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PHASE DIAGRAMS OF UREA INCLUSION COMPOUNDS
3. Pentadecanoic acid and urea

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Abstract

The phase diagram of the pentadecanoic acid and urea system consists of a combination of a binary system with two incongruently melting compounds and a system with a miscibility gap of the liquid phases. The first compound is a molecular addition compound of 1 molecule of pentadecanoic acid and 4 molecules of urea, which forms three polymorphic modifications. The second compound is a channel inclusion compound, which is known to be in a ratio of 1:12.2. In addition to the thermoanalytical investigations, FTIR spectroscopic and X-ray diffractometric analyses were also conducted for the inclusion compound as well as the stable form of the molecular addition compound.

Keywords: binary systems, inclusion compounds, miscibility gaps of liquid phases, pentadecanoic acid, urea

Introduction

It has long been known that urea forms channel inclusion compounds with long-chain aliphatic acids [1, 2]. Phase diagrams of these two-component systems, however, have only recently been examined [3, 4]. As a result, it has been seen that the inclusion compounds are transformed to urea in a peritectic reaction, which, for its part melts to a miscibility gap in the liquid phases. The present article differs from the papers cited above, insofar as in addition to the non-stoichiometric inclusion compound in the system, a stoichiometric molecular addition compound is formed, which is polymorphic and is transformed into an inclusion compound at higher temperatures.

As a result of the appearance of a miscibility gap in the liquid phases on the one hand and the polymorphism of the addition compound on the other, it was difficult to create the phase diagrams. Through the use of DSC analysis and thermomicroscopic methods, it was finally possible to produce these results.

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Experimental

Materials

Urea puriss. cryst., pentadecanoic acid, modification II, both from Merck, Darmstadt, Germany.

Methods and instruments

The DSC analyses were done with a DSC-7 model from Perkin-Elmer, Norwalk, CT, USA.

For the thermomicroscopic investigations we used a Kofler hot stage microscope Thermovar (Reichert, Vienna) and a Kofler hot bench (Wagner and Munz, Munich).

The FTIR spectra were recorded with a Bruker FTIR spectrometer connected with a Bruker FTIR microscope (Bruker Analytische Meßtechnik GmbH. Karlsruhe, Germany).

The X-ray diffractograms were produced with a Siemens D-5000 X-ray diffractometer. All of the methods and equipment mentioned here have been described in another article [5].

Results and discussion

Description of the two components

Pentadecanoic acid

Three polymorphic modifications of this aliphatic acid have long been known [6]. The enantiotropy between form II, which is stable at room temperature, and

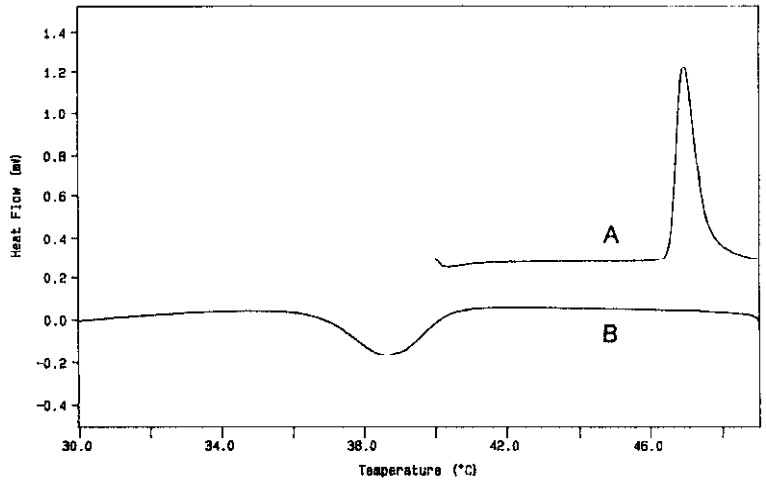

Fig. 1 DSC curves of the enantiotropic transformation of pentadecanoic acid: A on heating, B on cooling

the high temperature form I (*m.p.* 52°C) has already been described earlier. These two forms correspond to mod. B and mod. C described by Sato and Kobayashi [7]. Mod. A or III is irreversibly transformed to mod. B or II, respectively. The transformation of mod. II to mod. I occurs spontaneously at 47°C, the re-transformation begins only after a delay at 40°C (Fig. 1) and the transition point lies at 46°C [7]. Therefore, the polymorphism of this compound is relevant for the phase diagram.

The commercial product used results from mod. II, which transforms to mod. I on heating. Figure 2 shows the FTIR spectra of mod. I and mod. II, and Figure 3 shows the X-ray diffractograms of both of these mods.

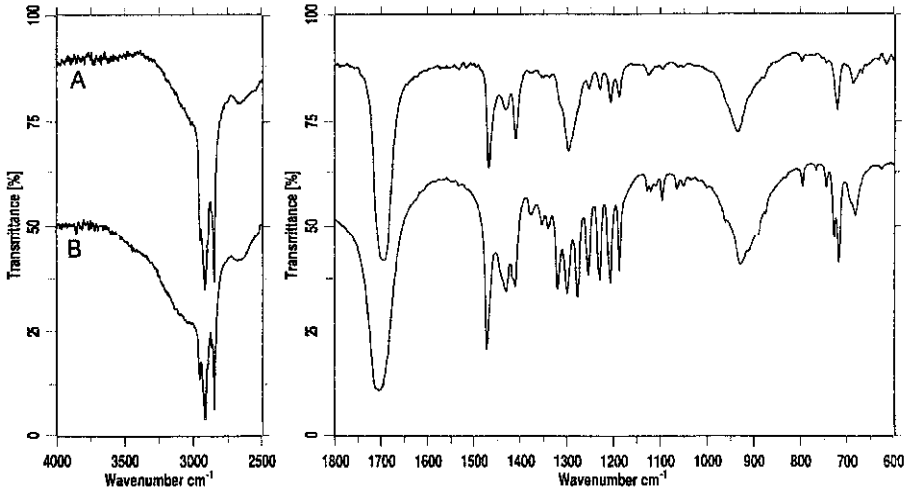

Fig. 2 FTIR spectra of mod. I (A) and mod. II (B) of pentadecanoic acid

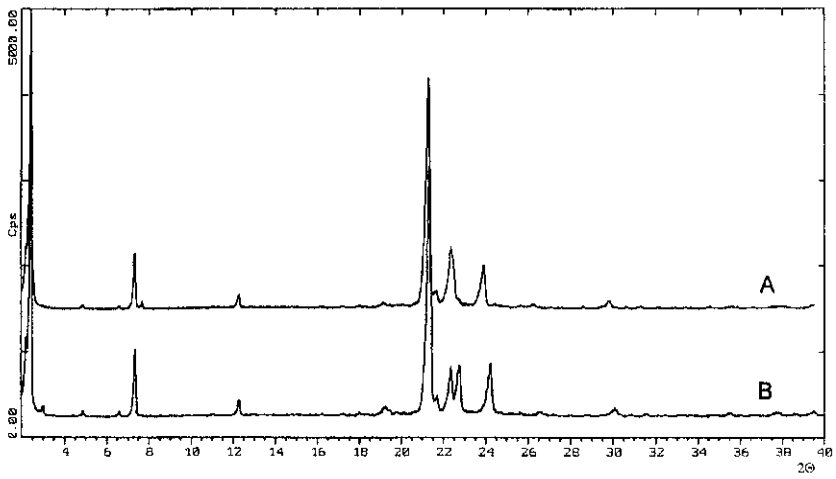

Fig. 3 X-ray diffractograms of mod. I (A) and mod. II (B) of pentadecanoic acid

For the transformation of mod. I to mod. II, an interesting phenomenon was observed in the microscope in the solidified drops of the melt. After being stored for several days, the plate-like crystals that were transformed to mod. II formed numerous zig-zag stripes, which displayed an irregular zig-zag pattern varying in width and height. Some plates were completely disintegrated to parallel zig-zag stripes, which resemble the folder structure of proteins (Fig. 4). If a melting film is allowed to cool slowly, along with the plates many fan-shaped crystals form out of mod. I, which, after transformation to mod. II, displays a similar zig-zag pattern. Rhombic structures can also be identified in the plates after transformation, which can well be considered the precursors of the zig-zag stripes. It is assumed that this phenomenon established through the use of a polarizing microscope is connected to the lattice displacement in the transformation mod. I → mod. II, because during transformation to mod. I narrow zig-zag stripes are stretched again to straight fibres.

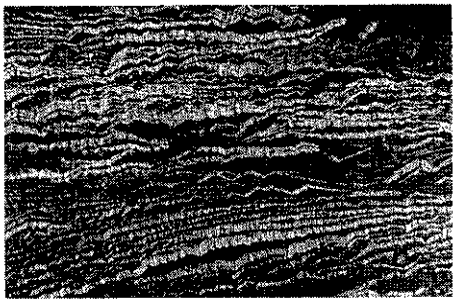

Fig. 4 Photomicrograph of a pentadecanoic acid crystal film with zig-zag pattern

Urea

As the polymorphism of urea can only be effected through the use of high pressure [6], only one modification could be noticed in our experiments (*m.p.* 134°C).

The pentadecanoic acid and urea binary system

The pentadecanoic acid and urea system is more complicated than that of palmitic acid [3] and stearic acid [4] with urea, described earlier.

Contact preparation

As in previous cases, the examination of a contact preparation [8–11] was the reason for recording the phase diagram. In order to retard the transformation of mod. I of pentadecanoic acid to mod. II, which is connected with a clouding of the crystal film, the film of melt is not brought to crystallization by laying it on a

metal plate, but rather is transferred from the hot bench on a hot stage preheated to 45°C. As a result, urea and mod. I of pentadecanoic acid crystallize. On the crystal front of urea a metastable molecular compound (MC III) forms as a narrow, bright stripe under polarized light, which grows together with pentadecanoic acid into a eutectic. When the preparation is heated, a eutectic stripe appears at 51.5°C, followed by the melting of pentadecanoic acid at 52°C. MC III melts without forming a eutectic at 56°C (peritectic point P_3). Sometimes new crystals of another phase appear between the MC III and urea; the preparation very often has to be reheated until a seam of needles forms on the crystal front of urea, which belongs to a compound with a different composition. As further studies have revealed, this is an inclusion compound (IC). It reacts in the contact preparation similarly to the IC of stearic acid with urea [4]. While the first IC crystals grow slowly as the temperature increases, the entire melt of pentadecanoic acid suddenly flows over the crystal film of urea between 80 and 100°C, during which the IC grows very rapidly. Numerous spontaneous nuclei of the IC are also formed, which generally grow in the form of large, terraced hexagons in the urea crystals. At ca. 120°C the crystallization of the IC comes to a standstill, from 125°C it melts incongruently while the urea crystals grow (peritectic point P_1). The miscibility gap is visible at 133°C. If a contact preparation that contains the IC is allowed to cool slowly, the above-described MC III which forms the eutectic with pentadecanoic acid nucleate on the crystal front of IC. It is not possible to bring the IC in contact with pentadecanoic acid. This means that below P_3 the MC III, within its region of existence, is stable in comparison the IC.

The results of the examination of the contact preparation (with the exception of the miscibility gap, which is not registered in the DSC curves) are in accord with the DSC analysis of the powder mix (first run), but cannot be found in the analysis of the solidified melts (second run). In the last analysis, additional peaks appeared which have yet to be explained.

Phase diagram of the pentadecanoic acid and urea system

As has already been described in detail, the phase diagrams of long-chain aliphatic acids with urea present great difficulties due to the miscibility gaps of the liquid phases [3]. In particular, the segment of the aliphatic acid curve which increases steeply cannot be satisfactorily determined through DSC analysis or thermomicroscopic investigations. In this case, then, the possibility of a deviation between 0 and 7% (m/m) (i.e. mole fraction of 0.0 and 0.2) of urea must be taken into account (Fig. 5).

The DSC analysis of the mixtures resulted in several surprises regarding the contact preparation. At first the curves of the first run seemed to support the results of the contact preparation. However, as we by chance conducted new DSC-analyses after approximately one year for several mixtures which had displayed

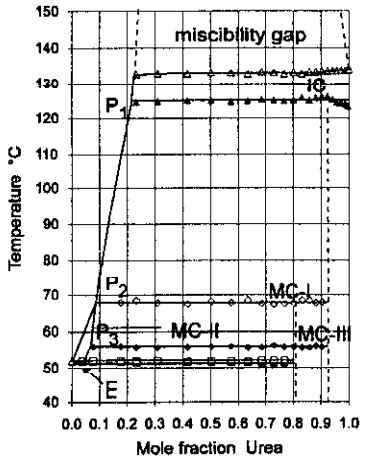

Fig. 5 Phase diagram of the pentadecanoic acid and urea system

an endothermal peak at 56°C, we found that this peak disappeared and was replaced by a new one at 68°C.

In Fig. 6 the DSC curves of the mixture of 70% pentadecanoic acid and 30% urea are shown. In curve A (recorded in 1995) P_1 stands for the polymorphic transformation of pentadecanoic acid mod. II to mod. I, P_2 for the melting of the eutectic. P_3 indicates the solidification of the melt forming MC III, P_4 signals the peritectic reaction with formation of IC, while P_5 stands for the peritectic transformation of IC to urea. Finally, P_6 shows the melting point of urea. In curve B (recorded in 1996) P_1 and P_3 of curve A are not found, because during storage

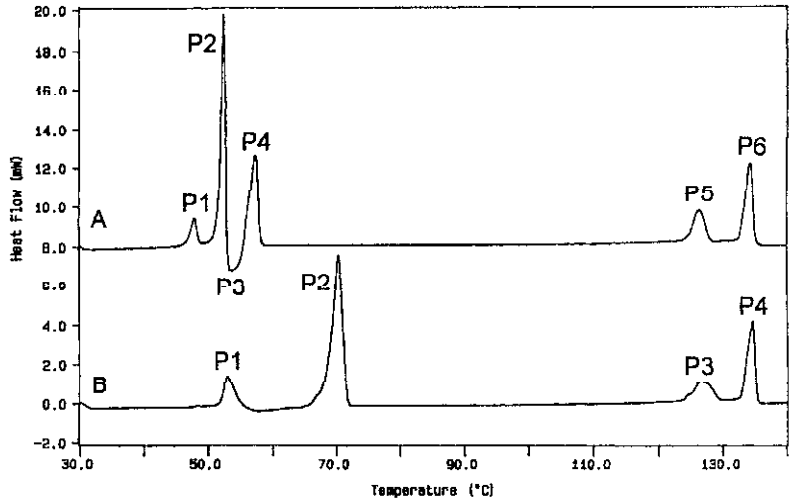

Fig. 6 DSC first-run curves of the mixture containing 70% pentadecanoic acid and 30% urea taken, A: immediately, B: after one year storage

MC I developed in the powder mixture. Due to the borderline case of the eutectic point between pentadecanoic acid and MC I, P_1 corresponds to the melting point of the acid (monotectic), while P_2 indicates the peritectic reaction MC I/IC. P_3 and P_4 have the same significance as P_5 and P_6 in curve A. In contrast to these two first-run curves, the second-run curve of the same mixture displays peaks for both modifications of the MC (Fig. 7, curve A). Because the pentadecanoic acid did not re-transform to mod. II in the solidified melt, the corresponding peak is missing. Here P_1 indicates the monotectic melting, P_2 signals the melting of MC III, P_3 the crystallization of MC I, and P_4 the peritectic reaction, in which MC I is transformed to IC. P_5 and P_6 again indicate the peritectic reaction and the melting of urea. In mixtures containing between 5 and 20% of urea an additional peak appears in the second run at 61°C, for which thermomicroscopic investigations reveal a further modification of MC. In Fig. 7, curve B illustrates the DSC curve of the mixture containing 85% pentadecanoic acid and 15% urea. In comparison to the 30% mixture (curve A), P_2' is an additional peak, which as peritectic reaction of mod. II of the MC must be interpreted. All other peaks correspond to each another.

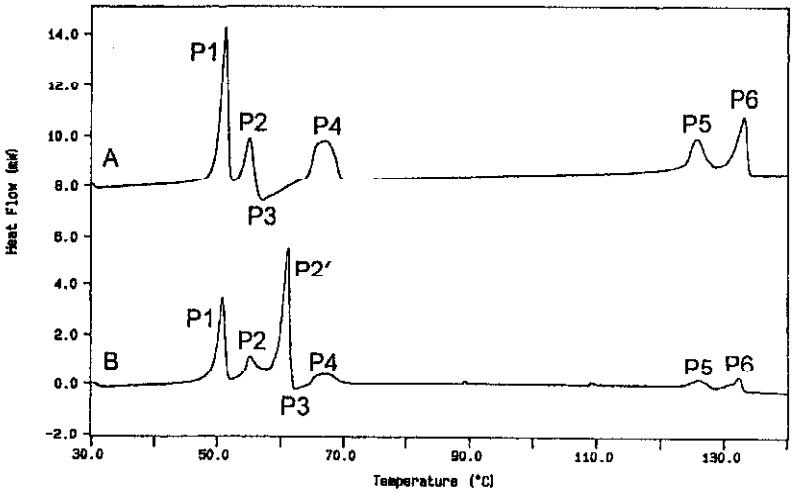

Fig. 7 DSC second-run curves: of a mixture containing 70% pentadecanoic acid and 30% urea (A), and of a mixture containing 85% pentadecanoic acid and 15% urea (B)

In Table 1 the data resulting from the DSC analyses of the mixtures are listed. These data form the foundation for the construction of the unusual phase diagram (Fig. 5). The inclusion compound (IC) is formed at a ratio of 1:12.2, the molecular compound (MC) at 1:4. Mod. II of the MC, which was only partly detectable, was not recorded in the table. Its inhomogeneous melting occurs at 61°C. The composition of the IC is in accord with the results of Schlenck [2], determined in studies of the dependence of the composition on the length of chain.

Table 1 Eutectic temperature (*ET*), monotectic temperature (*MT*), peritectic points of the polymorphic forms III (P_3), I (P_2) of the molecular compound, peritectic point of the inclusion compound (P_1), melting points (*m.p.*) of the pentadecanoic acid and urea system

Urea	*ET*/	*MT*/	P_3/	P_2/	P_1/	*m.p.*/
% (m/m)	°C					
0	–	–	–	–	–	52
1	51.7	52.0	–	–	–	–
2	51.7	52.1	56(ca.)	–	–	–
5	51.7	52.0	56.1	68(ca.)	–	–
7	51.5	51.9	55.8	68.5	124.5	132.8
10	51.8	52.0	55.7	67.9	124.7	133.0
15	51.5	51.8	55.8	67.6	125.0	133.0
20	51.5	51.9	56.0	68.2	125.0	133.2
25	51.5	51.9	56.0	67.9	124.6	133.1
30	51.5	51.8	55.7	68.5	124.8	132.8
35	51.3	52.1	55.7	67.7	125.4	133.4
40	51.4	52.0	56.2	67.4	125.0	133.1
45	51.4	52.0	55.8	67.6	124.8	132.9
50	–	–	55.8	67.8	125.0	133.2
55	–	–	55.7	68.5	125.8	132.9
60	–	–	55.7	68.4	125.0	133.4
65	–	–	56.1	67.9	125.7	133.4
70	–	–	55.8	68.0	126.0	133.6
75	–	–	–	–	126.1	133.6
80	–	–	–	–	125.2	133.7
85	–	–	–	–	124.4	133.7
90	–	–	–	–	124.2	133.8
95	–	–	–	–	124.0	133.8
98	–	–	–	–	123.4	133.9
100	–	–	–	–	–	134

The composition of the MC was difficult to determine, because the normal competent maximum for it is missing in the melting curve of the phase diagram. However, the presence of the pure MC I could be determined by the absence of a monotectic melting peak in the 50% mixture in the DSC curve (after one year of storage). The heating on the hot stage produces the same results: no melt was ob-

served below the peritectic reaction P_2 of mod. I and quantitative transformation of MC I to IC.

Inclusion compound and molecular addition compound of pentadecanoic acid and urea

The channel inclusion compound (IC) was produced by stirring a cold-saturated solution of urea in methanol and pentadecanoic acid crystals for 3 h. The DSC curve of the IC (Fig. 8) exhibits two peaks, P_1 for the peritectic reaction and

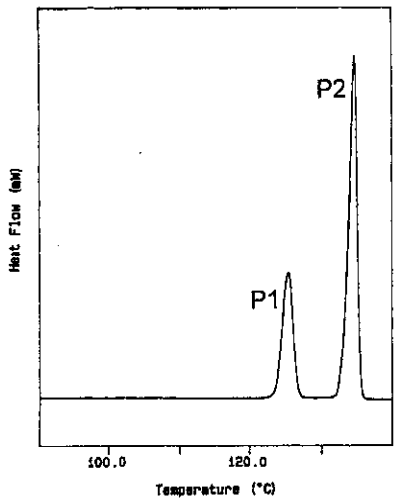

Fig. 8 DSC curve of the inclusion compound of pentadecanoic acid and urea

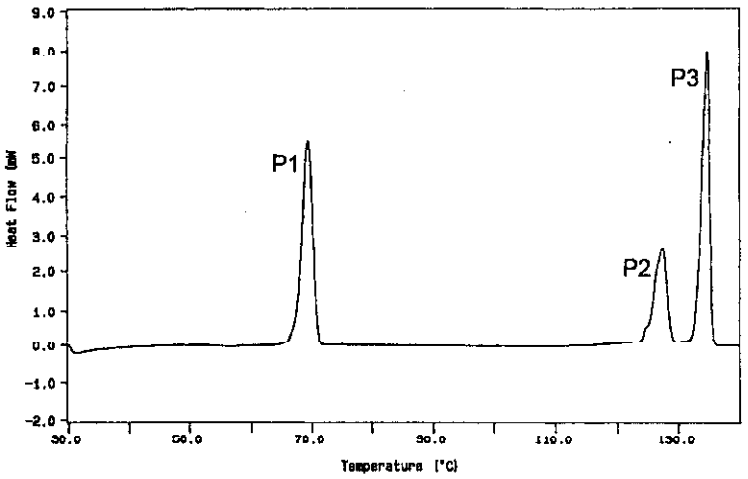

Fig. 9 DSC curve of the molecular addition compound of pentadecanoic acid and urea

P_2 for the melting of urea. The DSC curve of MC I, which resulted from the solid–solid reaction of the 50% mixture, shows three peaks of which P_1 indicates the peritectic between MC I and IC, P_2 the peritectic between IC and urea, and P_3 the melting of urea (Fig. 9).

In Fig. 10, the FTIR spectra for urea (A), pentadecanoic acid (B), IC (C) and MC I (D) appear. It is apparent that the IC is more similar to urea, whilst the MC

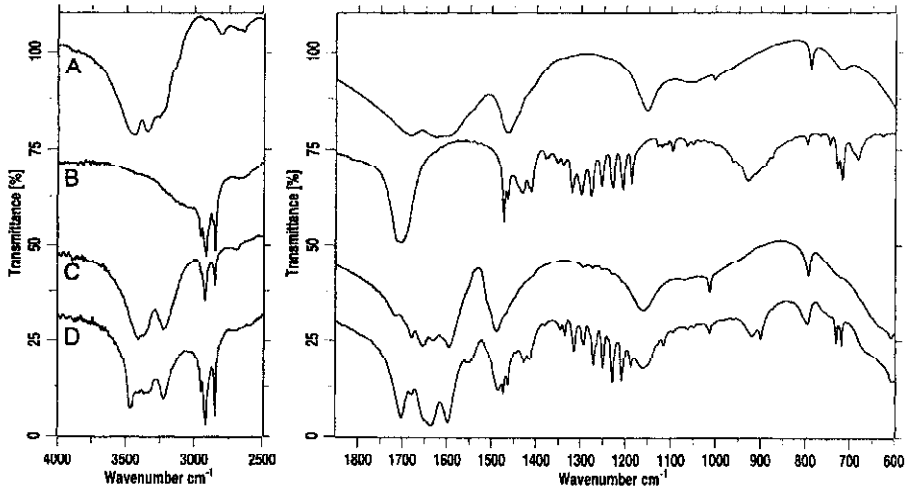

Fig. 10 FTIR spectra of urea (A), pentadecanoic acid (B), inclusion compound (C) and molecular addition compound (D)

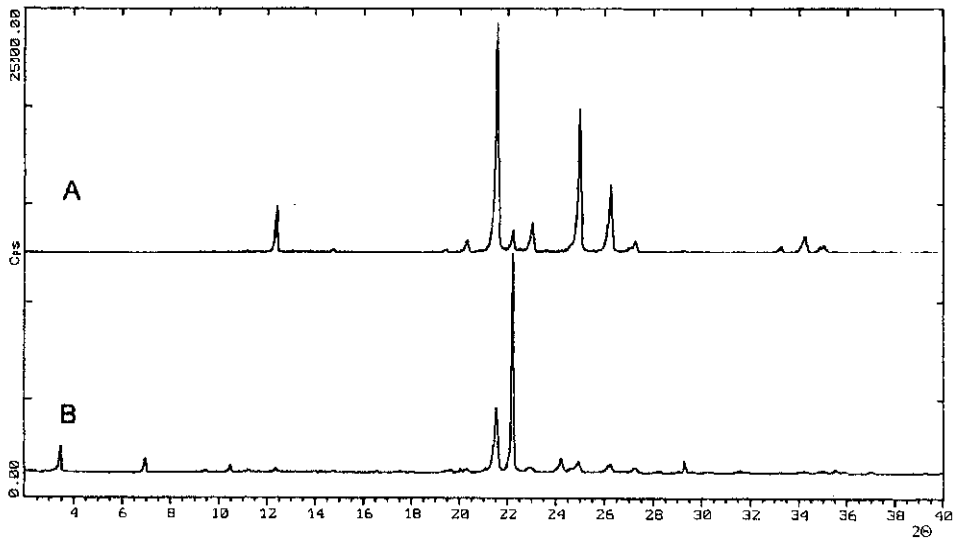

Fig. 11 X-ray diffractograms of the inclusion compound (A) and the molecular addition compound (B) of the pentadecanoic acid and urea system

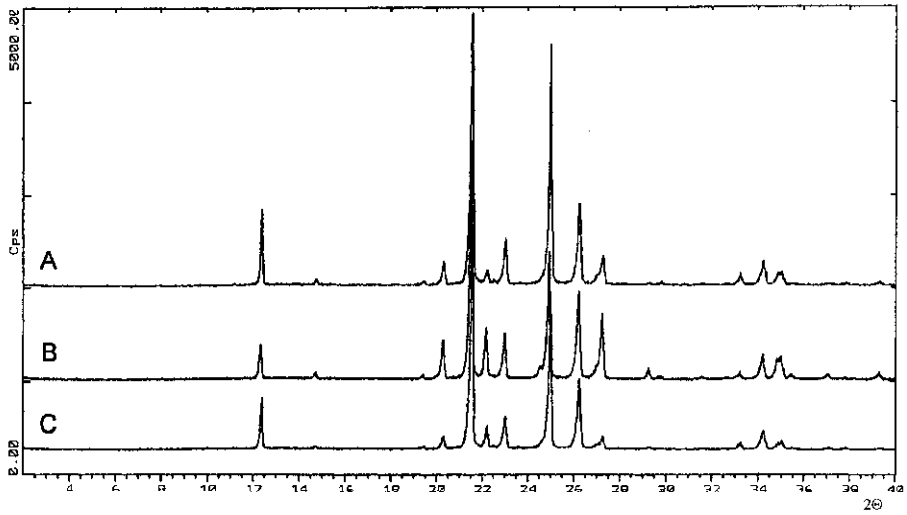

Fig. 12 X-ray diffractograms of the inclusion compounds of urea and palmitic acid (A), stearic acid (B), pentadecanoic acid (C)

displays characteristic combinations of the bands of urea and pentadecanoic acid. The X-ray diffractograms are also very well suited for differentiating between the IC and the MC (Fig. 11). In contrast, the channel inclusion compounds of palmitic acid [3], stearic acid [4] and pentadecanoic acid with urea reveal no differences, neither with regard to the FTIR spectra nor the X ray diffractograms (Fig. 12). They can only be identified by their DSC curves.

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