Anwendung kalorimetrischer und kryometrischer Methoden gemessen und die Phasendiagramme der festflüssigen Gleichgewichte von Stearinsäure + A (wobei A eine aromatische Verbindung oder eine Dicarbonsäure oder I_2 ist) bestimmt.

Резюме — Методами и криометрии измерены энтельпии плавления и предплавления стеариновой кислоты и определены диаграммы фазы равновесия твердое тело-жидкость стеариновая кислота + A (где A ароматическое соединение или дикарбоновая кислота или I_2).