Purification and thermal analysis of perfluoro-*n*-alkanoic acids

Minami Tsuji [a], Tohru Inoue [b], Osamu Shibata [a,c,*]

[a] *Division of Biointerfacial Science, Graduate School of Pharmaceutical Sciences, Kyushu University;*
3-1-1 Maidashi, Higashi-ku, Fukuoka 812-8582, Japan
[b] *Department of Chemistry, Faculty of Science, Fukuoka University, 8-19-1 Nanakuma, Johnan-ku, Fukuoka 814-0180, Japan*
[c] *Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University,*
Huis Ten Bosch, Sasebo 859-3298, Japan[1]

Abstract

Purification of perfluoro-*n*-alkanoic acids ($C_nF_{2n+1}COOH$, $n = 7$, 9, 11, 13, 15 and 17) was made by repeated recrystallizations from *n*-hexane/acetone mixed solvent, and their purity was found to be more than 99.5% by GC–MS, NMR, and elemental analysis. The thermal behaviors such as melting point and enthalpy change of fusion were investigated using differential scanning calorimetry (DSC). The melting point monotonously increased with increasing carbon number (n) of the acids, while the enthalpy change showed irregularity at $n = 14$. The crystal structure of these acids was found to be dependent upon solvent used for recrystallization; that is, the acids recrystallized from the above solvent becomes more stable energetically, indicating their higher enthalpy change of fusion than that of the solidified acids from fused ones. The solid state was also found to vary depending upon the thermal history, indicating that a few crystal structures of the solid state are quite similar energetically. The melting points (T_m) of perfluoro-*n*-alkanoic acids are higher than those of corresponding *n*-alkanoic acids, and the difference in T_m increases with increasing carbon number in the acids.
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Keywords: Fluorinated amphiphiles; Perfluoro-*n*-alkanoic acids; Purification of perfluoro-*n*-alkanoic acids; Differential scanning calorimetry (DSC); Melting point (T_m); Enthalpy change of fusion

1. Introduction

Fluorocarbons are now in widespread use not only for scientific fields but also for practical purposes because of their hydrophobicity, oleophobicity, stability against acid and base, and thermal stability [1–5]. In particular, perfluoro-*n*-alkanoic acids have been most commonly employed to examine whether alkanoic acids can be replaced by perfluoro-alkanoic acids due to their excellent physico-chemical properties and to see their new functions. In addition, perfluoro-alkanoic acids whose carbon number is from 10 to 14 seem to have a high potential for bioaccumulation [6]. Although perfluoro-*n*-alkanoic acids have been used in many fields, it is quite questionable that

the acids used were truly purified. If they were contaminated, their physico-chemical characteristics cannot be applied to other fields in safety and with confidence. Indeed, molecular surface areas of insoluble perfluoro-*n*-alkanoic acid monolayers at the air/water interface are quite dispersed [7–10], where ca. $20 \, nm^2$ is also reported in spite of a cross-sectional area of ca. $30 \, nm^2$ for a fluorocarbon chain. In addition, properties on binary mixture of fluorocarbon species and another component have been examined and reported in many papers, but reports on properties of perfluoro-*n*-alkanoic acid only are quite few in number, as far as the authors know. For example, thermal behavior of mixing of perfluoro-carboxylic acids with dipalmitoylphosphatidylcholines [11], silver perfluorocarboxylates [12] and fluorinated frallen [13] were studied, but perfluorocarboxylic acids themselves have not been reported much.

This paper is aimed to present the method to prepare highly purified perfluoro-*n*-alkanoic acids and to make clear their thermal behavior for further study on perfluoro-*n*-alkanoic acids.

* Corresponding author at: Department of Biophysical Chemistry, Faculty of Pharmaceutical Sciences, Nagasaki International University, Huis Ten Bosch, Sasebo 859-3298, Japan. Tel.: +81 956 20 5686; fax: +81 956 20 5686.
 E-mail addresses: wosamu@niu.ac.jp, wosamu-s@hotmail.co.jp
(O. Shibata).
[1] http://www.niu.ac.jp/~pharm/lab/physchem/indexenglish.html.

2. Experimental

2.1. Materials

Perfluorooctanoic acid (FC8: $n = 7$), perfluorodecanoic acid (FC10: $n = 9$), perfluorododecanoic acid (FC12: $n = 11$), perfluorotetradecanoic acid (FC14: $n = 13$), perfluorohexadecanoic acid (FC16: $n = 15$), and perfluorooctadecanoic acid (FC18: $n = 17$) were obtained from Fluorochem (United Kingdom). These acids were purified (see below) and their purity was checked by ^{19}F NMR measurement (UNITY INOVA 400 Spectrometer, Varian, USA), GC–MS (QP-1000, Shimadzu, Kyoto) and by elemental analysis, where the observed and calculated values were in satisfactory agreement ($< \pm 0.3\%$ for carbon atom). As a result, their purity was found to be more than 99.5%. *n*-Hexane of analytical grade and acetone of highest grade were from nacalai tesque. Both solvents, *n*-hexane and acetone, were freshly distilled once for removing involatile admixtures. They were used as a solvent for recrystallization.

2.2. Purification

The obtained perfluoro-*n*-alkanoic acid was made soluble in hexane/acetone mixtures, containing 20% of acetone (v/v) for FC18, 5% for FC16 and a few % for FC14. Difference in composition of solvent is related with different solubility into the solvent of perfluoro-*n*-alkanoic acids (shorter length of hydrophobic chain is more soluble in general). For the first crystallization, small amount of CF_3COOH was added to the solvent (200–500 mol% relative to amount of FC*n*) to be sure that FC*n* is in a form of free acid (neither salt nor ester). Maximum amount of FC*n* was dissolved in hot solvent close to boiling; that is, the solution with high solubility was cooled to 10–20 °C. The crystalline was separated from mother solvent by centrifugation. The above operation was repeated at least three times. The purity of FC*n* was monitored via recording ΔV–A and π–A isotherms of mother solution [10]. Judging from ΔV–A and π–A isotherms, FC*n* thus purified are much purer than that for crude samples [7–9]. This means that all extrapolated areas of FC*n* ($n = 12, 14, 16$ and 18) in the ordered state are approximately $0.30 \, \text{nm}^2$ and their surface potentials of those also show ca. $-1000 \, \text{mV}$ at the closest packing state [10]. This large negative value of surface potential results from the strong electronegative fluorine atoms. In addition, the molecular surface area and surface potential values above are characteristics of quite pure perfluorocarboxylic acids.

2.3. Thermal analysis

EXSTAR 6000 /DSC 6100 (SII) was used for the DSC studies. Five to ten milligrams of the solid samples was placed in 70 μL aluminum pans, and then these pans were sealed with a hermetic sealer. Purified indium and water were used as the standard calibration sample for enthalpy change. Samples were heated and cooled at the rate of 1 and 3 K/min, respectively. All samples were examined at least two times by repeating the heating-cooling cycles. When the same curve was not observed
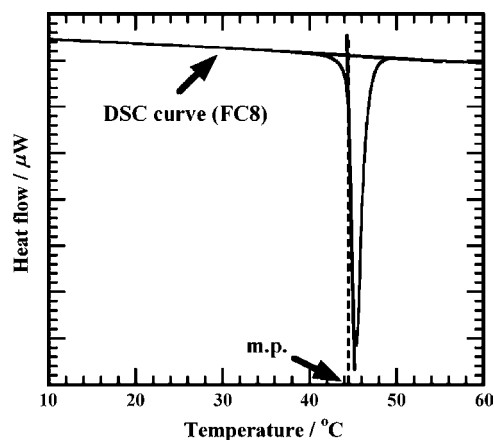

Fig. 1. The way to determine the melting point from DSC curve; no hysteresis was observed for FC8 through cyclic heat treatment.

for cyclic heat treatment, the melting temperatures (T_m) were determined from the corresponding endothermic peak. They were determined as the temperature at the intersection point between the endothermic peak line for phase transition and the baseline as reported previously [14,15] (Fig. 1).

3. Results and discussion

The DSC curves for the recrystallized FC*n* from solvents (1st heating, Fig. 2) were different from those for the molten solids (2nd heating, Fig. 3). It is because the crystal structures are different due to the polymorphism. There are pre-transition (phase transition of solid), which is followed by the main transition (melting) for the most samples. It is often the case that a recrystallized solid from a solvent is different in a crystal structure from a solid from the molten (molten solid). There are three types of crystalline, A, B, and C for long-chain *n*-alkanoic acids.
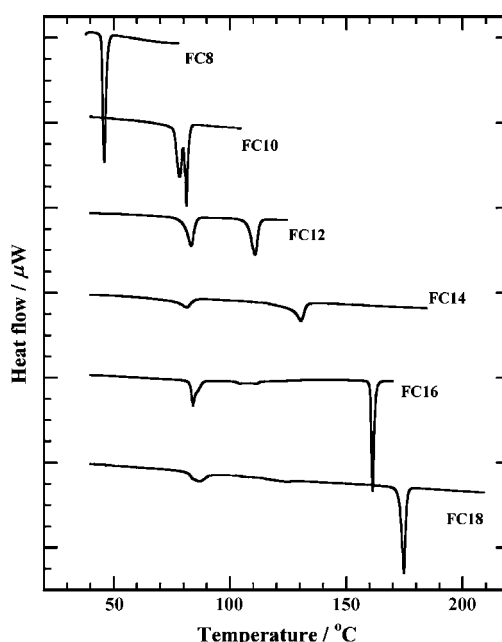

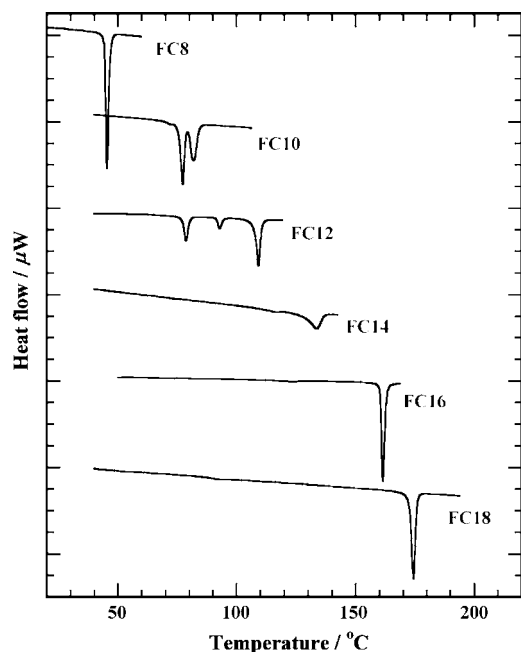Fig. 2. DSC traces of recrystallized perfluoro-*n*-alkanoic acids (1st heating).

Fig. 3. DSC traces of molten perfluoro-*n*-alkanoic acids (2nd heating).

Fig. 5. Change in melting point of FC*n* and *n*-alkanoic acids against the number of carbon atoms.

with the data reported by David et al. [17], Lehmler et al. [18] and Brace [19]. In addition, there is another phase transition before the melting except FC8, where the transition temperatures remain almost the same irrespective of the number of carbon atoms. The fact suggests that the transition relates with some structural change in −COOH group for the acids having a longer fluorocarbon.

As for FC8, DSC curve for the molten solid is quite similar to that for the recrystallized one. There exists only one endothermic peak. Most samples except FC8 have one or two interim pre-melting endothermic peaks for the molten-solid, where it is hard to say that FC16 and FC18 have the pre-melting (Fig. 6). As for FC10, the second endothermic peak is sharper than the first peak for the 1st heating, while the first peak is sharper than the second one for the 2nd heating. However, the temperatures at the two endothermic peaks remain the same. As for FC12, there are two endothermic peaks for the 1st heating, while there are three peaks for the 2nd and further heatings. This is also due to difference in solidifying process. The phase transitions of FC12 was examined by a polarizing microscope, and then, vigorous movement of the molecules was seen above the second transition temperature, although such movement was not observed above the first transition. The fact proves that the 1st transition is a phase transition of a solid state, the 2nd transition

The type C is the one from the molten acid, while the other two are those from recrystallization from solvent. The melting temperature should be determined for the molten solid, because the melting and solidification are reversible and the melting temperature is invariant at atmospheric pressure. The transition point (temperature) for the recrystallized solids from the solvent was obtained from the DSC curve for the first increasing temperature (the 1st heating), which are shown in Fig. 4 against the number of carbon atoms in the acids, where the transition temperatures were quite reproducible except FC14. The transition point was determined as mentioned above (see Fig. 1). The 2nd transition temperature (melting point, T_m) of the perfluorinated carboxylic acids are higher than those of hydrocarbon fatty acids [16], which supports that fluorocarbon acids are more stabilized energetically than hydrocarbon acids. The melting points (2nd transition) monotonously increase with increasing carbon atoms (Fig. 5), and the melting points of FC12 and 14 nearly agreed
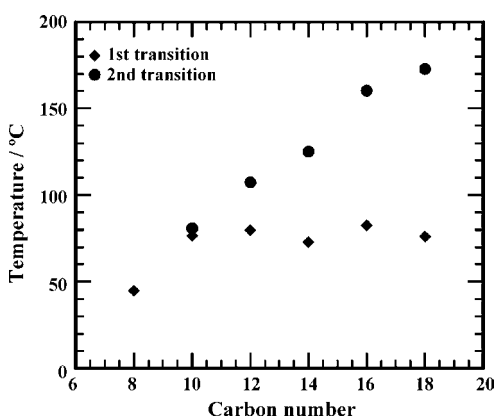

Fig. 4. Change in phase transition temperature against the number of carbon atoms for the recrystallized perfluoro-*n*-alkanoic acids (1st heating).
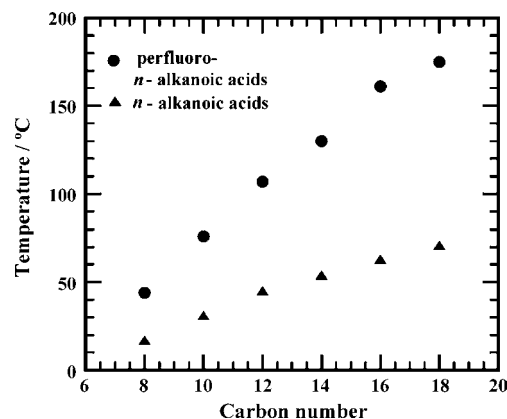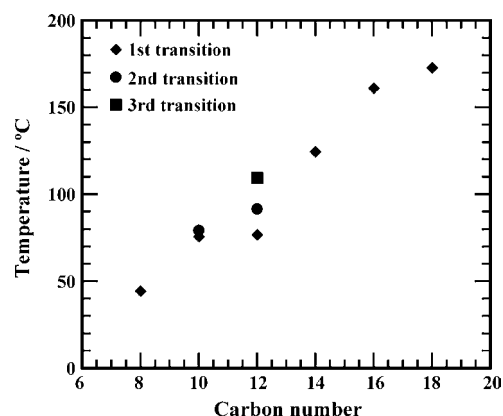

Fig. 6. Change in phase transition temperature against the number of carbon atoms for the molten perfluoro-*n*-alkanoic acids (2nd heating).
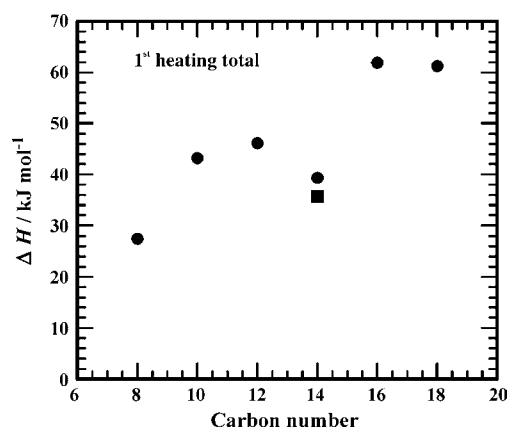
Fig. 7. Total enthalpy change (●) of 1st and 2nd phase transitions for the recrystallized perfluoro-*n*-alkanoic acids (1st heating), where the enthalpy change varies depending upon the thermal history for FC14 (●, ■).
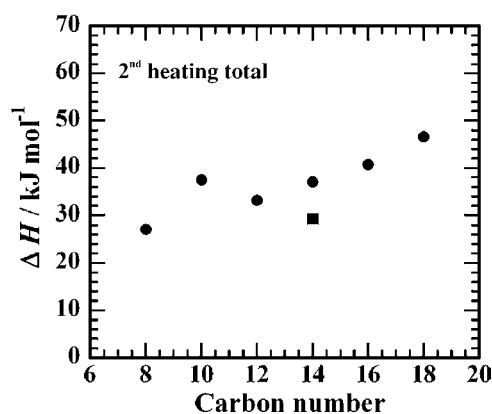

Fig. 8. Total enthalpy change (●) of 1st and 2nd phase transitions for the molten perfluoro-*n*-alkanoic acids (2nd heating), where the enthalpy change varies depending upon the thermal history for FC14 (●, ■). The standard deviation of the values is within the size of the circle.

corresponds to pre-melting, and the 3rd transition is complete melting.

As for FC14 whose purity is almost 100%, there are two patterns for the DSC curve, which are not reproducible. The temperature and the shape of the endothermic peak in the 2nd heating depend on the thermal history of the 1st heating; that is, the polymorphology is based upon the ways to heat and to cool. The gentle slope of the peak suggests low crystalinity, which may be related to an easy change in crystalline structure or small difference in energy between polymorphic forms.

FC16 and FC18 resemble each other with respect to the number and shape of the peaks. In the 1st heating, there are two quite small peaks and one main peak, while one main peak remains but two other peaks almost disappear in the 2nd heating, which also indicates that once the recrystallized solid melts, the morphology easily takes place for the molten solid.

As a whole, there happens an easy polymorphic transition due to small difference in energy between polymorphic forms. Hence, peaks appear or disappear with no reproducibility or with clear hysteresis. At present, however, the most important finding is that the recrystallized solids are more stable energetically than the molten solids. This must be verified from the enthalpy change of melting in the following section.

As for evaluation of enthalpy change of phase transition, a baseline is a matter of discussion [20]. In the present paper, however, the base line was drawn between the onset and the end of the peak of the DSC curve. As for the recrystallized solids, the sum of the enthalpy change of phase transition and the enthalpy change of fusion (the total enthalpy change) monotonously increases with increasing the number of carbon atoms in the acids, although an irregularity appear at the carbon number 14 (Figs. 7 and 8). The irregularity is quite hard to elucidate judging from the monotonous increase in the melting point. However, the irregularity is highly reproducible; the total enthalpy change was determined seven times totally, and then, two different values were obtained. This irregularity in the enthalpy change (ΔH) against the number of carbon atoms was also observed for hydrocarbon fatty acids (the minimum for palmitic acid) [21].

As for the total enthalpy change for the molten solid, on the other hand, two groups seem to be present (Fig. 8); one for FC8 and FC10 and the other for the acids with larger number of carbon atoms. In other words, the former has one crystalline structure and the latter does the other one. Judging from smaller total enthalpy change for longer FC*n* than expected, perfluoro-*n*-alkanoic acids with larger number of carbon atoms are less stable energetically than the ones with smaller ones. Interaction among fluorocarbon chains should be different between the former and the latter groups. What is an important finding here is that the total enthalpy change for the recrystallized solids is larger than that for the molten solids. The reason of the present consistent results should be made clarified using other techniques. Indeed, additional X-ray study can make clear the crystalline structure and the degree of crystallinity, which must be done in future.

4. Conclusions

Purification of perfluoro-*n*-alkanoic acids was made by repeated recrystallizations from *n*-hexane/acetone mixed solvent, and especially their purity for $n = 12$, 14, 16, and 18 was checked by the ΔV–A and π–A isotherms whose values were found quite reasonable. All the perfluoro-*n*-alkanoic acids thus obtained were found to be more than 99.5% by GC–MS, NMR, and elemental analysis, too.

The present DSC analyses revealed that there was pretransition (phase transition of solid), which is followed by the main transition (melting) for almost all the samples. As for FC14 whose purity is almost 100%, however, there are two patterns for the DSC curve, which are not reproducible. The DSC curves for the molten solids (2nd heating) were different from those for the recrystallized ones (1st heating). These observations originate from the small difference in crystal structures, the polymorphism. The solid state varied depending upon the thermal history, indicating that a few crystal structures of the solid state are quite similar energetically. As a whole, there happens an easy polymorphic transition due to small difference in energy between polymorphic forms.

The melting point (T_m) of the perfluorinated carboxylic acids are higher than those of hydrocarbon fatty acids, which supports that fluorocarbon acids are more stabilized energetically than hydrocarbon acids.

The total enthalpy change for the recrystallized solids is larger than that for the molten solids. At this present, it is thought that the recrystallized solids are more stable energetically than the molten solids, but its precise reason should be made clarified by further study using detailed X-ray analysis.

Acknowledgments

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