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Differential Scanning Calorimetry Studies on Urea–Carboxylic Acid Inclusion Complexes

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Abstract. Inclusion complexes of urea with several long chain fatty acids (of up to 30 C atoms) were prepared and their thermal behavior was investigated by differential scanning calorimetry (DSC). The host–guest ratios in these complexes were determined by titration against standard NaOH solution using pH to determine the end point. The DSC thermograms showed that complexes of the higher saturated acids (with 23 or more C atoms) are stable even above the melting point of urea. This is contrary to the currently accepted view that for complexes of urea and fatty acids, the outer urea lattice simply melts when the melting point of urea is reached, causing the complex to decompose.

Key words: Inclusion compounds, urea–fatty acid complexes, differential scanning calorimetry.

1. Introduction

The thermal behavior of inclusion complexes of urea with long-chain compounds has received considerable attention [1–9]. Among the techniques used have been differential scanning calorimetry (DSC), differential thermal analysis and thermogravimetric analysis. On the basis of these investigations, it is generally concluded that the inclusion complexes decompose either below the melting point of urea (132.7°C) or at this temperature when the urea melts, releasing the guest molecules. This conclusion has been drawn mostly on the basis of the observed transitions in the thermal curves which occur around the melting point of urea for several complexes. We extended the study to fatty acids with up to 30 carbon atoms and our results indicate that some complexes are stable well above the melting point of urea.

2. Experimental

The inclusion compounds were prepared following the procedure described in the literature [10–14]. A convenient amount of the carboxylic acid was added to a methanolic solution containing an excess of urea, with continuous stirring and heating (to boiling, if necessary) to obtain a clear solution. Cooling to room temperature (or 0°C, if necessary) afforded the inclusion compound. Table I lists specific literature references to the method of preparation of all the known complexes used in this study. The experimental details of the preparation of new compounds follow.

TABLE I. Symbols used for the carboxylic acids, and the host–guest ratios in the inclusion compounds of urea with these acids. Literature references for the known complexes are given in the last column

Symbol	Acid	Host–Guest Ratio in complex	Reference
C10	Decanoic acid	8.18	[10]
C12	Dodecanoic acid	9.76	[10]
C14	Tetradecanoic acid	11.0	[10]
C16	Hexadecanoic acid	12.2	[10]
C17	Heptadecanoic acid	13.8	[11]
C18	Octadecanoic acid	14.2	[10]
C20	Eicosanoic acid	14.5	[12]
C22	Docosanoic acid	15.6	–
C23	Tricosanoic acid	17.1	[11]
C24	Tetracosanoic acid	18.8	[11]
C28	Octacosanoic acid	23.7	–
C30	Triacontanoic acid	25.4	–
C13(2E)	(*E*)-2-Tridecenoic acid	10.1	–
C18(9,12,15Z)	(*Z*, *Z*, *Z*)-9,12,15-Octadecatrienoic acid	13.3	[13]
C18(9,12Z)	(*Z*, *Z*)-9,12-Octadecadienoic acid	12.9	[14]
C18(9E)	(*E*)-9-Octadecenoic acid	13.6	[14]
C18(9Z)	(*Z*)-9-Octadecenoic acid	13.3	[14]
C22(13Z)	(*Z*)-13-Docosenoic acid	16.4	–
C18(12OH)	(*R*, *S*)-12-Hydroxyoctadecanoic acid	13.4	–

U-C22: Docosanoic acid (C22) (1.00 g, 2.94 mmol) was added to a solution of urea (4.564 g, 75.99 mmol) in methanol (31 mL). This mixture was stirred and heated to boiling. Then the clear solution was allowed to cool slowly with continuous stirring to afford the white adduct (yield 3.488 g). Elemental analysis: C, 34.97; H, 8.58; N, 34.84.

U-C28: Octacosanoic acid (C28) (0.1037 g, 0.2441 mmol) was heated and stirred with methanol (100 mL) until the solution was boiling. The solution was filtered hot and urea (12.019 g, 200.1 mmol) was added to the filtrate. The mixture was reheated to boiling to give a clear solution, then cooled slowly with continuous stirring to afford the white adduct (yield 0.3591 g). Elemental analysis: C, 33.38, H, 8.26; N, 36.29.

U-C30: Triacontanoic acid (C30) (0.1033 g, 0.2281 mmol) was heated and stirred with methanol (50 mL) until the solution was boiling. The solution was filtered hot and urea (7.5 g, 0.12 mol) was added. The mixture was reheated to boiling and filtered hot. The clear filtrate was cooled slowly with stirring to afford the white

adduct (yield 0.2945 g). Elemental analysis: C, 32.98; H, 8.44; N, 37.32.

U-C13(2E): 2-Tridecenoic acid (C13(2E)) (1.031 g, 4.856 mmol) was dissolved in a solution of urea (2.931 g, 48.80 mmol) in methanol (20 mL) at room temperature. White crystals of the adduct appeared almost immediately. This mixture was stirred for 1d and then cooled to 5–10°C. Yield 1.708 g. Elemental analysis: C, 33.80; H, 7.98; N, 34.75.

U-C22(13Z): (*Z*)-13-Docosenoic acid (C-22(13*Z*)) (1.011 g, 2.986 mmol) was dissolved in a solution of urea (3.728 g, 62.08 mmol) in methanol (28 mL) at room temperature to afford white crystals of the adduct (yield 2.024 g). Elemental analysis: C, 35.50; H, 8.33; N, 34.80.

U-C18(12OH): 12-Hydroxyoctadecanoic acid (C18(12OH)) (1.001 g, 3.331 mmol) was dissolved in methanol (25 mL) and the solution was filtered to remove insoluble, suspended particles. Urea (3.522 g, 58.64 mmol) was added to the filtrate and the mixture was stirred at room temperature for about 2 h to afford the white adduct (yield 1.210 g). Elemental analysis: C, 33.40; H, 7.85; N, 34.50.

The complexes were shown to be free from co-included methanol through chromatographic analysis. Approximately 20 mg of the complex was dissolved in about 0.5 mL of A.R. quality 95% ethanol and the solution was examined using a Perkin-Elmer Sigma 3B gas-liquid chromatograph. By preparing a standard solution of methanol in ethanol and injecting it into the chromatograph, the lower limit of detectability of methanol was established. It was estimated that, if present at all, the amount of methanol must be less than 0.01 mole per mole of the fatty acid.

The host (urea)–guest (acid) ratios were obtained by determining the amount of acid in a weighed amount of the complex through pH titrations against a standard NaOH solution. The complex (about 200 mg) was dissolved in 50 mL of 95% ethanol/water (4 : 1 in most cases) by stirring and heating, if necessary (adducts with C18, C20, C22, C23, C24, C28, and C30). The temperature of the solution was maintained on a hot-plate stirrer during titration with standard sodium hydroxide (about 0.1 M in most cases) using a pH meter calibrated with buffer solutions of pH 7.02 and 4.00. The manual temperature compensation on the meter was set to the initial temperature of the solution.

D.S.C. measurements were made on a Shimadzu DT 30 thermal analyzer, using an aluminum sample holder in which a weighed amount of the dry compound was placed. A similar cell was used as the blank. An atmosphere of nitrogen was maintained around the cells, with the gas flowing at a rate of 5 mL/min. The heating rate was 10°C/min. The calorimeter was calibrated by making a run with a weighed amount of indium metal, whose heat of fusion is known accurately. A precision planimeter was used to measure the area under the peak at the transition point. In

TABLE II. Onset temperatures and enthalpies of transition of urea–fatty acid complexes. For the complexes for which only the total enthalpy is given, the individual peaks were not resolved

Urea–Acid Complex	Transition Temp. °C	Fusion Temp. °C	$\Delta H_{trans.}$	ΔH_{fusion}	ΔH_{total}
				[kJ/mol of acid]	
U-C10	105	130	54.8	108	
U-C12	113	130	81.9	124	
U-C14	121	130	90.4	170	
U-C16	125	130	99.0	208	
U-C17	126	132	–	–	302
U-C18	129	132	–	–	307
U-C20	130	134	–	–	325
U-C22	131	136	–	–	365
U-C23	133	139	–	–	414
U-C24	135	139	–	–	433
U-C28	135	141	191	245	
U-C30	136	141	207	283	
U-C13(2E)	119	130	86.1	161	
U-C18(9,12,15Z)	87	130	71.4	187	
U-C18(9,12Z)	88	130	98.0	190	
U-C18(9E)	111	130	97.9	191	
U-C18(9Z)	111	130	95.1	194	
U-C22(13Z)	114	131	109	254	
U-C18(12OH)	123	131	99.5	190	

different runs on the same complex, the enthalpies of transition were reproducible to within ±1%.

3. Results and Discussion

The general feature of the thermograms (Figure 1) is that there is an endothermic transition which takes place at a temperature that increases with the number of carbon atoms in the guest fatty acid molecule, followed by another endothermic transition which for the lower carbon number complexes, corresponds to the melting point of urea. Table II lists the temperatures and the enthalpies associated with both the peaks for each complex. Where the two peaks were not resolved, the sum of the two enthalpies is given. In each case, the temperature quoted is the onset temperature. For complexes of saturated acids, the lower transition temperature ranges from 105°C for urea–decanoic acid (U-C10) to 136°C for urea–triacontanoic acid (U-C30). The complexes between urea and C24 and higher acids show no transition corresponding to the melting point of urea, their first transition being well above 132.7°C. This suggests that even if these complexes are heated to the nor-

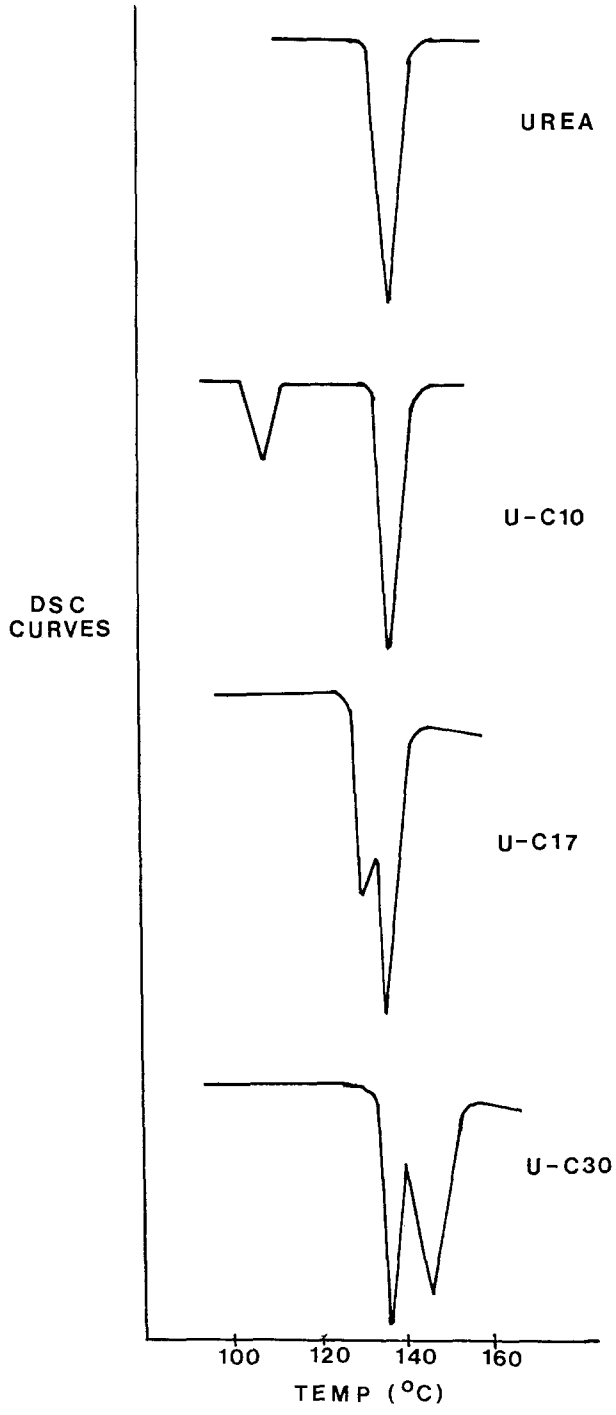

Fig. 1. DSC curves for urea, urea–decanoic acid, urea–heptadecanoic acid and urea–triacontanoic acid.

mal melting point of urea, the urea lattice remains intact. This is contrary to the accepted view (formed on the basis of the studies on acids C20 and below) that such complexes cannot be stable above the melting point of urea because the outer urea lattice simply melts at 132.7°C [3]. Stability at temperatures higher than this has been reported with certain polymers. For example, the adduct of the polyether poly(ethylene oxide), which has a molecular weight as high as 4 000 000, dissociates near 140°C [15].

If heating is stopped after the lower temperature transition, the complex allowed to cool and the thermogram rerun on the same sample, the same transition is observed again showing that it is a reproducible, reversible transition and, therefore, cannot correspond to decomposition or dissociation of the complex. If, on the other hand, the heating was continued beyond the second peak before the sample was cooled and reheated, the lower temperature transition was not observed, confirming that the complex had decomposed and melted. Since for higher saturated fatty acid adducts, this temperature is above the melting point of urea, this must be a congruent melting process. However, since the existence of the complex presupposes a urea lattice with the fatty acid trapped in it, the melting process implies the decomposition of the adduct to its constituents, urea and the acid.

The central point of this study, (i.e., the melting point of urea does not necessarily set an upper limit to the temperatures at which these compounds are stable), was confirmed by observing the physical appearance of the complex U-C30 as it was heated in an ordinary melting point apparatus. The complex did not melt or change in appearance till it reached 146°C, when a smaller liquid layer appeared over an opaque white layer. This temperature corresponds to the second peak of the thermogram, the onset of the first peak being at 136°C.

Previous investigations on the nature of the pre-melting transition in these complexes [3,4,9,18] have identified it with decomposition or dissociation before melting. However, our observation that this transition is reversible confirms that it does not represent decomposition of the complex.

A transition at much lower temperatures (around 205 K to 250 K depending on the chain length of the acid) has been reported for urea–acid complexes [6,12]. X-ray investigations showed this transition to correspond to transformation from an orthorhombic lattice to the ordinary hexagonal lattice as the complex was heated [6]. This transition has also been studied by NMR (^{1}H, ^{2}H) [6,16,17] and vibrational spectroscopy (infrared and Raman) [12]. It is regarded as an order–disorder transition of the included guest molecules involving concomitant changes in the urea lattice structure. It is possible that a similar but higher energy transformation in the structure of the complex occurs at the pre-melting transition discussed in the present study.

The host–guest ratios determined by titrating the acid are given in Table I. In principle the elemental analyses should have been sufficient for determining the host–guest ratios. However, in practice, the propagation of errors in the calculations makes this an unreliable method for the purpose. An error of 0.5% in the value

for C, which is generally considered permissible in elemental analyses, propagates to an error of 0.7 units in the host–guest ratio. An error of 0.7% in the value for N translates to an error of about 1.4 in the host–guest ratio. Within these limits, however, the host–guest ratios calculated from the elemental analyses agree with the values obtained by titration.

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