J. Chem. Eng. Data 1984, 29, 211-214

Solubility of the A, B, and C Polymorphs of Stearic Acid in Decane, Methanol, and Butanone

Wolfgang Beckmann,*[†] **Roland Boistelle, and Kiyotaka Sato**[‡]

Centre de Recherche sur les Mècanismes de la Croissance Cristalline, Campus de Luminy, Case 913,
13288 Marseille Cedex 9, France

The solubility of the A, B, and C polymorphs of stearic acid is measured in decane, butanone, and methanol. The experiments were carried out between 6 and 38, -2 and 39, and 8 and 33 °C for decane, methanol, and butanone, respectively. The enthalpies and entropies of dissolution for decane and butanone agree well with those derived from fusion data. The enthalpies check with those directly determined by calorimetry. The entropies for the polymorphic transitions B-C and A-C are found as 4.6 ± 0.5 and 1.3 ± 0.7 kJ mol^{-1}, respectively. The stability regions of the polymorphs are deduced within 2 K. The B and C polymorphs coexist at 29 °C; B is stable below this temperature whereas C is stable above it. The A polymorph is unstable at all temperatures. As an example, at 25 °C, the solubility of the B polymorph in 100 g of solvent is 0.698, 1.608, and 4.575 g for decane, methanol, and butanone, respectively.

Introduction

In some respects stearic acid, $CH_3(CH_2)_{16}COOH$, is an interesting substance to investigate the solubility of different polymorphic modifications: (i) the different modifications can be separately crystallized; (ii) the heats of polymorphic transformation are sufficiently high to give differences in solubility; (iii) the transitions between the polymorphs occur well below the melting point but are kinetically hindered, so that all polymorphs can be observed at the same temperature.

Stearic acid mainly crystallizes from solution in three polymorphic modifications A, B, and C (*1*). The B and C polymorphs are easily crystallized in lozenge-shaped, thin crystals, whereas the A polymorph forms needlelike crystals and is difficult to crystallize. Thus, we drew our attention to the B and C polymorphs, while only a few experiments were carried out with the A polymorph. Bailey et al. (*2*) first pointed out the differences in solubility of the stearic acid polymorphs. In a following paper (*3*) they pointed out that the C polymorph is stable above 40 °C and the B polymorph below 40 °C. Below 10 °C they suspect the E form to be stable. This latter polymorph has nearly the same macroscopic crystallographic features as the B one. However, its occurrence conditions are not well-defined. No quantitative information about the differences in solubility was given (*2*, *3*).

Solubilities for stearic acid are quite abundantly given in the literature. The data are nearly completely accumulated by Singleton (*4*). However, a closer examination shows a varying accuracy, which is often insufficient. Furthermore, the difference in solubility of the polymorphs is not quantitatively clarified. Since exact solubility data are needed for experiments concerning the crystallization of the B and C forms of stearic acid, we undertook careful measurements of the polymorph-specific solubility and selected decane, methanol, and butanone as solvents.

The solid-state transitions between the polymorphic modifications are kinetically hindered, so that solubility measurements provide a means to determine stability regions.

Experimental Section

The purities and the suppliers of the chemicals used are as follows: stearic acid (Fluka, >99.6%), decane (Fluka, >99%), methanol (Prolabo, >99.6%, <0.1% water), and butanone (Merck, >99.5%, <0.05% water). All chemicals were used without further purification. Crystals of the three polymorphs were obtained by careful crystallization from decane at room temperature. We selected the desired polymorph from the precipitate by means of an optical microscope. The solubilities have been determined by two different techniques. In both cases we started from solution prepared by using weighed amounts of stearic acid and solvent. The solutions were put into thermostated cells. The temperature could be read to 0.1 K. We used two slightly different techniques to determine the solubilities:

(i) The bulk solubilities were determined by directly nucleating the crystals in the cells. By lowering and raising its temperature, we could observe the appearance and disappearance of crystals. By using the "bracketing technique" we decreased the temperature intervals of successive crystallization/dissolution cycles. This technique has been used to determine the solubility of paraffins in alkane solutions (*5*). There the reproducibility was ≈200 mK. During our measurements it became rapidly clear that the reproducibility was less. Depending on the solvent we found the saturation temperature to vary as much as 700 mK. In addition, with this technique no influence on the polymorph precipitated could be excercised. From the determination of the occurrence domains of stearic acid (*6*) it can be assumed that the C polymorph is mostly precipitated in decane and other nonpolar solvents, if mean supersaturations are used. From a study, which is in progress, it appears that in methanol and other polar solvents mixtures of the polymorphs are precipitated more commonly.

(ii) The individual solubilities of the three polymorphs were determined by a new technique. After the prepared solutions had attained thermal equilibrium, small single crystals of the polymorph in question were added. Then the temperature of the solution was lowered and raised as above. At the same time we observed the crystal edges and interference colors by means of a polarizing microscope. Especially the change in interference colors gave a sensitive means to determine exactly the temperature at which the crystal was in equilibrium with the solution. However, the experiments could not be carried out in the entire temperature range. If the unstable polymorph, which has a higher solubility, is investigated far from the temperature of equal solubility, the stable polymorph may spontaneously precipitate and grow. Thus, the concentration in the solution is changed, which leads to incorrect results.

Results

The bulk and polymorph-specific solubilities obtained by us have been summarized in Tables I-III. For decane we compared the bulk solubilities with those of the C polymorph and found a very good accordance. We conclude that in the

---

[†] On leave from the Institut für Physikalische und Theoretische Chemie der TU, D-3300 Braunschweig, West Germany.

[‡] On leave from the Faculty of Applied Biological Science, Hiroshima University, 2-17 Midori-machi, Fukuyama 720, Japan.

0021-9568/84/1729-0211$01.50/0

Table I. Bulk and A, B, and C Polymorph-Specific Solubilities of Stearic Acid in Decane

θ/°C	C/(g (100 g of solvent)$^{-1}$)	$-\ln x_2$[a]	θ/°C	C/(g (100 g of solvent)$^{-1}$)	$-\ln x_2$[a]
		Bulk			
17.9	0.204	6.888	33.1	2.887	4.252
22.4	0.411	6.190	33.8	3.335	4.110
26.0	0.825	5.494	35.0	4.002	3.931
27.9	1.207	5.116	37.1	4.996	3.714
29.8	1.666	4.796	37.6	5.999	3.536
32.1	2.399	4.435			
		A Polymorph			
18.6	0.225	6.790	29.5	1.534	4.878
25.6	0.766	5.569	33.7	3.282	4.126
		B Polymorph			
5.7	0.014	9.578	30.4	1.733	4.757
17.3	0.168	4.085	34.5	3.899	3.957
20.0	0.307	6.480	35.8	4.779	3.757
25.0	0.699	5.660			
		C Polymorph			
19.5	0.275	6.590	35.5	4.278	3.866
24.7	0.696	5.663			

[a] x_2 is the monomer mole fraction.

Table II. Bulk and B and C Polymorph-Specific Solubilities of Stearic Acid in Methanol

θ/°C	C/(g (100 g of solvent)$^{-1}$)	$-\ln x_2$[a]	θ/°C	C/(g (100 g of solvent)$^{-1}$)	$-\ln x_2$[a]
		Bulk			
13.5	0.299	7.595	23.5	0.994	6.796
15.2	0.358	7.817	24.5	1.273	6.549
17.6	0.398	7.711	27.8	1.793	6.207
19.7	0.600	7.301	32.8	3.553	5.525
		B Polymorph			
−2.2	0.090	9.2010	18.8	0.672	7.1871
6.3	0.213	8.3342	21.2	1.035	6.7554
11.75	0.384	7.7469	27.2	1.993	6.1014
13.4	0.445	7.5991	31.0	3.251	5.6136
16.5	0.604	7.2933	34.4	5.155	5.1547
		C Polymorph			
11.0	0.389	7.7336	29.2	2.435	5.9018
15.7	0.607	7.2887	35.1	5.085	5.1684
20.4	1.041	6.7495	35.5	5.792	5.0389
27.0	2.010	6.0931	39.0	9.181	4.5821

[a] x_2 is the monomer mole fraction.

Table III. B and C Polymorph-Specific Solubilities of Stearic Acid in Butanone

θ/°C	C/(g (100 g of solvent)$^{-1}$)	$-\ln x_2$[a]	θ/°C	C/(g (100 g of solvent)$^{-1}$)	$-\ln x_2$[a]
		B Polymorph			
8.5	0.725	6.3015	20.7	2.770	4.9657
15.0	1.547	5.5455	26.1	5.190	4.3440
18.5	2.274	5.1620	29.5	7.441	3.9894
		C Polymorph			
7.5	0.734	6.2885	23.5	4.036	4.5927
14.2	1.586	5.5208	32.8	10.195	3.6813
18.0	2.353	5.1281			

[a] x_2 is the monomer mole fraction.

bulk experiments the C solubility was measured. Thus, we treated bulk and C solubilities as the same. We note that decane was the only solvent in which the bulk solubilities could be measured with an acceptable accuracy (≈300 mK). In all other tested solvents (methanol, cyclohexane, benzene) the dispersion was at least twice. At temperatures below ≈27 °C the bulk solubility determined for methanol as solvent is significantly lower than that of all polymorphs. As we have no explanation of the effects, we discard the bulk values. No bulk data were measured for butanone.

The solubility of any solute (index 2) in any solvent can be represented as

$$-\ln x_2\gamma_2 = \Delta_d H/RT - \Delta_d S/R \qquad (1)$$

where x_2 and γ_2 are the solute mole fraction and activity, respectively, and $\Delta_d H$ and $\Delta_d S$ are the enthalpy and entropy of dissolution. Depending on the nature of the solvent, which determines the degree of dimerization of the stearic acid, x_2 has to be taken as the monomer or dimer mole fraction. A discussion of the involved thermodynamics is given as supplementary material. (See paragraph at end of text regarding supplementary material.)

Stearic acid dissolves nearly completely as dimers in decane (*7*); thus we replace x_2 by x_D:$x_D = x_2/(2 - x_2)$. By means of eq 1 we obtain $\Delta_d H$ and $\Delta_d S$. The results of the least mean square fits are compiled in Table IV. As all numerical values are referred to 1 mol of monomeric stearic acid, the dimer mole fraction is to be calculated from the values in Table IV by

$$x_D = \exp[2(-\Delta_d H/RT + \Delta_d S/R)] \qquad (2)$$

Stearic acid is completely dissociated in butanone (*8*). A straight-line fit according to eq 1 using the monomer mole fraction gives the values for $\Delta_d H$ and $\Delta_d S$ displayed in Table V. Our experimental values indicate no deviation from a straight line. The mole fraction is given by

$$x_2 = \exp(-\Delta_d H/RT + \Delta_d S/R) \qquad (3)$$

The data for methanol as solvent cannot be represented by a straight line. For a treatment we can assume the same deviations from ideality for both polymorphs, i.e., $\gamma_B = \gamma_C$, at constant temperature. These nonidealities cannot be explained by a difference Δc_p, because these corrections do not apply in decane and butanone. The excess entropies and enthalpies of both polymorphs must be equal as the difference in enthalpy and entropy of both polymorphs does not depend on the solvent. Thus, we add the same correction term for both polymorphs to eq 1: $k(1/T - 1/T_0)^2$. The constant T_0 is chosen as 300 K to transform the correction into the range of our work. We fitted k for both polymorphs simultaneously with $\Delta_d H$ and $\Delta_d S$ using multiple regression techniques and obtained $k = (5.96 \pm 0.18) \times 10^6$ K^2. The values for $\Delta_d H$ and $\Delta_d S$ are given in Table VI. (Note that at 300 K the correction is zero.) With this correction the saturation temperatures are predicted within 300 mK, which is within the limit of the experimental error. The mole fraction is given by

$$x_2 = \exp[-\Delta_d H/RT + \Delta_d S/R + k(1/T - 1/300\ \text{K})^2] \qquad (4)$$

Consideration of Errors

In the following we consider the error in saturation temperature T_S (as calculated from concentrations) and supersatura-

Table IV. Enthalpy and Entropy of Dissolution of the A, B, and C Polymorphs of Stearic Acid in Decane Derived from Solubility, Calorimetry, and Fusion Data Using Ideal Solution Theory

	$\Delta_d H$/(kJ mol^{-1})			$\Delta_d S$/(J mol^{-1} K^{-1})		
polymorph	A	B	C	A	B	C
solubility	65.7 ± 0.5	69.0 ± 0.3	64.4 ± 0.2	193.4 ± 1.8	205.0 ± 0.9	189.9 ± 0.6
calorimetry		70 ± 1	64 ± 1			
fusion		68.6 ± 0.2	62.6 ± 0.2		202.0 ± 0.9	183 ± 0.9

Table V. Entropy and Enthalpy of Dissolution of the B and C Polymorphs of Stearic Acid in Butanone Derived from Solubility Data and Calorimetry

polymorph	$\Delta_d H/(\mathrm{kJ\ mol^{-1}})$		$\Delta_d S/(\mathrm{J\ mol^{-1}\ K^{-1}})$	
	B	C	B	C
solubility	77.9 ± 0.4	73.2 ± 0.4	224.1 ± 1.3	208.7 ± 1.4
calorimetry		74.0 ± 0.8		

tion β ($\beta = x/x_S$) caused by the uncertainties of the values.

(1) The error in saturation temperature will be caused by the error in $\Delta_d H$:

$$\sigma_{T_S} = T_S \sigma_{\Delta_d H} / \Delta_d H \tag{5}$$

To evaluate the error caused by $\Delta_d S$ we note that $\Delta_d S$ is extrapolated to $1/T = 0$, which is far from the investigated interval. Thus, $1/T$ is transformed to the temperature range of interest (≈300 K) by $1/T' = 1/T - 1/300$ K. This transformation of the coordinates considerably reduces the error in ΔS (the intercept). The error in T_S as caused by the error in the intercept $\Delta_d S$ or $\Delta S'$ will be

$$\sigma_{T_S} = T^2 \sigma_{\Delta S} / \Delta_d H \tag{6}$$

The sum of both errors (eq 5 and 6) leads to uncertainties in the saturation temperature T_S of 60–90 mK for decane and 90–140 mK for butanone. For methanol as solvent we deduced above the uncertainties in T_S from our fits as 300 mK.

(2) The error in β is only caused by the error in $\Delta_d H$:

$$\sigma_\beta / \beta = (\sigma_{\Delta_d H} / R)(\Delta T / T^2) \tag{7}$$

where ΔT is the subcooling. This error will be less than 0.2%, if we take $\Delta T < 4$ K and $T = 300$ K.

Discussion

We compare the entropies and enthalpies of dissolution with those of fusion and heats of dissolution directly determined by calorimetry (Tables IV–VI). The heat of fusion of the B polymorph was obtained by adding to the heat of fusion of the C polymorph the heat of the B–C transition $\Delta_{tr}H_{BC} = 6$ kJ mol^{-1}, as obtained by DTA. The entropies were calculated by $\Delta_f S_C = \Delta_f H_C / T_f$ and $\Delta_f S_B = \Delta_f S_C + \Delta_{tr} H_{BC} / T_{tr}$ with $T_{tr} = 302$ K.

The check for decane is very satisfactory. We note a good agreement of the dissolution data (solubility and calorimetry) for butanone. The enthalpy of fusion is by ~11 kJ mol^{-1} lower, which we explain by the difference in enthalpies of the dissociation of the stearic acid dimer and the formation of the stearic acid–butanone complex. The total disagreement for methanol cannot be due to the uncertainties in the measurements. As pointed out above, the thermodynamics of this solution are very involved and not quantitatively known. We cannot build up a valuable physical model from our measurements. The fit is only a mathematical representation of the experimental data.

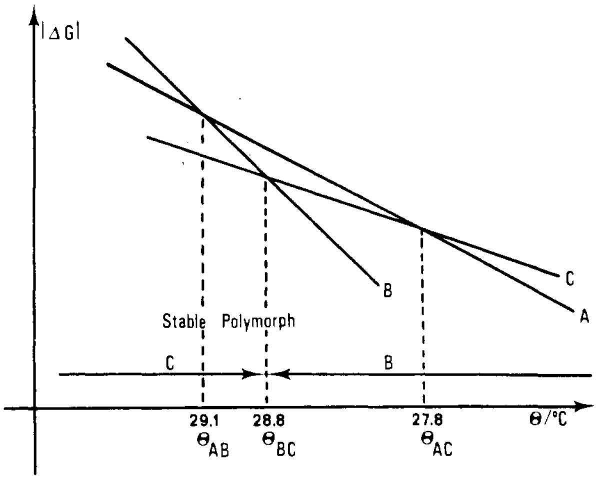

Figure 1. Schematic representation of the free enthalpies ΔG of the A, B, and C polymorphs of stearic acid as a function of temperature.

Our solubility measurements allowed for the calculation of transition enthalpies, entropies, and temperatures for the three polymorphic transitions (A–B, A–C, B–C) as summarized in Table VII. The dispersion in the temperatures is on the order of 2 K. We compare the differences in enthalpies with the heats of the solid-state transition. For the B–C transition $\Delta_{tr}H_{BC} = 6$ kJ mol^{-1} as determined by DTA (*9*, *10*). Defects formed upon heating may be at the origin of the slightly higher transition enthalpy. A difference of 6 kJ mol^{-1} is also obtained from calorimetric measurements of the heats of dissolution (*7*). No exact direct determination for the A–C transition is available. By DTA Garti (*9*) found the heat to be smaller than for the B–C transition but did not give any quantitative value.

We exaggerated the differences in ΔG of the three polymorphs as a function of temperature, in order to illustrate the stability region, (Figure 1). It can be seen that the A polymorph is unstable at any temperature. Furthermore, it becomes evident from Figure 1 that the solid-state transitions are only from A to C and B to C. At temperatures >30 °C, where the ki-

Table VI. Enthalpy and Entropy of Dissolution of Stearic Acid in Methanol at 300 K[a]

polymorph	$\Delta_d H/(\mathrm{kJ\ mol^{-1}})$		$\Delta_d S/(\mathrm{J\ mol^{-1}\ K^{-1}})$	
	B	C	B	C
solubility (300 K)	88.9 ± 0.8	84.4 ± 0.7	245.7 ± 0.4	230.9 ± 1.3
calorimetry (304 K)	81.3 ± 0.7	75.4 ± 1.6		

[a] For other temperatures the corrections given by eq 1d apply. The enthalpies are compared with those obtained by calorimetry at 304 K.

Table VII. Comparison of the Enthalpies, Entropies, and Temperatures of the A-B, B-C, and A-C Polymorphic Transitions[a]

solvent	transition A-C			transition B-C			transition A-B θ/°C
	$\Delta_{tr}H$/ (kJ mol^{-1})	$\Delta_{tr}S$/ (J mol^{-1} K^{-1})	θ/°C	$\Delta_{tr}H$/ (kJ mol^{-1})	$\Delta_{tr}S$/ (J mol^{-1} K^{-1})	θ/°C	
decane							
SOL[b]	1.3 ± 0.7	4.1 ± 0.1	27.9	4.6 ± 0.5	15.2 ± 0.1	28.8	29.1
GRO[c]				4.2 ± 1.3	13.8 ± 4.3		
methanol				4.5 ± 1.5	14.9 ± 0.1	30.1	
butanone				4.7 ± 0.8	15.4 ± 0.2	29.1	

[a] The dispersion of the temperatures is on the order of 2 K. [b] SOL = solubility. [c] GRO = growth kinetics.

netically hindered solid-state reaction may occur, the C polymorph is the most stable.

All described measurements were performed in a stagnant system. We would additionally deduce the differences in saturation temperatures between the B and C polymorphs from measurements of the growth and dissolution rates in a flow system (for the system, see ref *11*). This difference is 0.6, 0.5, and 0.0 K at 19.4, 23.9, and 28.3 °C, respectively. The precision of the temperatures is on the order of 200 mK. We deduced the differences in enthalpy and entropy of dissolution of the B–C pair additionally given in Table VII. The values have a higher dispersion, but check with those obtained in the stagnant system. We conclude that the differences in $\Delta_{tr}H_{BC}$ between solubility experiments ($\sim$4.7 kJ mol^{-1}) and direct calorimetric and DTA experiments ($\sim$6.0 kJ mol^{-1}) are not due to the use of a stagnant system (i.e., influence of diffusion).

To our knowledge for decane no solubility data are published. The few data published for butanone (*12*) are higher than ours. Those published for methanol (*2*, *13–15*) agree qualitatively at temperatures higher than 10 °C. In both cases no reference was given to the polymorphic modification.

Conclusion

We have undertaken careful measurements of the solubility of the A, B, and C polymorphs of stearic acid in decane, butanone, and methanol. The attained precisions are very good. In decane we found stearic acid to dissolve nearly ideally in the form of dimers. We found great deviations from ideality in methanol. In butanone, stearic acid dissolves as monomers followed by a formation of a solvent–solute complex, the nature of which is unknown. In all solvents the point of equal solubility of the B and C polymorphs is at 29 °C.

A comparison of Δ_dH calculated from solubility data with direct calorimetric determination (*7*) reveals two noteworthy facts: (i) the absolute values for the heats of dissolution check for decane and butanone, but largely deviate for methanol; (ii) in all solvents the difference in the heats of dissolution between the B and C polymorphs is 4.7 kJ mol^{-1} from solubility data, while 6.0 kJ mol^{-1} is obtained from calorimetry and DTA.

We have shown that in all solvents the differences in solubility of the B and C polymorphs are equal and we obtained quantitative values for the differences in solubility of the A, B, and C polymorphs. Thus, if the solubility of only one polymorph has been determined, the solubilities of the remaining two can be easily calculated.

Acknowledgment

We thank Mrs. Heidi Volkert for a critical correction of the English.

Glossary

H	enthalpy, kJ mol^{-1}
k	correction constant, K^2
R	universal gas constant, 8.314 J mol^{-1} K^{-1}
S	entropy, J mol^{-1} K^{-1}
T	absolute temperature, K
x	mole fraction

Greek Letters

β	supersaturation
Δ	difference operator
γ	activity coefficient

Subscripts

2	solute
B	B polymorph
C	C polymorph
d	dissolution
D	dimer
f	fusion
S	saturation
tr	polymorphic transition

Registry No. Stearic acid, 57-11-4.

Literature Cited

(1) von Sydow, E. *Ark. Kemi* **1956**, *19*, 231.
(2) Bailey, A. V.; Harris, J. A.; Skun, E. L. *J. Am. Oil Chem. Soc.* **1969**, *46*, 583.
(3) Bailey, A. V.; Mitcham, D.; Pittman R. A.; Sumrell, G. *J. Am. Oil Chem. Soc.* **1972**, *49*, 419.
(4) Singleton, W. S. In "Fatty Acids"; Markley, K. S., Ed.; Interscience: New York, 1960; Part 1, p 600 ff.
(5) Lundager Madsen, H. E.; Boistelle, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1078.
(6) Sato, K.; Boistelle, R. *J. Colloid Interface Sci.* **1983**, *94*, 593.
(7) Beckmann, W.; Rouquerol, F.; Beckmann, H. *Thermochim. Acta* **1983**, *66*, 295.
(8) Murata, Y.; Motomura, K.; Matura, R. *Mem. Fac. Sci., Kyushu Univ., Ser. C.* **1976**, *11*, 29.
(9) Garti, N.; Sarig, S.; Wellner, E. *Thermochim. Acta* **1980**, *37*, 131.
(10) Garti, N.; Wellner, E.; Sarig, S. *J. Cryst. Growth* **1982**, *57*, 577.
(11) Boistelle, R.; Doussoulin, A. *J. Cryst. Growth* **1976**, *33*, 335.
(12) Ralston, A. W.; Hoerr, C. W. *J. Org. Chem.* **1942**, *7*, 546.
(13) Foreman, H. D.; Brown, J. B. *Oil Soap (Chicago)* **1944**, *21*, 183.
(14) Kolb, D. K.; Brown, J. B. *J. Am. Oil Chem. Soc.* **1955**, *32*, 357.
(15) Hoerr, C. W.; Ralston, A. W. *J. Org. Chem.* **1944**, *9*, 329.

Received for review May 25, 1983. Accepted October 31, 1983. Two of the authors received stipends to visit the CRMC2, for which they would like to thank the Deutsche Forschungsgemeinschaft (W.B.) and the Centre International des Etudiants Stagiaires (K.S.).

Supplementary Material Available: A discussion of the thermodynamics of the polymorph-specific solubility of stearic acid in the solvents covered (8 pages). Ordering information is given on any current masthead page.