Journal of Thermal Analysis, Vol. 50 (1997) 559-567

PHASE DIAGRAMS OF UREA INCLUSION COMPOUNDS
2. Stearic acid and urea

Maria Kuhnert-Brandstätter and A. Burger

Institute of Pharmacognosy, University of Innsbruck, Josef-Moeller-Haus, Innrain 52
A-6020 Innsbruck, Austria

(Received October 10, 1996)

Abstract

The stearic acid-urea binary system exhibits an unusual phase diagram, which, on the one hand, indicates an incongruently melting inclusion compound and on the other hand a miscibility gap in the liquid phases. The peritectic point lies near the melting point of urea and the unstable congruent melting point of the inclusion compound coincides with the melting point of urea. In addition to the processing of the phase diagram, the pure inclusion compound was prepared and its DSC curve, FTIR spectrum and X-ray diffractogram were recorded.

Keywords: binary systems, inclusion compounds, stearic acid, urea

1. Introduction

In an earlier paper the binary system of palmitic acid and urea was described and the unusual nature of the phase diagram of a long-chain aliphatic acid with urea was further explained [1]. The point worth mentioning was that two types of phase diagrams were combined, that of an incongruently melting addition compound and a miscibility gap in the liquid phases. According to Schlenck [2], long-chain aliphatic compounds and urea form nonstoichiometric channel inclusion compounds. The combination with miscibility gaps was unknown.

In addition to the binary system discussed in the above-mentioned paper and this one, other long-chain compounds have been found, which form with urea inclusion compounds as well as miscibility gaps in the liquid phases. Lauric acid, myristic acid and 1,10-decanediol [3] were tested with the contact method [4–6], while the pentadecanoic acid and urea system, which is particularly complicated, will be discussed in a later study.

A further and so far unknown phenomenon related to channel inclusion compounds is the formation of liquid crystals. The inclusion compound of octadecanedioic acid (*m.p.* 126°C) melts at 137°C to a smectic liquid phase with a focal-conic fan texture, for which the clearing point lies at 152°C [3]. As octadecanedioic

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

acid is no longer on the market and our supply only met the needs for testing contact preparations, no phase diagram was produced for this interesting binary system.

2. Experimental

2.1 Materials

Urea puriss. cryst., and stearic acid for biochemistry, were supplied by Merck, Darmstadt, Germany.

2.2 Methods and instruments

2.2.1

For thermal analysis differential scanning calorimetry was mainly used, because thermomicroscopy was extremely disturbed by the miscibility gaps in the liquid phases [1]. We used a Perkin-Elmer DSC7-model (Norwalk, CT, USA). The sample mass was 1.5 to 2±0.0005 mg, weighed on Mettler ultra-micro balance UM3 (Greifensee, Switzerland). The heating rate was 5 K min^{-1}.

2.2.2

The thermomicroscopic investigations were carried out by using a Kofler hot stage microscope (Reichert, Vienna, Austria) by means of the contact method. In this case it was necessary to use more urea than usual to produce a contact preparation, so that 2/3 of the space between the object slide and the cover glass were filled with melt. The reason for this is that, during the formation of the compound, at a higher temperature the whole melt of stearic acid flows over the crystal film of the urea. If too much stearic acid is present, the contact zone between the urea and the inclusion compound is lost, and a crystal film results, which only comes from the inclusion compound. In addition, it was helpful to place the urea crystals under the cover slip just before melting, so that sublimation and decomposition could be kept to a minimum. After crystallization of the urea, some crystals of the lower melting stearic acid were melted alongside the cover slip, so that the liquid filled the remaining space under it.

2.2.3

For recording the FTIR spectra we used a Bruker FTIR spectrometer, connected with a Bruker FTIR microscope (Bruker Analytische Meßtechnik GmbH, Karlsruhe, Germany). The X-ray diffractograms were created with a Siemens D-5000 X-ray diffractometer. Details of the two instruments and methods described in section 2.2.3 have been published elsewhere [7, 8].

3. Results and discussion

3.1 Description of the components

3.1.1 Stearic acid

Quite some time ago, four polymorphic forms of stearic acid were described and enantiotropy between mod. I and mod. II was determined [9]. Since then, many studies of the crystal structure, the thermodynamic stability and the crystallization requirements of polymorphic forms have been published, which were discussed along with other long-chain aliphatic compounds in a review paper by Sato and Kobayashi [10]. According to the opinions of these authors, stearic acid demonstrates an unusual stability relationship between forms B (mod.II) and C (mod.I), similar to palmitic acid, for which four modifications are known. While the solubility curves of B and C intersect at 32°C, which allows enantiotropy to bread down, the solid to solid transformation of B to C is irreversible. The absence of the retransformation of C to B was designated as a steric hindrance. A and E, the two other forms are also considered due to their solubility as unstable and are irreversibly transformated to mod.C.

The substance we used was mod. C with *m.p.* 69°C. In the context of the present studies, the polymorphism of stearic acid is meaningless, because in the melt and also in the phase diagram with urea only mod.C appears.

3.1.2 Urea

The polymorphism of urea can only be realized by high pressure; under normal pressure, only one modification with *m.p.* 134°C exists.

3.2 The stearic acid-urea binary system

3.2.1 Contact preparation

The contact preparation is generally an excellent possibility for studying the essential features of a phase diagram. In the particular cases of the miscibility gaps in liquid phases discussed here, it is especially important, because, for example, DSC does not register the miscibility gaps. Because of the absence of unlimited miscibility of the liquid phases, the contact zone remains necessarily narrow, even when the preparate is heated beyond the melting point of urea. After rapid cooling of the melt of stearic acid on a cold metal block, the two crystalline phases momentarily come into contact without forming the inclusion compound (IC). Changes in the contact zone can be observed only with slow heating on a hot stage: needles of IC fall out of the primary crystals bordering the stearic acid and on the crystal front of urea a faint, thin crystal stripe of IC forms under polarized light. Between the IC and the stearic acid, an eutectic stripe melts at 68.5°C, which is immediately followed by the melting of the pure stearic acid at 69°C. On increasing the temperature, the needles in the melt slowly dissolve, while in the urea crystals the compact stripe of the IC grows equally slowly. At temperatures between 80 and 100°C, the whole melt of the stearic acid flows over the urea crystal film, at which point the crystal stripe of the IC grows rapidly in the urea

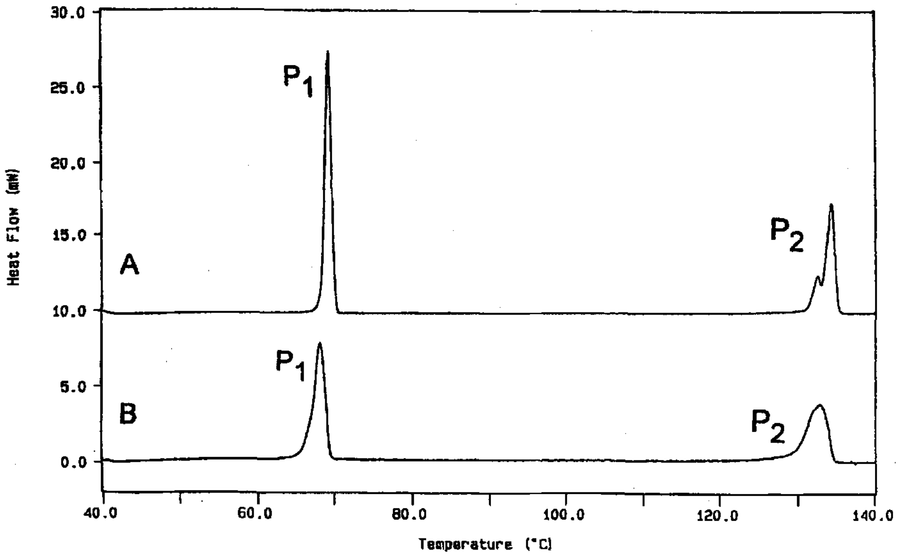

Fig. 1 DSC curves of the 30% urea and 70% stearic acid mixture: A first run, B second run

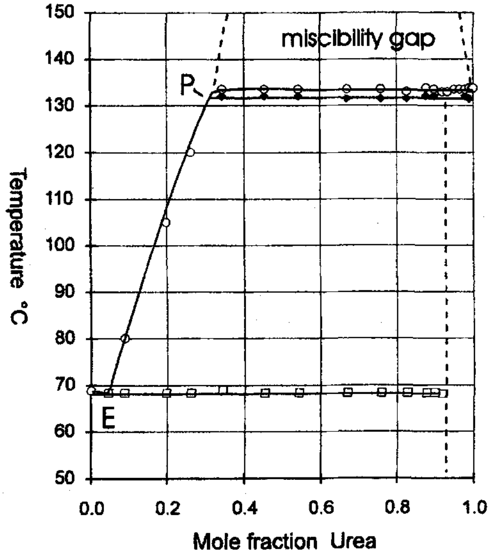

Fig. 2 Phase diagram stearic acid and urea

and a great number of IC nuclei form spontaneously in the crystal film. The contact zone between the IC and the urea can be observed only when relatively little stearic acid melt is present. The re-transformation of the IC through urea first occurs at 132°C. At 133.5, after removal of a polarization filter and restriction of the light bulb with the help of an iris diaphragm, on the remaining urea crystals the formation of a separation line between the liquid phases can be seen. The melt around the crystals consists of urea saturated with IC, and the IC melt outside the separation line is saturated with urea.

It can occur that in isolated places the re-transformation of IC through urea does not appear and the congruent melting point of IC can be observed. This practically coincides with the melting point of urea, at which in some places the IC can melt 1 to 2 tenths of a degree higher than urea, and in other places urea can melt at a slightly higher temperature than the IC. Because of the intensive study

Table 1 Eutectic temperature (*ET*), peritectic point (*P*) and melting point (*m.p.*) of the system stearic acid and urea

Urea/mass %	*ET*/°C	*P*/°C	*m.p.*/°C
0	–	–	69
1	68.5	–	–*
2	68.5	–	ca. 80*
5	68.5	–	ca. 105*
7	68.5	–	ca. 120*
10	69	132	133.5
15	68.5	132	133.5
20	68.5	132	133.5
30	68.5	131.5	133.5
40	68.5	131.5	133.5
50	68.5	131.5	133
60	68.5	132	134
65	68.5	132	133.5
70	68	shoulder	133
75	–	shoulder	133
80	–	shoulder	133.5
85	–	shoulder	133.5
90	–	132	133.5
95	–	131.5	134
98	–	–	134
100	–	–	134

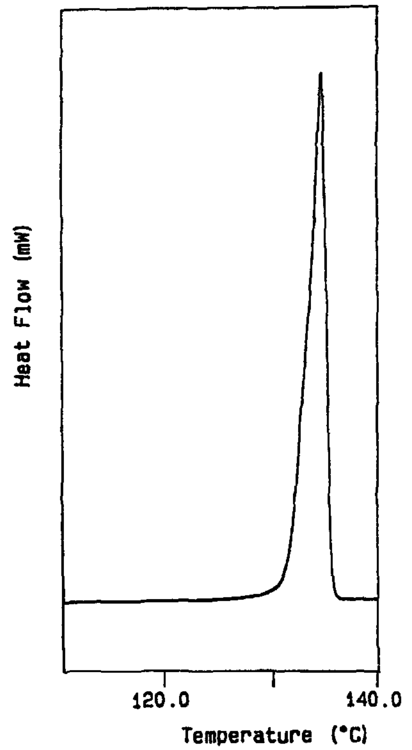

Fig. 3 DSC curve of the inclusion compound stearic acid-urea

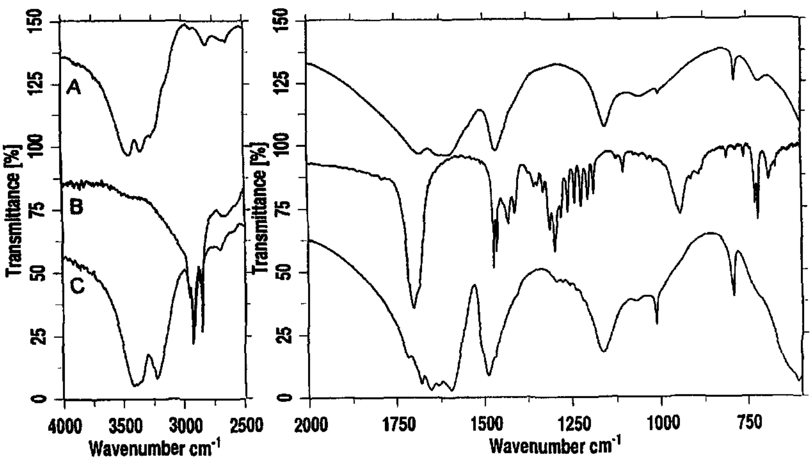

Fig. 4 FTIR spectra of urea (A), stearic acid (B), inclusion compound (C)

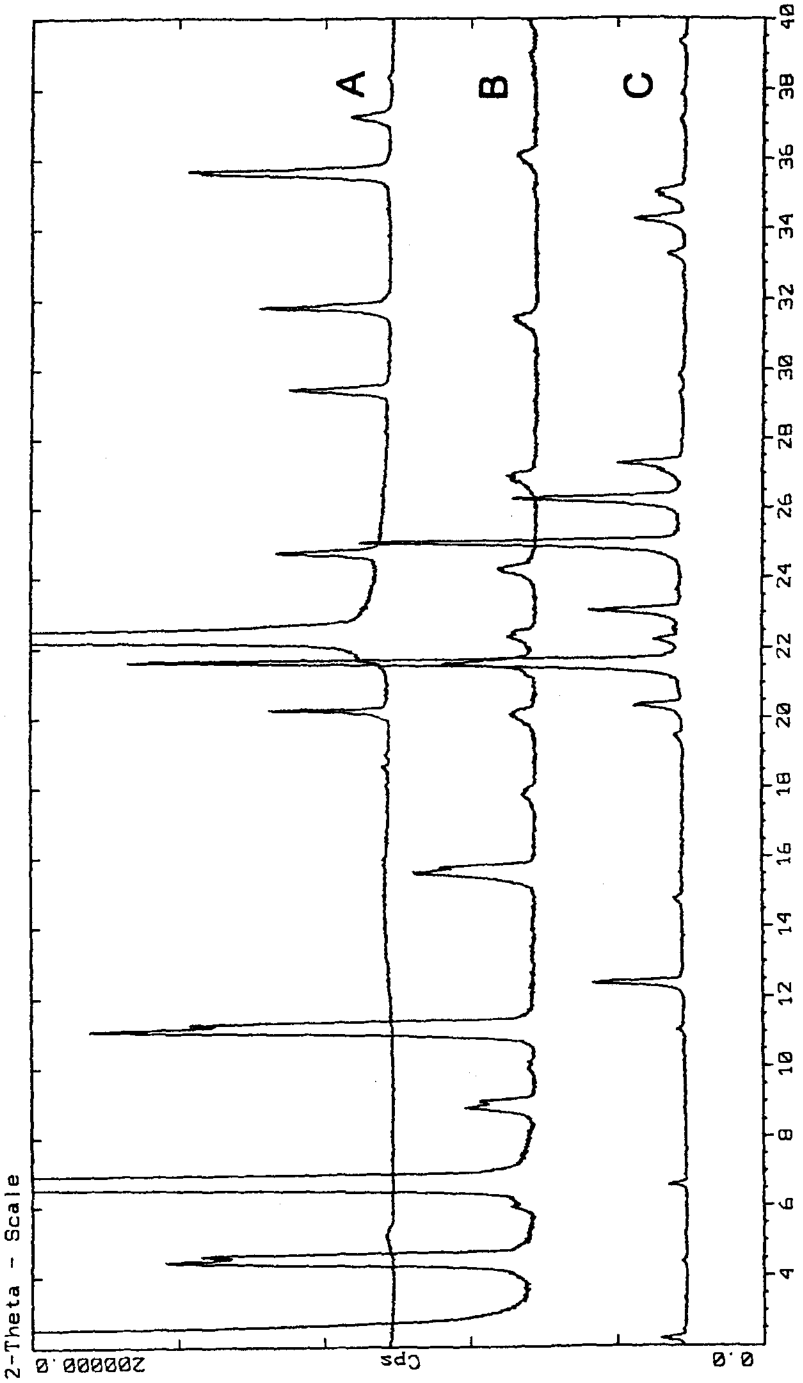

Fig. 5 X-ray diffractograms of urea (A), stearic acid (B), inclusion compound (C)

of the contact preparation it was possible to clarify the contradictions which occur with the DSC-analysis of powder mixtures and solidified melts.

3.2.2 Phase diagram of the stearic acid-urea system

We have already reported the general difficulties caused by the miscibility gaps that occur in the recording of a phase diagram in another paper [1]. With few exceptions (1 to 7%), the values ascertained in the DSC analysis could be used. While we normally analyze the peaks of a phase diagram that are obtained from the solidified melts of the mixture (second run), this was not ideal for this system, because the peritectic reaction and the melting of urea only result in one common peak. In contrast, the peritectic reaction in the first run can be clearly seen as a small peak before the melting peak in most mixtures. In Fig. 1, the DSC curves of the mixture of 30% urea and 70% stearic acid appear (A: first run, B: second run). P1 is the signal for the eutectic temperature and P2 for the peritectic reaction and the melting point of urea. The reason for the difference lies in the limited decomposition of the urea melt, as a result of which the melting point after resolidification is lowered by approximately 1 K, so that the peritectic reaction and the beginning of the melting of urea overlap. In Table 1 the temperatures inferred from the DSC curves for the eutectic temperature, the peritectic reaction and the melting points are listed. The values are rounded to the nearest 0.5 K. Figure 2 shows the phase diagram. The composition of the IC, which, according to the results of Schlenck (2) is formed in a proportion of 14.2 molecules of urea to one molecule of stearic acid, is correspondingly drawn at a mole fraction of urea of 0.93.

3.3 Inclusion compound stearic acid/urea

The channel inclusion compound (IC) from stearic acid and urea, which is already known in the literature, was produced by stirring for three hours a cold-saturated solution of urea in methanol after addition of stearic acid crystals. The DSC curve of the IC (Fig. 3) has only one peak and its ascending part displays a slight bend. The latter was interpreted as an indication of the peritectic reaction. The FTIR spectrum of IC shows great similarity with urea in the fingerprint area, two bands in the area between 2750–3000 cm^{-1} refer to stearic acid (Fig. 4). In Fig. 5, the X-ray diffractograms of urea, stearic acid and IC are shown opposite to one another. The diffractogram of the IC also clearly displays more similarity with that of urea. Namely, with the urea inclusion compounds, the urea molecules are sitting at the edges of the length forming regular six-sided prisms, which form continuous cavities. In these channels of the basic network structure the long-chain molecules are positioned head to tail. The decisive element for the IC is therefore the urea, although in the IC it is not in the normal, tetragonal arrangement of molecules, but rather forms a hexagonal lattice.

References

1 M. Kuhnert-Brandstätter and A. Burger, Pharmazie, 51 (1996) 288.
2 W. Schlenck jr., Organische Einschlußverbindungen in: Fortschritte der chemischen Forschung, Vol. 2, Springer Verlag, Berlin, Göttingen, Heidelberg 1951, p. 92.
3 M. Kuhnert-Brandstätter, unpublished.
4 L. Kofler and A. Kofler, Thermomikromethoden, Universitätsverlag Wagner, Innsbruck 1954.
5 M. Kuhnert-Brandstätter, Thermomicroscopy of Organic Compounds in: Wilson and Wilson's Comprehensive Analytical Chemistry, Vol. XVI (Gy. Svehla, ed.) Elsevier, Amsterdam 1982, p. 329.
6 M. Kuhnert-Brandstätter, Thermomicroscopy in the Analysis of Pharmaceuticals, Pergamon Press, Oxford 1971.
7 M. Kuhnert-Brandstätter and U. J. Griesser, J. Thermal Anal., 45 (1995) 559.
8 A. Burger, J.-O. Henck and M. N. Dünser, Microchim. Acta, 122 (1996) 247.
9 L. Deffet, Répertoire des Composés organiques polymorphes, Editions Desoer, Liège 1942.
10 K. Sato and M. Kobayashi, Structure, Stability and Crystal Growth of Polymorphs and Polytypes of Long-Chain Aliphatic Compounds in: Organic Crystals I, Springer-Verlag, Berlin, Heidelberg 1991, p. 65.