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DETERMINATION OF PHYSICAL CHARACTERISTICS OF FOOD FATS

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirement of the degree of Master of Science

Department of Food Science and Agricultural Chemistry
Macdonald Campus of McGill University

March, 1998

Short Title: Physical Properties of Food Fats

By Younes Zamani

Note: This thesis is presented as conventional format and not as a manuscript format.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to my supervisor, Dr. Inteaz Alli, whose belief in me, constant guidance, inspiration, and encouragement were indispensable in conducting this research.

My grateful acknowledgment is extended to Dr. Kermasha S. for his financial assistance during my research.

I am very thankful of Dr. H.S. Ramaswamy for letting me to use his facilities in his laboratory.

My special thanks are extended to Mr. K. Yeboah, Mr. E. Noroozy, and Mr. A.R. Taherian for their friendship and encouragement.

Also, my appreciations go to all staff members, graduate, and undergraduate students of the Department of Food Science and Agricultural Chemistry for wonderful family like atmosphere.

Last but not least, I am indebted to my wife Nasim for her patience and my son Shawnlee who brought joy and happiness to our lives.

This thesis is dedicated to all mothers specially to my kind mother.

ABSTRACT

Polymorphic crystal forms in food fats contribute to physical characteristics of the fats and consequently to their performance in fat based foods. In the present study the phase transitions associated with polymorphism behavior of common food fats were investigated. The polymorphism of butters, margarines, cocoa butter and cocoa butter products were determined and the effects of certain ingredients and conditions of temperature were studied. The following polymorphic forms were detected: sub-α, α, β', β'_3, β'_2, β, β_2, and β_1; however, not all forms were observed in all fats. Margarines contained β' and β forms depending on their fat constituents, while butter, cocoa butter, and fat blends consisted of α, β' and β; only the β' form of butter showed a sharp melting point. Rapeseed oil exhibited α, β_1 and β_2 forms, depending on the degree of hydrogenation.

Addition of lecithin to cocoa liquor decreased the melting point of the α form. Its effect on crystallization point was minimal. Addition of sugar to cocoa liquor containing 0.2% lecithin resulted in an increase in the melting point of the α form from 18.7°C to 18.9, 19.8, and 21.1°C in cocoa liquor containing 30, 40, and 50% sugar concentrations, respectively. Neither lecithin nor sugar affected the melting point of the β' or β forms.

Temperature cycling experiments revealed that the β' and β-form was unstable and disappeared completely after the first heating cycle; the other polymorphic forms were affected only slightly by temperature cycling.

DSC measurements of fat blends were correlated with viscosity index measurements from Universal Material Testing Machine (UMTM) using a single cycle, back extrusion technique. A correlation of $R^2 = 0.70$ ($p=0.95$) was obtained. Viscosity index decreased as temperature increased, suggesting a possible relationship between viscosity index and solid fat fraction. This suggests that viscosity index could be a potential indicator of food fat textural properties which are evaluated by DSC.

RÉSUMÉ

Les cristaux polymorphiques se forment dans les gras alimentaires et contribuent à leurs caractéristiques physiques. Par conséquent, ils ont aussi un rôle dans les aliments à base de lipides. Dans la présente recherche, une étude a été réalisée afin de déterminer les différentes étapes de transition reliées au changement de polymorphisme dans le gras des aliments les plus communs. L'étude du polymorphisme a été faite sur différentes catégories de beurre, margarines, beurre de cacao et les produits dérivés. L'étude de certains paramètres tels que l'effet de divers ingrédients ou encore l'effet de la température, ont été étudiés. Les différentes formes de polymorphisme mis en évidence ont été les suivantes: sub-α, α, β', β'_3, β'_2, β, β_2, et β_1. Cependant, les formes citées n'ont pu être détectées dans tous les types de matières grasses. Les formes β' et β ont pu être déterminées dans les margarines et cela en fonction de leur constitution en lipides. Le beurre, le beurre de cacao et les mélanges de gras ont montré un contenu en formes α, β', et β. Seule la forme β' du beurre a montré un point de fusion précis. L'huile de canola apparemment contient les α, β_2, et β_1, dépendant de leur degrè d'hydrogénation.

Une diminution du point de fusion ainsi que du point de crystallisation de la forme α a pu être constatée après ajoût de lécithine. Cependant, l'ajoût de sucre à la liqueur de cacao contenant 0.2% de lécithine a permits de noter une augmentation de son point de fusion. La fourchette des températures sétant de 18.7°C jusqu'à 18.9, 19.8 et 21.1°C pour une concentration en sucre de 30, 40, et 50% respectivement. Les formes β' et β n'ont été affectées ni par l'ajoût de sucre ni par l'ajoût de lécithine. Des essais faisant appel à l'utilisation de cycles de température ont été réalisés et ont montré que les formes β' et β étaient instables et disparaissaient après le premier cycle d'augmentation de chaleur. Les autres formes polymorphiques ont seulement été légèrement affectées.

Les analyses obtenues par DSC sur des mélanges de lipides ont été corrélées avec des analyses d'index de viscosité obtenues avec la Machine Testant les Matériaux Universals (UMTM); ceci, en utilisant la technique de zephex à cycle unique. Le facteur de corrélation obtenu était de $R^2 = 0.70$ ($p = 0.95$). L'index de viscosité diminuait lorsque la température augmentait, suggérant une éventuelle relation entre l'index de viscosité et la portion gras solides. Cette analyse permet de conclure que l'index de viscosité pourrait être un indicateur potentiel concernant la texture des matières grasses alimentaires, évaluée à présent par DSC.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Fats impart a wide range of characteristics to foods, among which are texture (crunchiness, moistness, tenderness and juiciness), flavors, and aromas; they tend to absorb flavors, consequently contributing to overall acceptance and palatability of the diet. Fats are a major contributor of energy in human diet. Structural studies in the area of fats and fat-based spreads have become increasingly important. With the increasing knowledge of the structure of fats, a better understanding of the properties and ways to influence these can be obtained.

Over consumption of fat by certain populations has been linked to a number of chronic diseases including cardiovascular disease, cancer, and obesity. These findings have stimulated an interest towards reducing dietary intake of fat as well as substituting lower fat versions of food products. Therefore successful solutions for such problems require an understanding of physical and chemical characteristics of fats. Physical properties of oils and fats are of critical importance in determining its use. Indeed, the two words "fat" and "oil" shows a fundamental physical differences, whether the fat is liquid or solid at ambient temperature. Fat is a material that is composed of an intimate mixture of liquid and solid phases whose main constituents are tryglycerides. The physical state of a fat depends upon how these tryglycerides are packed. It has been known for over a century that tryglycerides have multiple melting points which is known as "polymorphism". Understanding of polymorphism of whether a pure tryglyceride, fatty acids or a fat

product is essential for a correct understanding of polymorphic behavior.

In recent years, the use of sensitive techniques such as differential scanning calorimetry (DSC), high performance liquid chromatography (HPLC), and gas chromatography (GC) has led to significant improvement in the understanding of structures and their effect on product properties. Fat and fat containing foods are dependent on the fat components of the food, where the nature of the fat microstructure determines the physical properties which include a number of functional properties. The microstructure of fats is temperature dependent and it also depends on temperature history (deMan, 1982). The water and water-phase ingredients (e.g. proteins) are emulsified in the fat continuous matrix which affect the emulsion stability (deMan, 1982). The addition of salt to the fats (e.g. butter) changes the melting of the aqueous phase from a single transition to a double transition, hence lowering the crystallization point (Sherbon and Dolby, 1972).

Objectives

The objectives of this study were to:

1) identify various polymorphic forms (sub-α, α, β', and β) in salted, semi-salted butter, margarines, commercial vegetable fat blends and rapeseed oils.

2) evaluate the effect of lecithin and sucrose as added ingredients on polymorphic behavior of cocoa liquor.

3) examine the effect of heating and cooling cycles on polymorphic behavior of cocoa butter and cocoa liquor.

4) evaluate relationship between rheological, namely viscosity and hardness, and thermal characteristics of commercial fat blends.

CHAPTER II

LITERATURE REVIEW

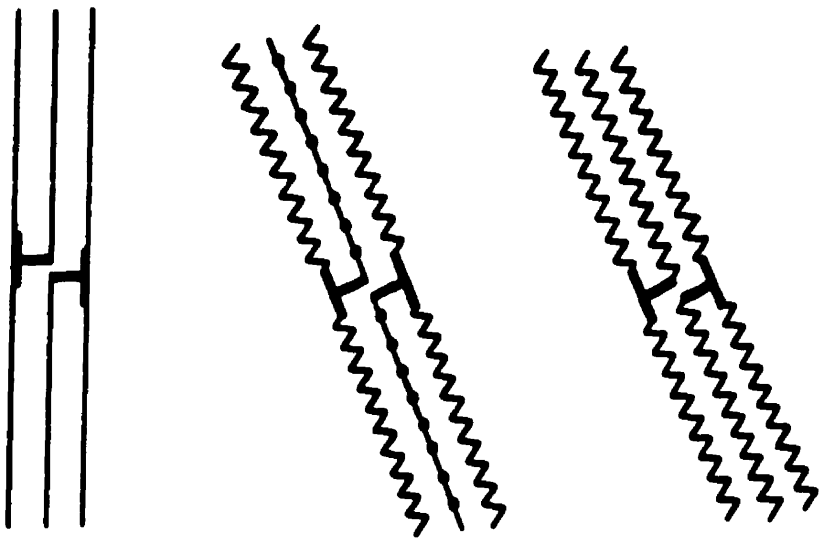
II. 1. PHYSICAL CHARACTERISTICS OF FOOD FATS

A basic understanding of the components of food fats, requires a complete description of the different aspects of their microstructure, such as the nature of the fat crystals, their interaction and distribution. In particular, the concept of polymorphism in fats needs to be defined. Polymorphism refers to the different packing arrangements of the hydrocarbon chains in the fat crystals originating from a variety of molecular configuration and packings; it has an important influence on the phase behavior of fat species (Small, 1986).

II. 1. 1. Fat Crystals and Their Transitions

As a typical example, the schematic diagram of the main characteristics of tristearin is shown in Figure 1. Triglycerides crystallize in four geometric forms designated as: sub-α, α ,β′ and β (Larsson, 1986). The sub-α and α are hexagonal forms which are unstable at ambient temperature (Juriaanse and Heertje, 1988). The sub-α form, if it exists, is lower in melting point and stability than the α form. In some cases sub-α and α transformation is reversible based on having identical *d spacing* (Lutton, 1972). However Riiner (1970) reported that sub-α had X-ray short spacings characteristics of β′ form. The β′-crystal form is orthorhombic, possesses two ethylene (CH_2) units in each subcell, in which the alternate chain planes are perpendicular to their adjacent planes The β-crystal form is

form is triclinic, has two ethylene units in each subcell, with parallel zigzag planes (Nawar, 1985).



Polymorph	α	β′	β
	Vertical oscillating chains	Tilted chains with adjacent zig-zags indifferent planes	Tilted chains, all zig-zags in same plane
X-ray short spacing	single at 0.414 nm	double at 0.418 and 0.378 nm	triple at 0.368, 0.386, and 0.459 nm
Melting Point	54°C	64°C	73°C

Figure 1. Schematic diagrams of polymorphic forms α, β′ and β in tristearin (Timms, 1984).

The transition point of a crystal form is the temperature at which the relative stability of the crystal form changes. For example, the polymorphic transition of cocoa butter, which has been the subject of several studies, revealed six forms of crystals, each having a different melting point (Wille and Lutton 1966). The melting points of the polymorphs ranged between 15°C and 36°C; all crystal forms were obtained from the liquid phase, except the VI form. The VI form can be obtained only by transformation from the V form. The α form is obtained when cocoa butter was cooled rapidly; supercooling of the melt causes the formation of liquid crystals (Larsson, 1982). The β′-form (III and IV) can be obtained directly by cooling the melt and maintaining the temperature a few degrees above the melting point of the α-form; the $\beta' \rightarrow \beta$ transition occurs when the β′-form is heated to its melting point (Larsson, 1982). Figure 2 illustrates a typical triglyceride curve showing the transitions of the polymorphic forms α, β'_2, β'_1, and β. Although fats are considered to have crystal structure, the contribution to their structure is actually dependent on the crystal structure of the component triglycerides and their component fatty acid.

The polymorphic transition of the fatty acids were described by Stenhagen and von Sydow in 1953 (Garti and Sato, 1988); they reported that all crystal forms (A, B, and C) of even number carbon saturated fatty acids can be obtained from solvents. However, the C form which is the most stable form at high temperature is present only in the melt. Based on the type of chain packing, the A, B, and C forms could be named β, β′ or β'_2 and β'_1 crystal forms, respectively (Garti and Sato, 1988). In odd number carbon fatty

acids, all crystal forms (A', B', and C') are obtained from solvents. The polymorphic behavior of odd number carbon fatty acids is explained by Figure 3.

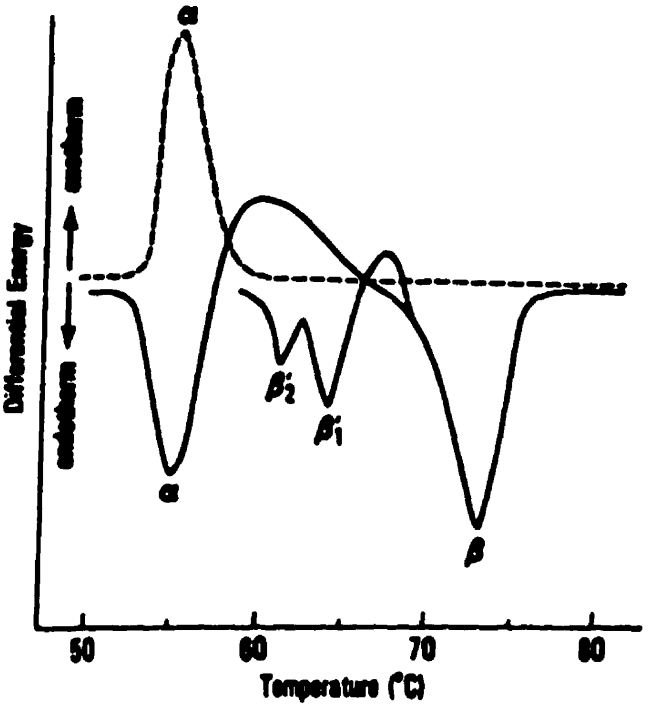


Figure 2. Typical DSC thermal analysis curves of stearin. Cooling (dashed line) rate from melt - 20°C min, heating (solid line) rate -2.5°C min. Intermediate crystals (β'1 and β'2) appeared after 30 min. of delay slightly above α-form (Hagemann, 1988).

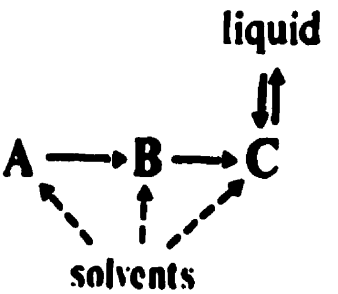


Figure 3. Polymorphic transitions of even carbon number (long chain) fatty acids. The possibility of growing crystals from solvents (dashed lines) (Garti and Sato, 1988).

In unsaturated fatty acids, the molecules are packed in a bilayer where a change in the direction of the tilt occurs at the cis double bond (Garti and Sato, 1988). A knowledge of the crystal structures is important for the understanding of the relation between the chemical composition of fats and crystallization properties. Chemical composition information provides an understanding of the physical structure which in turn determines the physical properties of fats. A number of factors affect the above interrelationships; these include the influence of temperature, thermal history, and polymorphic transformation (deMan, 1982).

II. 1. 2. Effect of Temperature on Polymorphism

In the consideration of the influence of temperature on crystal forms, it is important to define "tempering". Tempering is a thermal process by which fat crystals are formed in their desirable polymorphic forms. Chawla and deMan (1994) showed that in the production of shortenings, a final tempering procedure is crucial in order to stabilize the crystal structure and minimize changes during storage and transport . The effect of tempering on delaying $\beta' \rightarrow \beta$ transition has been reported by Moziar et al. (1989). The tempered samples showed a significant increase in hardness, firmness, and peak force. The increase was attributed to the growing together of crystals and formation of primary bonds (Moziar et al., 1989); it was also shown by DSC that the heat of infusion (ΔH) and melting behavior of the tempered shortenings did not change during 5 weeks of storage. Chawla and deMan (1994) showed that a transition of β to β' occurred in partially hydrogenated soybean and/or canola and palm oil. In a mixture of hydrogenated

vegetable oils, the β form content increased from 61% to 69% as a result of temperature cycling. These authors considered temperature cycling as 1) isothermal treatment of samples at 70°C, -15°C for 18 h, and 23°C for 22 days 2) consecutive 5 cycles started with an additional treatment at 30°C for 2 days then, at 23°C for 2 days. In shortening consisting of hydrogenated vegetable oil and palm oil, β′ crystals remained intact throughout the temperature cycling (Chawla and deMan, 1994). The polymorphic changes in the hydrogenated oils were explained by their low C16:0 content which is considered to be responsible for the soft characteristics of the oils.

II. 1. 3. Solid Fat Content (SFC) of Fats

SFC is commonly used as a measure of the textural properties of fats. It is a measure of the hardness of products stored under various conditions. Juriaanse and Heertje (1988) suggested that a coarse crystal structure in fat is associated with high hardness and that a high SFC was the major reason for high hardness; therefore, the hardness of a fat spread depends on the both amount and type of fat crystals. Haisghton (1976) described two kinds of bonds in crystal interaction which are responsible for hardness of fats. These were i) primary bonds which result from crystals growing together, are irreversible and do not re-form after rupture, and ii) secondary bonds which are weak London Van der Walls forces and re-form after rupture (reversible). Secondary bonds participate in the consistency whereas primary bonds are considered to be responsible for the hardness. Previously, Shama and Sherman (1970) suggested that crystal interactions are based on the concept of a spectrum of bond strengths and argued that in margarines, weak bonds

form only a minor proportion of the bond strength spectrum. In butter, on the other hand, a small proportion of strong bonds are present although butter appears harder than margarines under refrigeration conditions (Shama and Sherman, 1970).

II. 1. 4. Melting Point of Fats and Oils

Unlike pure compounds which exhibit melting points, fats and oils, because of their complex nature show melting ranges. Each component of a fat has its own melting point, but together the various components show a melting range which is loosely referred as melting point. Melting points of fats are determined by a variety of methods with different methods having different degrees of reliability. Moreover, different official analytical organizations recognize different methods as official methods; the AOAC (Association of Official Analytical Chemists) recognizes the Wiley and capillary tube methods and the AOCS (American Oil Chemists Society) lists the capillary tube, Wiley, softening point, and slipping point methods as official methods. In addition to the official methods, melting points of fats can be determined by Mettler dropping point (Keim, 1970), the photoelectric method (Keim, 1970), the conductivity method (Chabanne, 1969), and from DSC curve (deMan et al., 1983). Melting point of fats are altered by "internal" factors of fats; these include; i) degree of saturation (the greater the degree of unsaturation the softer the fats are, therefore the lower the melting point) ii) chain length of fatty acids (melting point increases as the chain length increases) iii) molecular configuration of triacylglycerols (a single triacylglycerol shows a sharp melting point, and triacylglycerols in a mix system show broad melting points (Potter, 1970). Melting

points of fats also depend upon "external" factors such as pretreatment of the fat, heating rate during experiment and storage condition. A more detailed consideration of "internal" and "external" factors is provided below.

II. 1. 5. Internal Factors :

II. 1. 5. 1. Degree of Unsaturation

Studies on polymorphism of triolein, trilinolein, and trilinolenin have shown that the greater the degree of unsaturation the lower the melting point. Table 1 shows the degree of unsaturation of these triglycerides, corresponding melting points as well as α, β, and β′ intermediates (β'_3, β'_2, and β'_1) polymorphic phases (Hagemann, 1988). Triolein and trilinolein each exhibit α, β, and three β′-forms. The intermediate forms of β′ of trilinolenin is uncertain; however, β'_3-form melts 20°C below the β'_2-form (Hagemann et al., 1972).

Table 1. *Melting points of unsaturated triglycerides.*

Triglyceride	POLYMORPHIC FORMS				
	α	β'_3	β'_2	β'_1	β
	MELTING POINT (°C)				
Triolein	-37,-32	-12,-13	-8	-5	5.5
C18:1	-32	-12	–	–	4.7,-5
Trilinolein	-84	-43,-47	-27,-29	-21	-11,-13
C18:2	–	-45.6	–	–	-12.9
Trilinolenin	-44.6	–	–	–	-24.2
C18:3	–	–	–	–	–

Source: Hagemann et al., 1972 (shaded values); Wheeler et al., 1940.

II. 1. 5. 2. Chain Length of Fatty Acid

Figure 4 shows the melting points of a homologous series of simple triglycerides as a

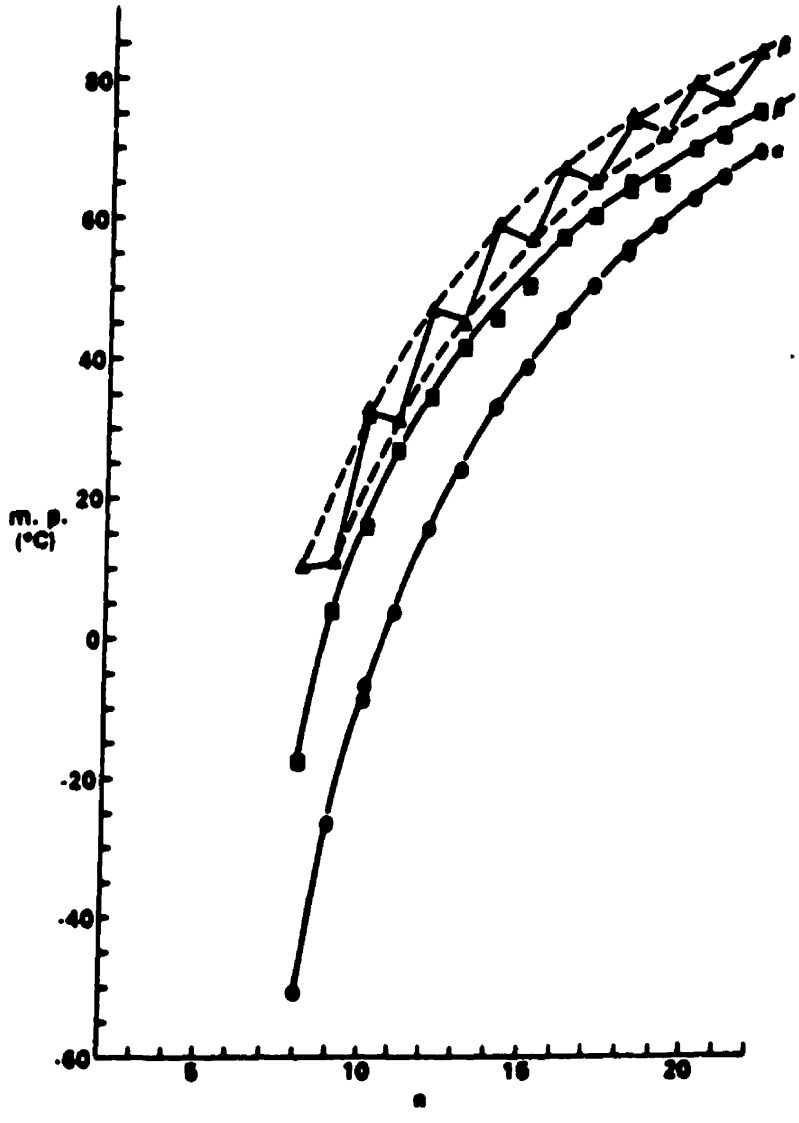


Figure 4. Melting points of simple triglycerides as function of number of carbon atoms in fatty acid chain. Odd number carbon triglycerides alternate with even number carbon in each polymorphic form starting with even number carbon. ●=α, ■=β', ▲=β *(Small, 1986).* n = number of carbons

function of number of carbons in each acyl chain for three polymorphic forms. There is an increase in melting point as the temperature increases (Lutton and Fehl, 1970). In each case, the β′-form is less stable than the β-form while the α-form is the least stable form. There is an alternating pattern for changes in melting points for even and odd homologues of the β-form while β′ and α-forms show smooth curves.

The thermal behavior of saturated triglycerides and fatty acids has been extensively examined. Table 2 shows data of relationship between chain length and melting point of some even carbon number saturated fatty acids. The β-form is the most stable of the three forms of any given fatty acid. Melting points of crystal forms increase as the number of carbon atoms increase in the fatty acid chain. Slightly different melting points have been reported by two group of researchers (Hagemann and Rothfus, 1983; Lutton and Fehl, 1970).

There is an increase in melting point as the temperature increases (Lutton and Fehl, 1970). In each case, the β′-form is less stable than the β-form while the α-form is the least stable form. There is an alternating pattern for changes in melting points for even and odd homologues of the β-form while β′ and α-forms show smooth curves.

II. 1. 5. 3. Position of Double Bonds

Thermal analysis by DSC of β-form of triglyceride of cis and trans series revealed an alternating pattern for change in melting points with double-bond position (Figure 5).

Table 2. Melting points of polymorphic forms of saturated fatty acids.

Fatty Acid Chain	POLYMORPHIC		
	α	β'	β
	MELTING POINTS (°C)		
14:0	31.0	41,45	56.0
	32.8	45.0	58.5
16:0	46.0	53,57	66.0
	44.7	56.6	66.4
18:0	55.0	61,64	73.0
	54.7	63.2	73.5
20:0	64.0	69,71	78.0
	61.8	69.0	78.1
22:0	69,70	74,77	83.0
	68.2	74.0	82.5

Source: Hegemann and Rothfus, 1983 (dashed values); Lutton and Fehl, 1970

This phenomenon is similar to the melting point alternation of β-form of saturated triglycerides (Lutton and Fehl, 1970). The alternating pattern in melting point of the cis configuration is caused by density differences in crystal packing as the number of methylene groups (-CH_2-) between the carboxyl group (-COOH) and double bond increases (Larsson, 1966). Lutton and Kolp (1951) related the alternating pattern of melting points in the trans series to the differences in the degree of tilt relative to end-group planes.

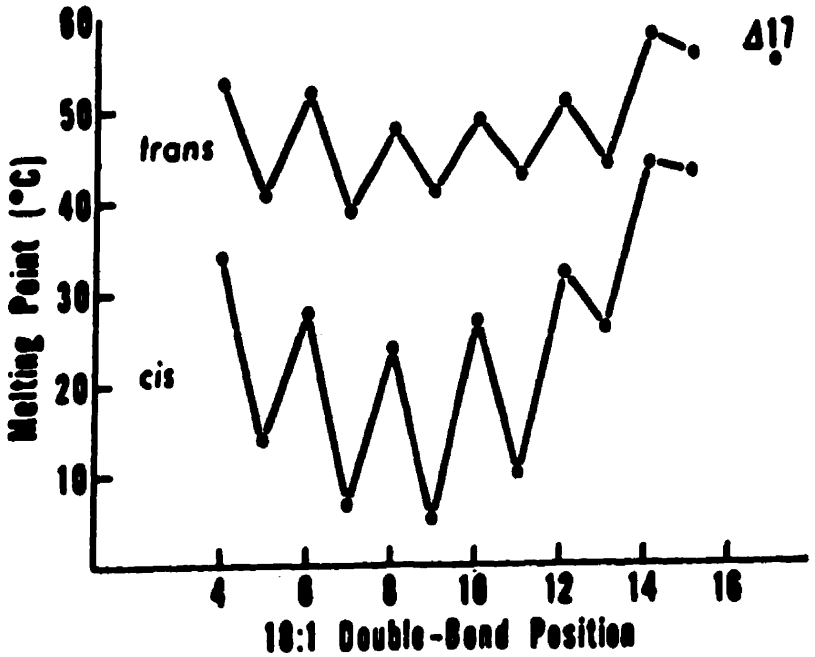


Figure 5. Melting point of oleic (C18:1, cis-9) and elaidic (C18:1, trans-9) acid (Hagemann et al., 1975).

II. 1. 5. 4. Molecular Configuration of Glycerides in the Fats

Glycerides, being major constituents of fats and oils, molecular configuration affect their properties. Phase transformation and melting points of fats vary depending on the number of different chemical entities present. Most triglyceride transitions follow first-order kinetics where large changes in terms of molecular movements occur. Second-order transitions occur over a wide range of temperature which merely involve an increase in molecular movement. In transition of sub-α → α a second-order transformation probably occurs (Hagemann, 1988).

II. 1. 5. 5. Aqueous Phase

Three different structural types of fats can be distinguished based on phase considerations: shortenings (100% fat), margarines and halvarines (80-60% fat), and butter (80% fat) (Juriaanse and Heertje, 1988). Margarines not only can be composed of a relatively wide range of triglycerides but also the aqueous phase may contain different ingredients. Margarines and butter contain 16-20% water as fine dispersed droplets (Juriaanse and Heertje, 1988). It is estimated that butter contains approximately 10^{10} to $3x10^{10}$ droplets/ml (Walstra, 1974; Mulder et al., 1956; Sato, 1988). Water droplets in margarines are formed during intensive mixing of fat and water during processing; the crystals orient themselves around the water droplet surface. Heertje et al. (1987) showed by scanning electron microscopy (SEM), that the "shells" of water droplets are surrounded by the fat crystals which is the continuous phase; the crystals are considered to be in the β′ form. In butter where both β and β′-crystals forms are present, the outer crystalline shell of high melting fat consists exclusively of β-crystals (Heertje et al., 1987). These "shells" are connected with the three-dimensional fat crystal network.

The contribution of the aqueous phase to melting characteristics was investigated by Sherbon (1972). In unsalted butter a single melting transition at -0.5°C associated with the aqueous phase was observed. Salted butter thermograms showed two melting transitions at -8°C and -22°C; the latter transition point represents melting of NaCl-H_2O eutectic mixture, while the former point is the final melting point of H_2O at temperatures controlled by salt concentration.

II. 1. 5. 6. Emulsifiers

The surfactant property of fat and water is due to the presence of free fatty acids and mono- and di-glycerides. In fats, the carboxyl or acid end of the fatty acid (-COO^-) as well as the -C=C- portion of the unsaturated fatty acid is polar or hydrophilic; the acid end, or the double bond, tend to orient itself towards the water. The hydrocarbon end of a fatty acid is nonpolar or hydrophobic and is oriented towards the oil. If the fatty acid has more than one double bond, not all the double bonds can orient themselves to the water because of structural limitations. Appropriate tempering during processing or addition of minute amount of emulsifiers (surfactants) have been suggested to clear up this problem. Emulsifiers will either prevent or retard blooming. Blooming is defined as the development of a new phase in the fat that disrupts the smooth surface and is manifested as clusters of crystals on the surface (Timms, 1984).

Emulsifiers are defined as amphiphilic molecules, consisting of a hydrocarbon chain and a hydrophilic moiety (Aronhime et al., 1990); they stabilize liquid emulsions and in terms of their effect on polymorphism, they are considered as "*crystal structure modifiers*", "*dynamic controllers of polymorphic transformations*", and "*crystal modifying agents*" (Perrin and Michel, 1973).

Niiya et al. (1973) examined the effect of both saturated and unsaturated fatty acid monoglycerides and other emulsifiers on the physical properties of hydrogenated edible fats . The saturated fatty acid monoglycerides such as monostearin (MS), monolaurin (ML), monopalmitin (MP), and monobehenin (MB) were incorporated into the fat and resulted in increased melting point of the fats; the crystal growth of vegetable fats

(hardened soybean oil and palm kernel) was slightly accelerated, whereas that of animal fats was unaffected (Figure 6).

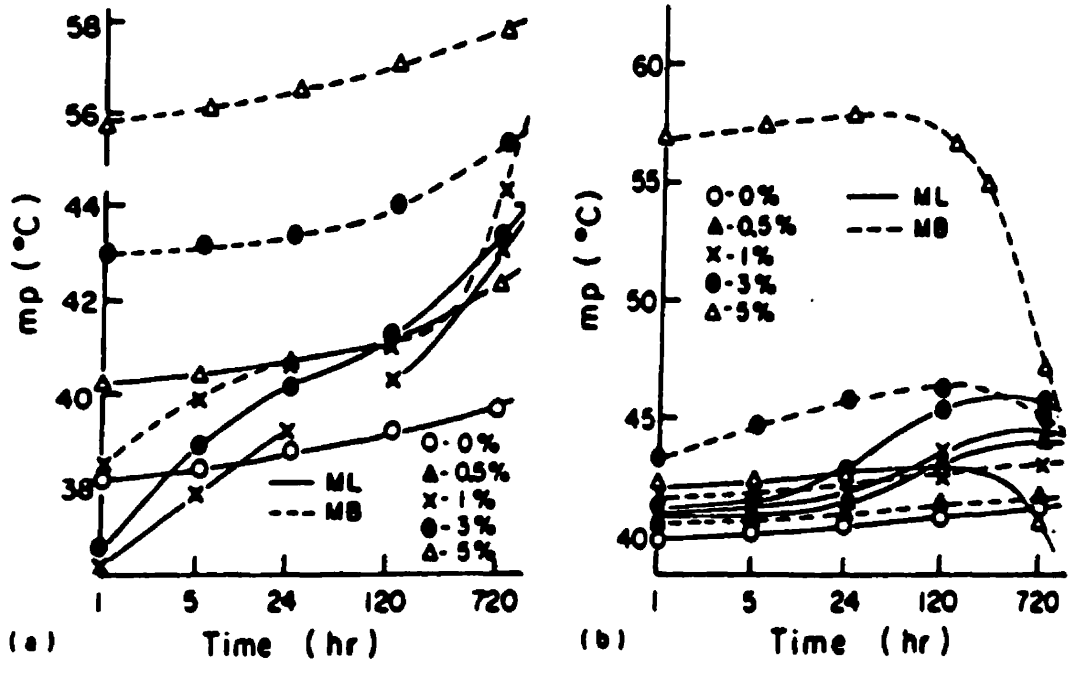


Figure 6. Change of melting point of hardened soybean oil by added (a) monostearin and (b) monolaurin and monobeheinin, samples aged at 30°C (Garti and Sato, 1988).

A slight increase in the melting point was detected at the presence of ML and a significant increase in the presence of MB in hardened whale oil (Figure 7); crystal growth was not accelerated by ML and MB.

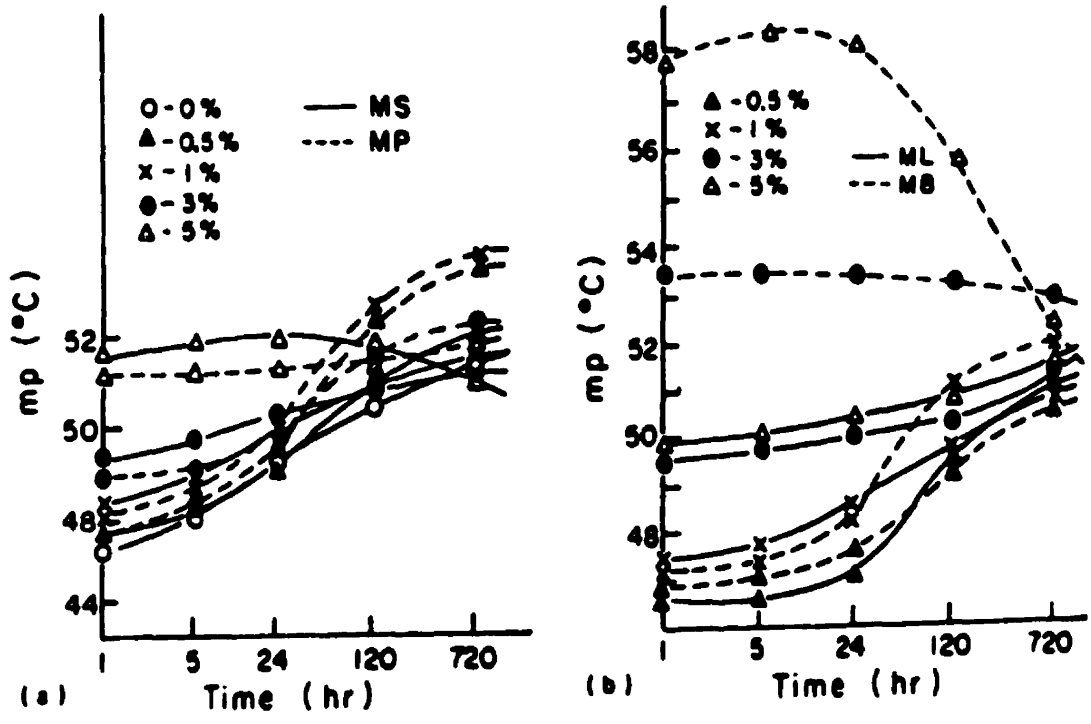


Figure 7. Change of melting point of (a) hardened palm kernel oil and (b) hardened whale oil by adding monolaurin and monobehenin (Garti and Sato, 1988).

Unsaturated fatty acid monoglycerides, monoolein (MO) and monolinolein (MLI) significantly affected both vegetable oils and animal fats; these surfactants decreased the melting point of hardened soybean oil and hardened palm kernel oil (Figure 8). Unsaturated surfactants also accelerated the crystal growth of the fats.

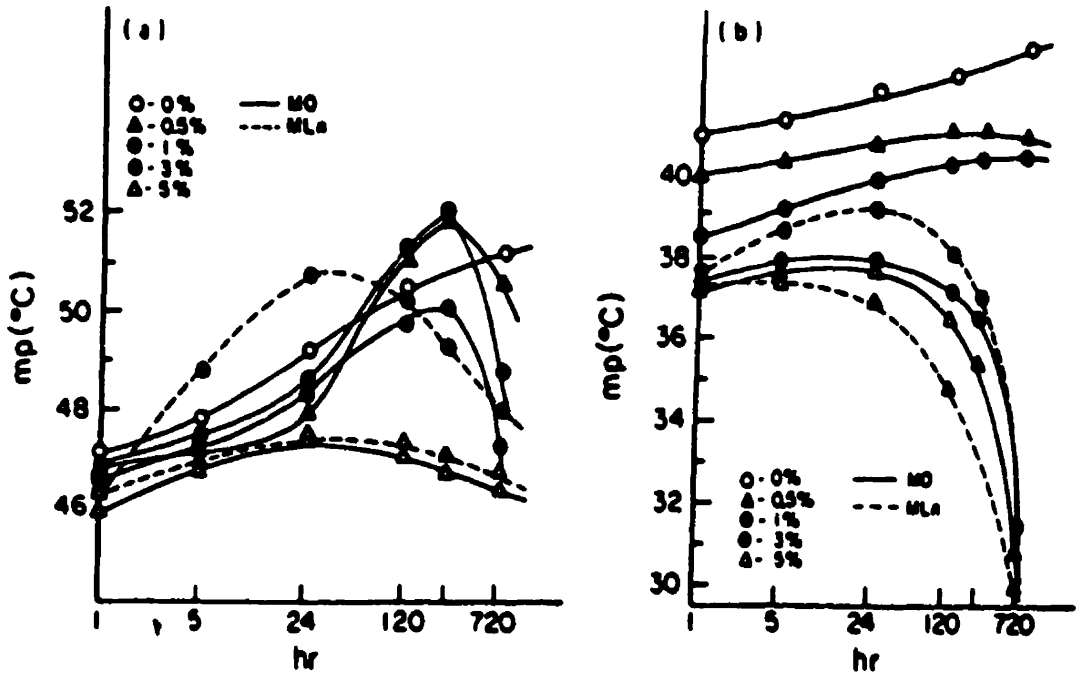


Figure 8. Change of melting point of (a) hardened soybean oil and (b) hardened palm oil, aged at 30°C in the presence of monoolein and monolinolein (Garti and Sato, 1988).

Several researchers have shown that sorbitan tristearate (STS) inhibited the β→β′ transition of vegetable oil (Madsen and Als, 1968; Hernqvist and Anjo 1983). Hernqvist et al. (1984) showed that the presence of diglycerides as surfactants stabilized the β′ form during storage of beef tallow and hardened whale oil. Lee and deMan (1984) studied the effects of STS (sorbitan tristearate), STO (sorbitan trioleate), SMS (sorbitan monostearate) and monoglycerides on the polymorphic behavior of canola oil; STS

appeared to be the most effective surfactant in delaying the transition β′→β; this effect was temporary. The packing of the chain plains in transformation of β′→β involves a 180° rotation of chains in every second double layer (Lee and deMan, 1984). The mechanism of action of emulsifiers on polymorphic transformations was explained to involve possible blockage of the rotation of the chains in the glyceride to a different packing within the fat (Lee and deMan, 1984).

The effect of surfactants on polymorphic transition of cocoa butter was examined by Garti et al. (1986). Addition of surfactant to cocoa butter accelerated the rate of transformation from I to V, but retarded the transformation from V to VI. It is believed that the transformation from polymorphs I to V are melt-mediated while the V to VI transformation is solid-mediated (Aronhime et al., 1990). Figure 8 summarizes the effect of emulsifiers on cocoa butter polymorphs; emulsifiers increase the liquid fraction and destabilize the metastable forms giving a kinetic orientation toward the stable form.

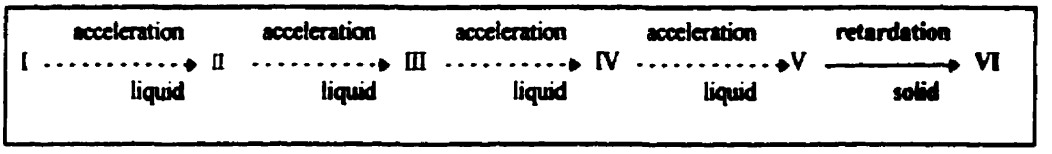


Figure 9. Effect of emulsifier on polymorphism of cocoa butter (Aronheime et al., 1990).

Mostafa and deMan (1985) and Mostafa et al. (1985) used 1,2- and 1,3-diglycerides of saturated long-chain fatty acids as crystal structure modifiers in β-tending fats; addition of 1 wt% of saturated diglycerieds did not retard the β′ transformation nor was β′-form stabilization achieved. A 3-5 wt% concentration was sufficient to drive polymorphic

behavior changes; 1,2-diglycerides were more efficient than 1,3-diglycerides in stabilizing the β′ form.

II. 1. 6. External Factors:

II. 1. 6. 1. Tempering of Fats

Tempering is a thermal process by which fats and fat products (e.g. butter, margarines, chocolate) are converted to the stable polymorphic forms. Inappropriate tempering results in poor quality characteristics of these products. Understanding of polymorphic changes are essential for satisfactory process and tempering of fats. Fats must maintain a certain physical appearance during process and storage. *Sandiness* of margarines and *blooming* of chocolate are long-known evidences of unwanted polymorphic changes. These phenomena occur when niddle-like β′-crystal (about 1μm long) convert to a thermodynamically most stable β-form (>20μm long), (Madsen and Als, 1968). Some vegetable oils such as partially hydrogenated sunflower oil and low-erucic rape seed oil have tendency to form β-form and cause sandiness. The conditions which are important for optimum tempering are considered below.

II. 1. 6. 2. Heating and Cooling Rates

Crystallization and melting behavior are physical properties of the fats. These properties can be measured by the use of various techniques. At the macroscopic level, thermochemical techniques such as differential scanning calorimerty (DSC), themogravimetry (TGA), differential thermal analysis (DTA), thermomechanical analysis

(TMA), and thermodilatometry can be used to observe changes of some gross physical condition of the oils and fats. The DSC has been used fairly extensively for at least four decades, measures energy changes as a result of changes of phase as material is either heated or cooled.

The effect of variations in cooling or heating rate of temperature on the shape of the thermograms of fats and oils are already known. For instance, peak broadening occurs progressively as the rate is increased. The faster rates also shift peaks to lower temperature in cooling and to higher temperature in heating. Sato et al. (1989) elucidated the details of the effect of temperature rate change on polymorphism. These researchers used cooling and heating to obtain various polymorphic forms. Cebula and Smith (1991) investigated effects of cooling and heating rate changes on polymorphism of pure triglycerides; they summarized their observations as follows: i) the number of polymorphic forms depends not only on the cooling and heating rate, but also on the individual triglyceride; ii) rapidly cooled samples underwent progressive polymorphic transitions on subsequent reheating; iii) the degree of transformation on heating was greater at slow heating rates.

II. 1. 6. 3. Thermal History or Storage Conditions

The thermal history of a fat is sometimes associated with the "memory" of the fats. Figure 10 shows the effect of thermal history on the polymorphism of pure POP. In a) the single endothermic peak represents the transition point of β-form when it was crystallized by an organic solvent, b) POP then cooled to 15-20°C below its melting

point, stored for 2 weeks. The identical endotherm when compared with a) indicates that recrystallization of β-form occurs under these conditions, c) an exothermic peak (freezing point) of α-form when POP cooled rapidly (≥10°C/min.), d) cooled material (in c) is reheated, endothermic peak (melting) of α-form will appear at about 12°C, e) the rapidly cooled POP (in c) is heated at a much slower rate (1.25°C/min.) the three basic crystal forms (α, β′, and β) will be apparent.

II. 1. 6. 4. Working of Fat

Mechanical and thermal agitation during process influence the transformation of crystals which have a marked effect on the melting point and performance of the fats in their applications. Heertje et al. (1988) reported that margarines and shortenings subjected to C-unit (a cylinder fitted with pins in inner wall induces strong working during fat crystallization) showed a more granular structure than samples processed only in A-unit (a scraped-surface tube induces fat and water mixing and fat crystallization). They also observed that in A-unit under strong shear a much finer emulsion was formed in which the crystalline were related to α-form reported by Haighton (1976).

II. 2. EFFECT OF PROCESSING AND CHEMICAL COMPOSITION ON PHYSICAL CHARACTERISTICS:

The processing and chemical composition of fats determine to a large extent the final properties of products containing the fats. In establishing a relationship between composition and desired product, processing plays a significant role. Animal fats are

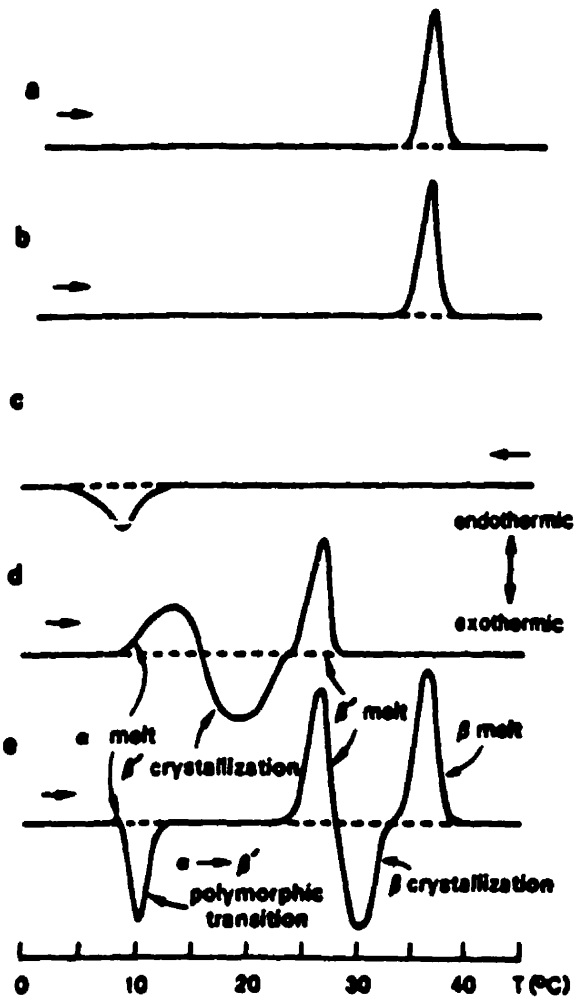


Figure 10. Effects of thermal history on the polymorphism of 2-oleodipalmitin, POP. a)β crystal melting formed in organic solvent, b)β crystal when material in (a) cooled and stored for 2 weeks and rcheated, c)formation ofα crystal, d)melting endotherm of α crystal followed by crystallization and melting of β' crystal at rapid heating rates, e)polymorphic transition of α →β' followed by melting of β', formation and melting of β crystal at slow heating rates, (Small, 1986)

generally extracted by dry or steam heat to separate them from other food compounds such as proteins. Vegetable fats are obtained by solvent extraction or expression of oilseed. Fats and oils obtained by above mentioned methods are known as "crude" fats and oils. Crude fats and oils undergo various refining processes e.g. degumming, bleaching, and deoderizing. The number of processing steps determine the final physical properties of fat products.

II. 2. 1. Modification of Fats

Modifications of fat have been useful for alteration of physical properties, such as spreadibility to increase oxidation stability, storability of fats. Modification is done by means of hydrogenation, interesterification, and fractionation.

II. 2. 1. 1. Hydrogenation

Hydrogenation involves introduction of hydrogen atoms to the double bonds of the unsaturated fatty acids (Hoffmann, 1989; Synder et al., 1986). It is a common belief that hydrogenation converts only unsaturated to saturated fats. In fact, hydrogenated vegetable shortenings, oils, and margarines may contain large amounts of unsaturated fatty acids (Ziller, 1994). The primary aim of hydrogenation however, is to achieve stability and control in physical properties of the final fat product. Fats are solidified to achieve correct hardness, melting point, and consistency. Another aspect of hydrogenation relates to the formation of trans isomers whose polymorphic behavior has been discussed earlier (in section II. 1. 5. 3).

II. 2. 1. 2. Interesterification.

Interesterification of fats and oils is another important process for modification of physical and functional properties (Young, 1985). Many reports have been published on chemical (Chang, 1990) and lipase-directed interesterification (Bloomer et al., 1990; Macrae, 1983). Most researchers agree that chemical interesterification (randomization) introduces fatty acid randomly on the glycerol moiety, while some lipases (enzymatic modification) exhibit interesterification in specific positions, mainly at 1,3-positions of the fatty acids in triglycerides.

II. 2. 1. 3. Fractionation

Fractionation is the separation process of the higher and lower-melting fractions of different physical characteristics. For example, fractionation of palm oil has resulted in fractions with different melting characteristics (Ng, 1990). The author reported that a high concentration of palmitic acid in palm oil exhibited a solid-state behavior which is a limitation in its use for frying oils or for margarine and shortening.

CHAPTER III

IDENTIFICATION OF POLYMORPHIC FORMS IN COMMON FOOD FATS AND OILS

III. 1. MATERIALS:

Commercial samples of: dairy fats (salted butter, semi-salted butter, and butter containing 1% salt), vegetable fats (margarines, commercial vegetable fat blends, cocoa butter, and cocoa liquor), and vegetable oils (rapeseed oils) were used.

Commercial margarines and butter were purchased from a local supermarket and labeled as follows:

A: margarine, 80% hydrogenated and liquid soybean oil,

B: light margarine, 35% canola or sunflower oil and 58% water and 3% modified palm and palm kernel oil,

C: margarine, canola, linola, and sunflower oil , and water ≤16% and 6% modified palm and palm kernel oil,

D: salt free margarine, canola, linola, and sunflower oil (75%) and water ≤16% and 7% modified palm and palm kernel oil,

E: salted butter,

F: semi-salted butter, and

G: butter containing 1% salt .

The margarines varied in salt, water, and oil content. Butter samples differed in their salt content.

A set of four commercial samples of vegetable fat blends were tested for polymorphic forms. The identification of the fats are as follows:

#1: partially hydrogenated soy bean oil and cotton seed oil,

#2: fractionated soy bean oil,

#3: hydrogenated palm kernel oil, and

#4: partially hydrogenated canola oil.

Hydrogenated rapeseed oils (R1, R2, R3, R4, R5, and R6) were also examined for polymorphic forms.

III. 2. METHODS:

III. 2. 1. Thermal Analysis:

To identify the presence of polymorphic forms, thermal analysis was performed using a differential scanning calorimeter (DSC) equipped with TC11 processor (Mettler TA 3000, Mettler Instrument Corporation, Switzerland). The DSC was calibrated using pure indium (ΔH_{fusion} = 28.5 J/g; melting point 156.4°C). An empty aluminum pinholed pan was used as a reference. Liquid air was used to cool to the desired temperatures in all cases. Approximately 15 mg of samples were used for all fats and oils.

Samples were encapsulated in aluminum pans and heated to temperatures between 50 and 70°C (depending on the sample) and held at this temperature for 5 min to destroy crystal nuclei; the samples were then cooled rapidly at a rate of 20°C/min to -40°C and

held at this temperature for another 5 min. The samples were then reheated to 60°C at rate of between 0.625 and 5°C/min (depending on the sample).

III. 2. 2. Calculation of ΔH, Transition Point, and Percent Liquid Fraction:

Results from DSC scan were recorded and processed using Graphware 72.5 TA software (Mettler Instrument Corporation, Highstown, NJ, USA). This software processes the data into ΔH (enthalpy change), melting or crystallization points (transition point), and percent liquid fraction.

The **change of enthalpy (ΔH)** represents the overall heat change resulting from possible phase transitions. The **transition point** (melting or crystallization) is registered as the midpoint temperature of a differential curve. The extent of reaction or **liquid fraction** corresponds to the ratio of partial area to the total area (fractional area) as a function of sample temperature.

III. 2. 3. Assignment of Polymorphic Forms:

The designation of polymorphic forms (sub- α, α, β′, and β) and their corresponding melting points was accomplished by comparing the transition points of DSC thermograms with melting points reported in the literature (Table 3).

Table 3. Polymorphic forms and corresponding melting transitions of some food fats.

Fat Products	Melting Point (°C)		
	α	β'	β
Cocoa butter[1]	17.3, 23.3	25.5, 27.5	33.8, 36.3
Butter[2]	-	16.5	32.4
Butter[3]	7.5	14.5	-
Rapeseed[4]	-21.0	-	-8.0, 5.0
Margarines[5]			
Soybean oil		32.7, 34.2	-
Canola oil	-	-	27.3, 31.4
Sunflower-palm-kernel-palm oil	-	33.0	-

1 = Wille and Lutton, 1966. 2 = Bornaz et al., 1994.
3 = Coni et al., 1994. 4 = Kawamura, 1981.
5 = deMan et al., 1991. (melting point by Mettler Dropping Point Method)

III. 3. RESULTS AND DISCUSSIONS

III. 3. 1. Margarines

Figure 11 and Table 4 show the thermograms and transition points of the commercial margarine samples with various compositions: A- margarine (hydrogenated and liquid soybean oil, 2.8% salt), B-margarine (canola or sunflower oil, 1.5% salt), C-margarine (canola, linola or sunflower oil, 1.8% salt), and D-margarine (canola, linola, and sunflower oil, no salt). Unsalted margarine, containing canola, linola and sunflower oil (D) showed a minor fraction with transition point of 31.1°C; no other transition points were observed in the temperature range of 5°C-40°C, which is associated with the common fat crystals α, β′, β. Comparison of these results with data reported in the literature (Table 3), suggests that the minor peak (31.1°C) represents the β-form. Salted (2.8%) margarine containing hydrogenated and liquid soybean oil showed minor peak with transition points of 12.9°C, 32.4°C, and 38.9°C. deMan et al (1991) assigned fractions with melting points of 32.7°C and 34.2°C as β′-forms in soybean margarine (Table 3); by comparison, the peak with transition point of 32.4°C (A) could represent the β′-form. The peaks with transition points of 12.9°C and 38.9°C have not been reported in the literature and could represent the α and β forms respectively based on their positions relative to β′. No polymorphic forms were identified in salted (1.5%) margarine containing canola or sunflower oil (B) or in salted (1.8%) margarine containing canola/linola or sunflower oil (C). The results from margarine show the presence of only small quantities of the common β crystal form (A, D) and the presence

of the α and β′ forms only in A. deMan et al (1991), based on melting point determinations identified only β′ and β forms in soybean and canola margarine. The presence of peak with transition point above 50°C (52.6, 69.9;C) (54.5; B) (67.9;D) represent **"sediment"**; similar transition points have been reported by Liu et al. (1996) and defined as "sediments". These researchers reported a higher melting point for sediments of Canadian canola (77°C), Australian canola (77°C) than sunflower oil (73°C); differences between these transition points and our data can be attributed to the different composition of margarines. Occurrence of sediments is due to the inefficient or lack of winterization, which is a technique to remove these sediments from oils such as sunflower, soybean, and canola during processing. These oils are used in manufacturing of margarines; Przybylski et al. (1993) and Hu et al. (1993) reported that winterization process does not guarantee a sediment-free product in refined canola oil. The sediments contain mainly wax esters (72-99%) of long chain fatty acids and alcohols (Liu et al., 1996). The transition points -22.0 to -22.8°C (Figure 11) and -0.3 to -10.3°C (Figure 11) are associated with eutectic form of salt and pure water, respectively and represent the melting of water and eutectic mixtures of water and salt: sample D which contained no salt showed a peak with transition point of -25.2°C; this could be an unidentified crystal form of the fat.

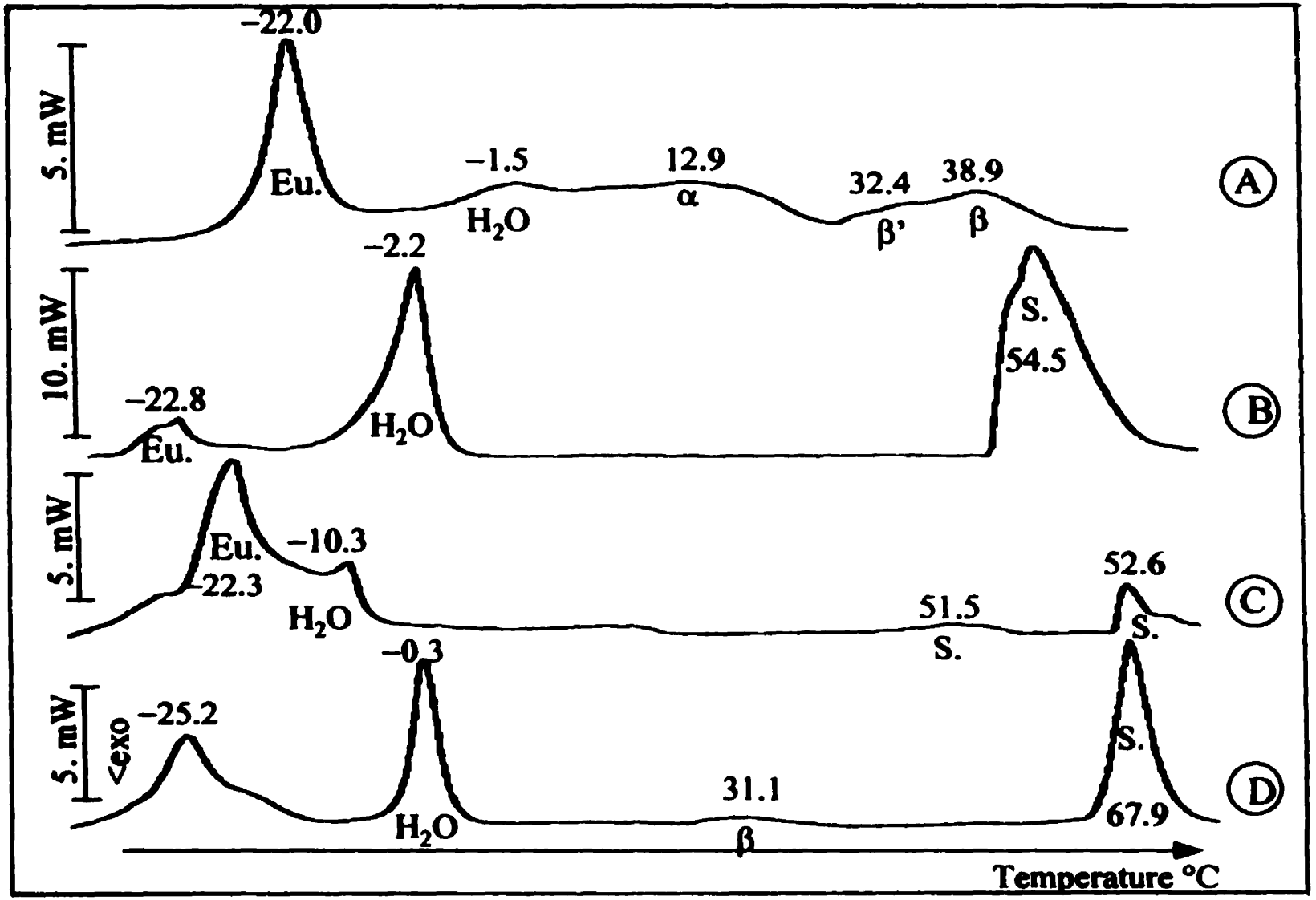


Figure 11. DSC thermograms of margarines: hydrogenated soybean oil (A), canola or sunflower oil (B), canola, linola, or sunflower oil (C), and canola, linola, & sunflower oil (D). Eu = eutectic S= sediment

Table 4. Melting points of polymorphic forms of margarine: hydrogenated soybean oil (A), canola or sunflower oil (B), canola, linola or sunflower oil (C), canola, linola, and sunflower oil (D); butter: salted (E), semi-salted (F), and 1% salted.

Samples	Melting Point (°C)			
	α	β'	β	Sediment
Margarine				
A	12.9	32.4	38.9	-
B	-	-	-	54.5
C	-	-	-	51.5, 52.6
D	-	-	31.1	67.9
Butter				
E	6.4	15.5	31.5	-
F	6.2	15.3	31.1	-
G	6.4	15.5	31.3	-

III. 3. 2. Butters

Figure 12 and Table 4 show the thermograms and transition points of butter with 1% salt (G), semi-salted butter (F), and salted butter (E). By comparison of the recorded transition points of 6.2-6.4°C, 15.3-15.5°C, and 31.1-31.5°C with data (Table 3), reported by Bornaz et al (1994) and Coni et al (1994) it can be suggested that the peak with transition point of 31.1-31.5°C is the β crystal, the peak with transition point of 15.3-15.5°C represents the β′ form and the peak with the transition point of 6.2-6.4°C represents the α form. Our results suggest that in the three samples of commercial butter, the three common crystal forms, α, β′, and β were detected. Other researchers have shown the presence of either α and β′ crystals or β′ and β crystals in butter (Garti and Sato, 1988). On the basis of percent area (Table 5), the β′ represents the dominant polymorphic form in butter samples. The peaks represented by transition points -22.0 to -23.2°C, and -5.7 to -9.3°C represent a eutectic form of salt and water and pure water respectively. On the basis of signal response (Figure 12) and percent area (Table 5), it is evident that sample E contains the highest amount of salt (Sherbon and Dolby, 1972).

Table 5. Area percent of polymorphic forms of : salted (E), semi-salted (F), 1% salted (G) and eutectic mixture (Eu.) butter samples.

Butter Sample	Eu.	α	β′	β
	Percent Area			
E	17.7	11.3	24.0	18.5
F	5.8	9.2	26.4	21.7
G	7.7	8.6	22.7	20.9

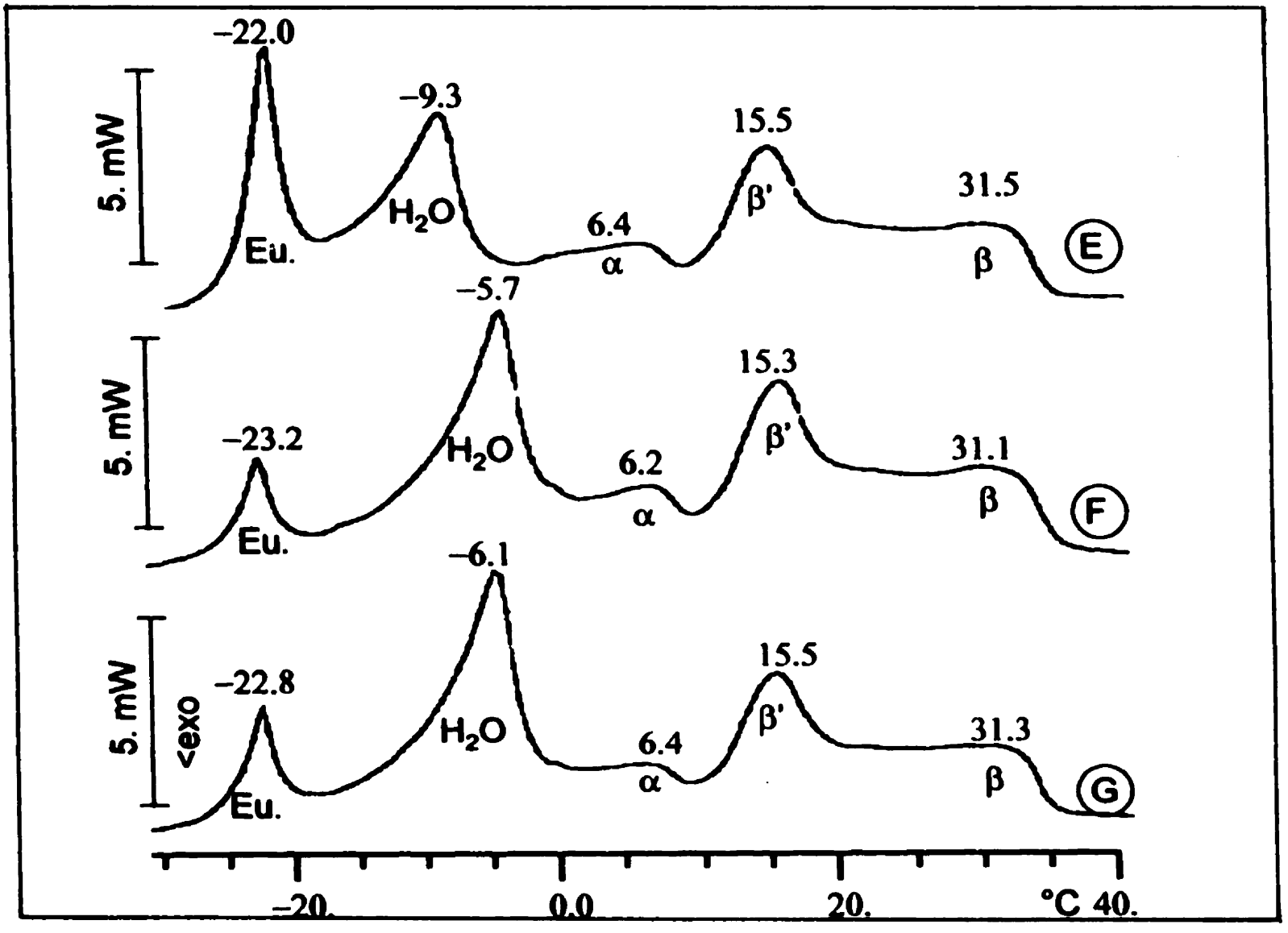


Figure 12. DSC thermograms of butters: salted (E), semi-salted (F), and 1% salted (G). Eu.= eutectic

III. 3. 3. Cocoa Butter and Cocoa Liquor

Figure 13 shows that untempered cocoa butter (C) gave two endothermic peaks at 17.7°C and 22.5°C which represent sub-α and α form crystals respectively (Table 3). Three polymorphic forms were identified for well-tempered (A) as well as poorly-tempered (B) cocoa butter. The transition points in both well-tempered (31.3, 23.5, and 16.4°C) and poorly-tempered (31.6, 24.1, and 18.7°C) cocoa butter correspond to β, β′, and sub-α forms respectively (Wille and Lutton, 1966, Table 3). Table 6 shows that the melting enthalpy (ΔH) of the β form in cocoa butter (A) was greater than the β form in cocoa butter (B). The melting enthalpy (ΔH) of β form was 11.8% in cocoa butter (B) and 14.7% for cocoa butter (A). This suggest that cocoa butter (A) was a better tempered cocoa butter than (B) (Merken et al., 1982). Cocoa liquor (D) showed sub-α (15.2°C), α (20.6°C), β′ (24.3°C), and a trace of β form (32.3°C).

Table 6. Transition points, enthalpy, and percent β content of well-tempered (A) and poorly-tempered (B) cocoa butter.

Cocoa Butter	sub-α	β′	β	Total	β	% β
	Transition Point (°C)			Enthalpy (J/g)		
A	16.4	23.5	31.3	86.0	12.6	14.7
B	18.7	24.1	31.6	85.8	10.1	11.8

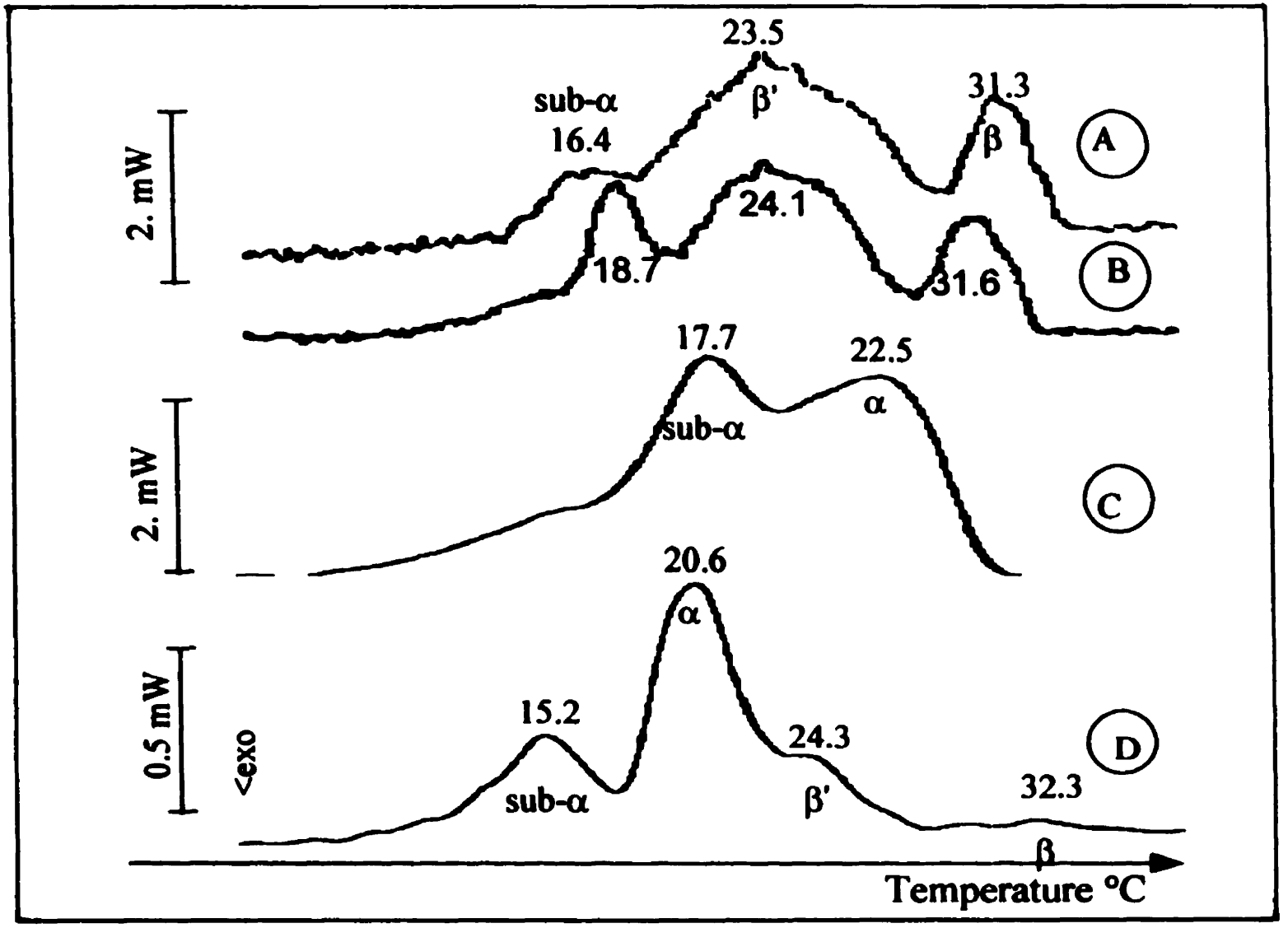


Figure 13. DSC thermograms of cocoa butter: well-tempered (A), poorly-tempered (B), untempered (C), and cocoa liquor (D).

III. 3. 4. Commercial Vegetable Fat Blends

Figure 14 shows that two samples of partially hydrogenated soybean oil, (#1 and #2) contained a crystal form which melted at 32.7°C to 32.9°C; based on literature values (deMan et al., 1991, Table 3), these polymorphs represent the β′ form of soybean oil. Hydrogenated palm kernel oil, (#3) showed three peaks at 20.4°C, 26.4°C, and 34.3°C. The transition peak at 34.3°C represents the β′ form of hydrogenated palm kernel oil (deMan et al., 1991, Table 3): the transitions points at 20.4°C and 26.4°C are unidentified peaks. Partially hydrogenated canola oil (#4) showed two peaks at 29.5°C and 5.1°C; the former represents the β form (deMan et al., 1991, Table 3) while the later, is an unidentified crystal form in canola oil.

III. 3. 5. Rapeseed Oils

Figure 15 shows the thermograms of rapeseed oil of different degrees of hydrogenation The samples varied according to the degree of hydrogenation from R1 to R6 (in order of increasing degree of hydrogenation). R2, R3, R4, and R5 exhibited two peaks corresponding to α and β forms. R1 and R6 showed a single peak representative of α and β form respectively (Kawamura 1991, Table 3).

The α form diminished as the degree of hydrogenation increased while the β form became enhanced (Figure 15); consequently, the enthalpy of α crystal decreased and enthalpy of β crystal increased as hydrogenation progressed (Table 7). Riiner (1970) reported that high euricic acid rapeseed (HEAR) oil crystallized to α and β_2-form which transformed to β_1-form as the temperature was increased.

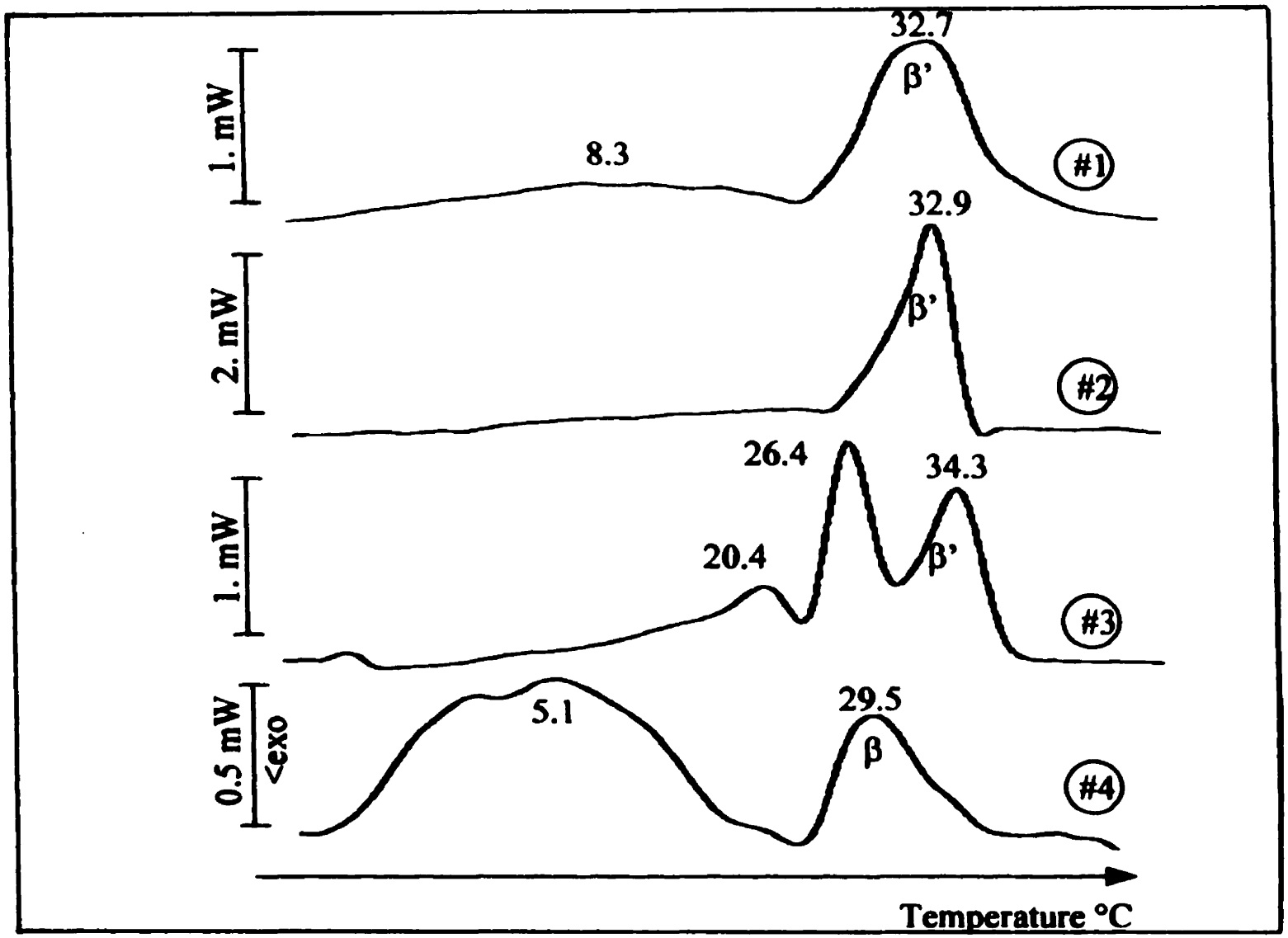


Figure 14. DSC thermograms of commercial fat blends: hydrogenated soybean & cottonseed oil (#1), fractionated soybean oil (#2), hydrogenated palm kernel oil (#3), hydrogenated canola oil (#4)

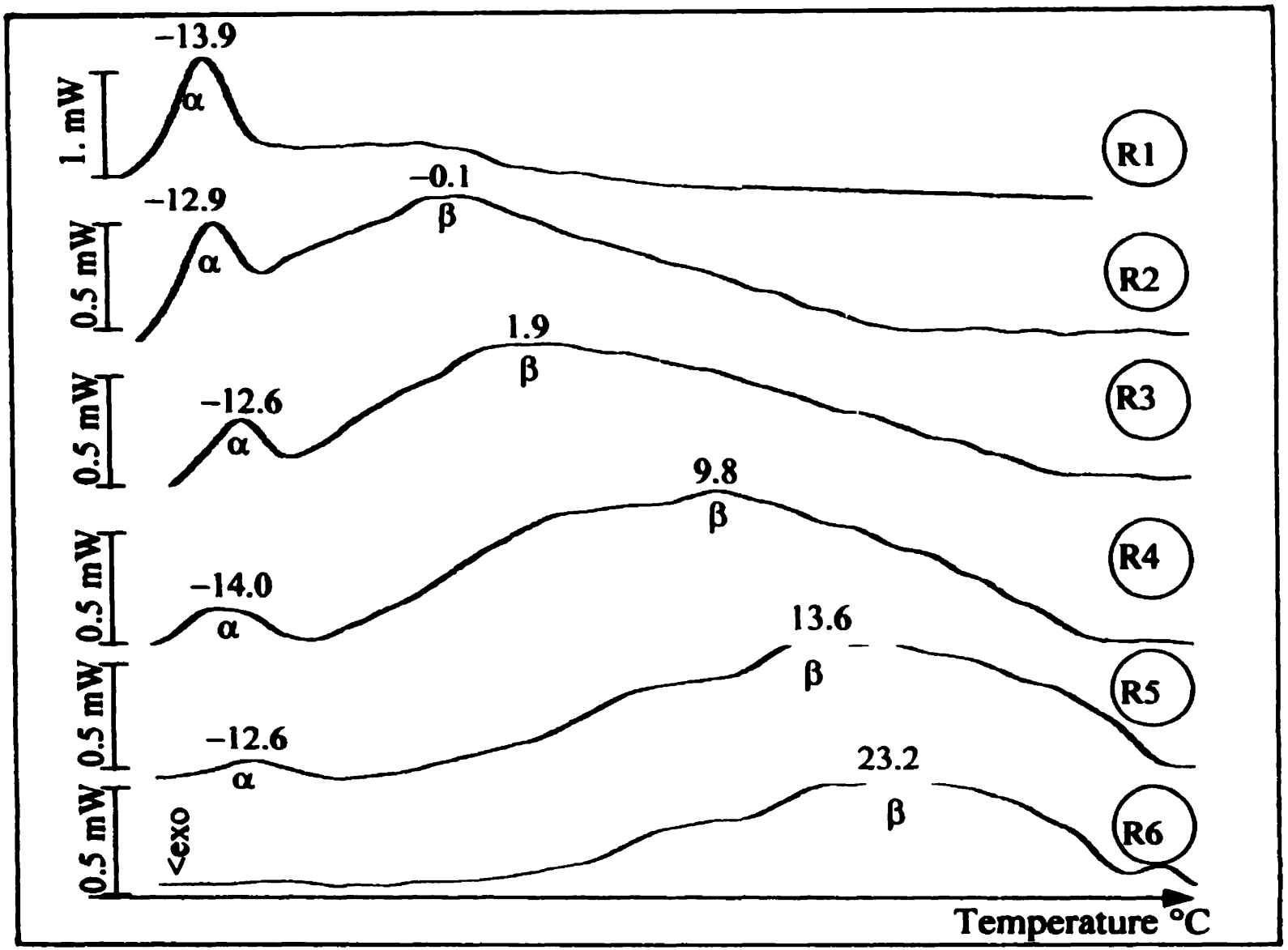


Figure 15. DSC thermograms of rapeseed oil (R1-R6) in increasing order of degree of hydrogenation.

Table 7. Enthalpy and melting point of samples of hydrogenated rapeseed oils.

Fat Sample	α		β	
	m.p. (°C)	ΔH (J/g)	m.p. (°C)	ΔH (J/g)
R1	-13.9	35.9	-	-
R2	-12.9	12.6	-0.1	62.4
R3	-12.6	7.5	1.9	66.7
R4	-14.0	5.0	9.8	77.8
R5	-12.6	2.5	13.6	102.1
R6	-	-	23.2	113.7

R = Rapeseed Oil
m.p. = Melting Point

III. 4. SUMMARY

Various commercial fats revealed common polymorphic forms sub-α, α, β′, and β. Butters contained α, β′, and β crystal forms; margarines and commercial vegetable fat had β′ and β according to their fat constituents. The DSC technique was shown to be limited in assigning any common fat crystals between -25°C and 0°C due to the presence of water in butter and margarine samples. Tempered cocoa butter contained sub-α, β′ and β forms; untempered cocoa butter showed sub-α and α forms while cocoa liquor revealed sub-α, α, β′ and traces of β forms. Hydrogenated rapeseed oils showed α and β forms in various amounts based on their hydrogenation levels.

CHAPTER IV

EFFECT OF INGREDIENTS ON POLYMORPHIC BEHAVIOR

IV. 1 MATERIALS:

Cocoa liquor was obtained from Barry-Callebaut Canada, St. Hyacinthe, Quebec; soybean lecithin was obtained from L. V. Lomas Ltd., Dorval, Quebec; margarine and butter samples were purchased from a local supermarket.

IV. 2 METHOD:

IV. 2. 1. Distribution of Polymorphic Forms

The distribution of polymorphic forms in the samples were determined by DSC analysis using the method described in section III. 2. 1.

IV. 2. 2. Calculation of Percent Liquid Fraction

The partial area under the melting peak is considered to be equivalent to the percentage of solid fat remaining at any given temperature (Md.Ali and Dimick, 1994); therefore

$$SFI = \frac{A_p}{A_T} \times 100$$

Where A_T is the total, A_p is partial area and SFI is solid fat index.

The effect of the following food ingredients were investigated:

i) Effect of lecithin on cocoa liquor

Cocoa liquor was heated in a 50°C water bath. Lecithin was added to liquid cocoa liquor at levels of 0.0, 0.2, 0.3, and 0.4%.

ii) Effect of sugar-lecithin mixture on cocoa liquor

The above samples were mixed with sugar and made as 30, 40, and 50% mixtures which were well mixed while heating in 50°C water bath.

iii) Effect of presence of salt in butter and margarine

Commercial margarines and butter containing no salt and different levels of salt were used.

IV. 3. RESULTS AND DISCUSSIONS

IV. 3. 1. Effect of Lecithin

Figure 16 shows the thermograms of cocoa liquor with added lecithin; the effect of lecithin on total enthalpy and melting points of cocoa liquor is shown in Table 8. Cocoa liquor with or without added lecithin melted as a single polymorphic form; however, addition of lecithin slightly decreased the melting point of cocoa liquor from 19.9°C to 18.7°C. The observed melting temperature is similar to melting point of sub-α form (Table 3). Lovegren et al. (1976) reported that a rapid solidification (similar to that observed in our experiment) of a fat or fat mixture results in a homogeneous solid that incorporates any liquid fat within the crystal matrix which melts as a single solid phase.

Table 8. Total enthalpy and melting point of cocoa liquor at the presence of lecithin concentrations (0.0, 0.2, 0.3, and 0.4%).

	Cocoa Liquor + Lecithin Concentration (%)			
	0.0	**0.2**	**0.3**	**0.4**
Total ΔH (J/g)	42.2	40.4	40.7	41.9
Melting Point (°C)	19.9	18.7	19.1	18.7

Soybean lecithin is a natural phospholipid that is used in confectionery for reducing the viscosity of chocolate. Surfactants such as lecithin are known to stabilize metastable polymorphs and delay the formation of stable crystals and may affect the rate of polymorphic transformation (Aronhime and Garti, 1988). Aronhime et al. (1988) proposed that the seeding effect might induce the formation of smaller crystals which is translated to slightly lower melting point of fat at the presence of emulsifier compared to pure fat. Our results are in agreement with those of Aronhime et at. (1988); however, we did not observe peak broadening reported by Aronhime and Garti (1988).

Figure 17 shows a typical plot of percent liquid fraction of cocoa liquor obtained by DSC. The influence of lecithin on percent liquid fraction of cocoa liquor is tabulated in Table 9. In general, the percent liquid fraction increased with lecithin added. The 0.3% lecithin concentration in cocoa liquor exhibited lower liquid fraction than that of 0.2 and 0.4% concentrations. The liquid fraction of cocoa liquor at the presence of 0.3 and 0.4% lecithin concentration (at given temperature between 17 to 21°C) was similar; the melting point of cocoa liquor at 0.3 and 0.4% lecithin concentrations also occurred at

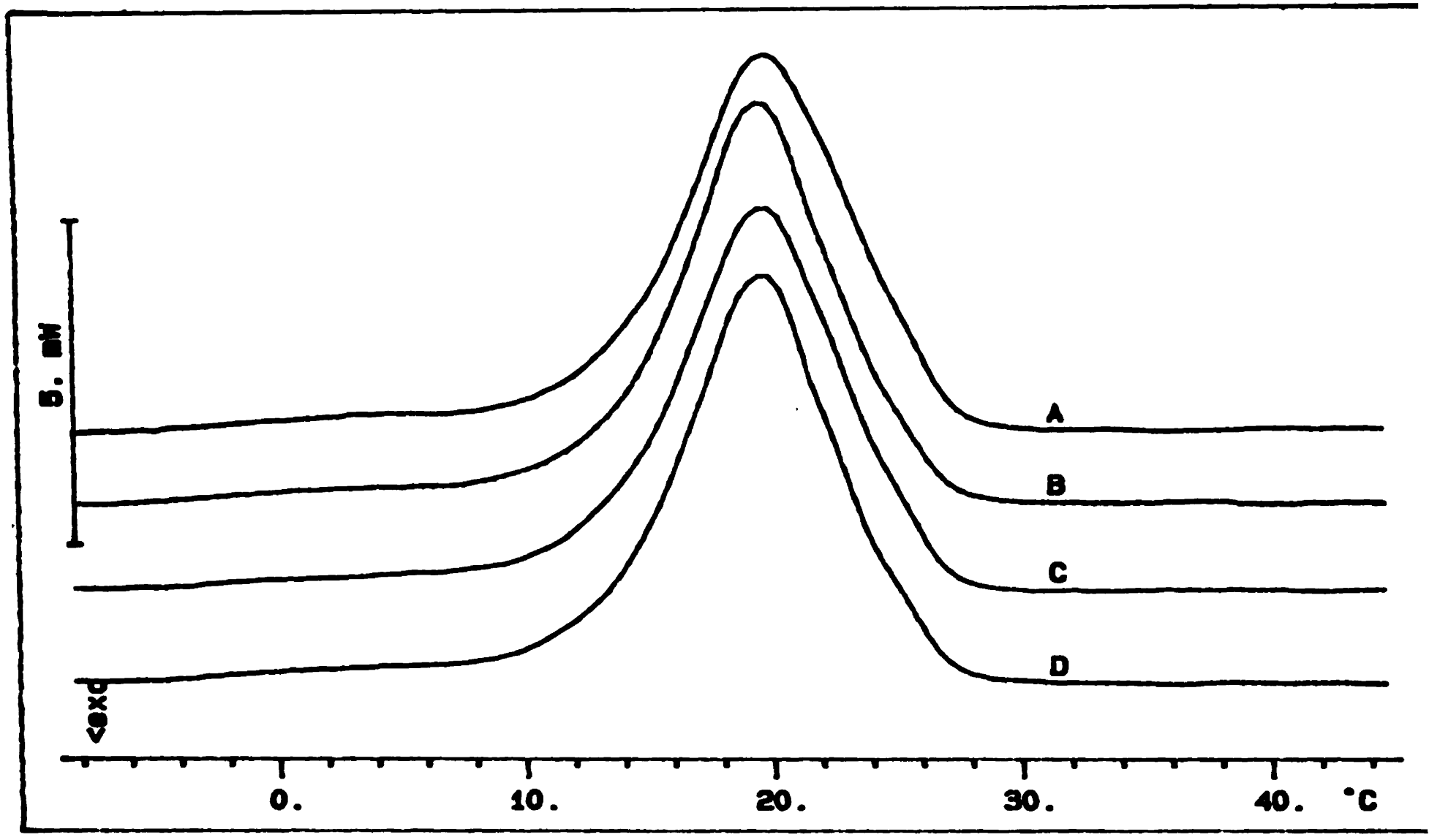


Figure 16. DSC melting thermograms of cocoa liquor with: 0.0% (A), 0.2% (B), 0.3% (C), and 0.4% (D) added lecithin.

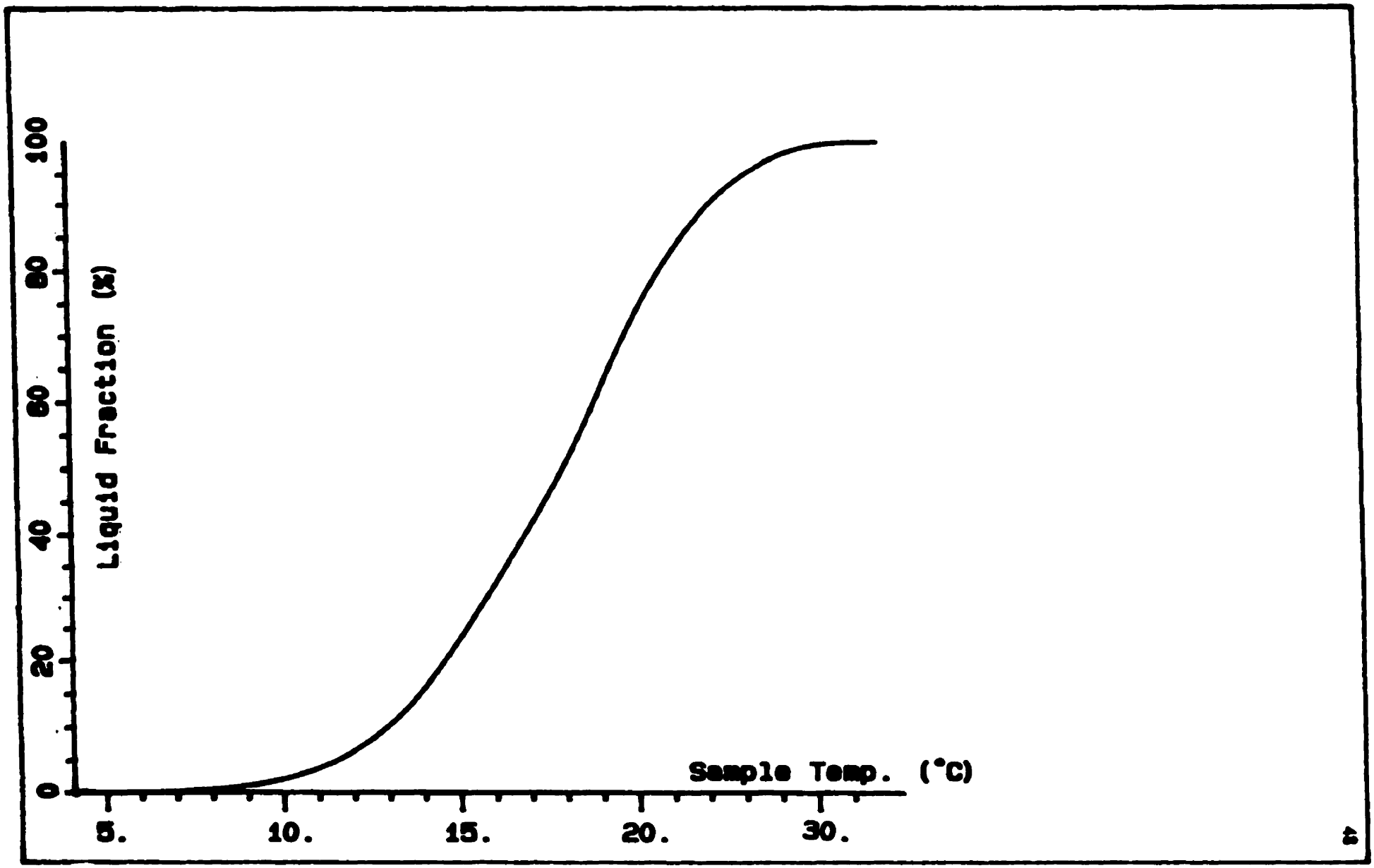


Figure 17. A typical plot of percent liquid fraction of cocoa liquor vs. temperature.

Table 9. Percent liquid fraction of cocoa liquor in the presence of various lecithin concentrations.

Temperature (°C)	Lecithin (%)			
	0.0	0.2	0.3	0.4
	Percent Liquid Fraction			
14	15.4	15.6	14.7	14.9
15	19.7	20.4	19.6	20.0
16	25.8	27.4	26.5	27.3
17	34.2	37.1	35.8	37.3
18	44.8	49.1	47.3	49.3
19	56.1	61.3	59.2	61.4
20	66.5	71.6	69.6	71.7
21	75.3	79.7	78.2	79.8
22	82.8	86.3	85.2	86.4
23	88.7	91.2	90.5	91.3
24	93.2	94.9	94.5	94.9
25	96.5	97.4	97.3	97.5
26	98.5	98.9	99.0	99.0

similar temperature (18.7°C). Aronhime and Garti (1988) reported that the percent liquid fraction of cocoa butter increased with emulsifier (Span 65) concentration.

The mode of action of emulsifiers has been postulated by Aronhime et al. (1990); the emulsifier molecule is incorporated in the crystal lattice which in turn increase molecular disorder and rotational freedom; therefore the thermal mobility of the molecules and liquid fraction is increased.

IV. 3. 2 Effect of Sugar

Figure 18 and Table 10 shows thermograms of cocoa liquor/lecithin/sugar and corresponding enthalpy and melting point temperatures, respectively. The effect of lecithin on cocoa liquor was observed to be weak; however, lecithin action is more pronounced on the sugar/cocoa liquor mixture. Our results are in agreement with those of Harris (1968) who reported that addition of sugar augmented the effect of lecithin on cocoa butter.

Table 10 showed that addition of sugar to cocoa liquor containing 0.2% lecithin caused an increased melting point from 18.7°C to 18.9, 19.8, and 21.1°C at 30, 40, and 50% sugar concentration, respectively. At 0.3% concentration the melting point of the α from was the lowest (18.9°C) when cocoa liquor contained 40% sugar. On the other hand, at 0.4% lecithin concentration the melting point of the α from was the lowest at 50% sugar. Unlike the effect of lecithin alone on cocoa liquor, presence of lecithin/sugar retarded the melting of crystals. This could be due to the less organized system of molecules that

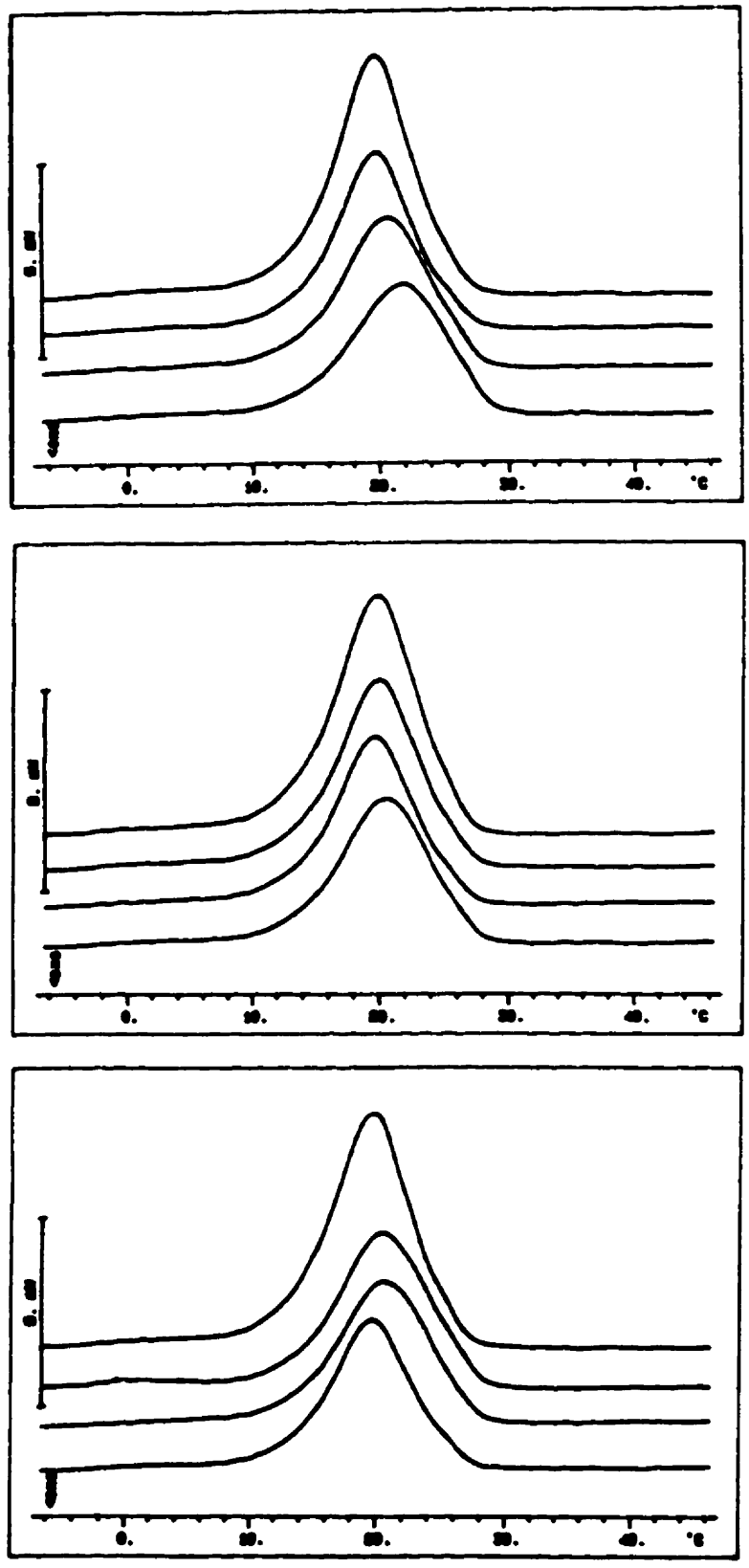


Figure 18. DSC thermograms of cocoa liquor and lecithin: 0.2% (B), 0.3% (C), and 0.4% (D) with respective sucrose.

Table 10. Total enthalpy and melting point of cocoa liquor in the presence of various sucrose and lecithin concentrations.

	Cocoa Liquor + 0.2% Lecithin			
	Sucrose concentration (%)			
	0	30	40	50
Total ΔH (J/g)	40.4	43.9	49.5	52.6
Melting Point (°C)	18.7	18.9	19.8	21.1

	Cocoa Liquor + 0.3% Lecithin			
	Sucrose concentration (%)			
	0	30	40	50
Total ΔH (J/g)	40.7	46.7	48.7	54.6
Melting Point (°C)	19.1	19.3	18.9	19.8

	Cocoa Liquor + 0.4% Lecithin			
	Sucrose concentration (%)			
	0	30	40	50
Total ΔH (J/g)	41.9	46.3	47.8	54.4
Melting Point (°C)	18.7	19.8	19.7	18.9

required more time and energy to melt as is evident by increased melting temperatures and enthalpies (Table 10).

Harris (1968) explained the action of sugar is such that the moisture at the surface of the sugar particles causes high friction between molecules resulting in a greater viscosity. With addition of lecithin the hydrophilic end of the molecules attach themselves strongly to the water molecules on the surface of the sugar particles and hydrophilic end to the fat crystals which reduces friction and increases particle mobility. Therefore, the effect of lecithin is due to its action on the sugar particles (Harris 1968).

IV. 3. 3. Effect of Presence of NaCl on Margarine and Butter

The DSC thermograms for margarine and butter samples are given in Figures 11 and 12 respectively, and their corresponding thermal data of eutectic and aqueous phases in Table 11. Two endothermic transitions appeared below 0°C in margarines (A, B and D), however margarine (C) showed more than two peaks in this region. Table 11 shows a eutectic melting temperature from -22.0 to -23.2°C of NaCl solutions. The shift in melting transitions of eutectic mixtures depends on NaCl content. Table 11 shows that hard margarine (A) contained the highest amount of salt (2.8%); this is consistent with highest enthalpy of NaCl (22.2 J/g). Margarine D, a salt free margarine, showed a transition point at -25.2°C and a low melting of the aqueous phase at -0.3°C suggesting the absence of salt; the transition point at -25.2°C is relatively high in comparison to the other products, suggesting the existence of a form of unidentified fat crystal.

Table 11. Enthalpy and melting points of eutectic mixture and aqueous phase of margarines (A, B, C, and D), and butters (E, F, and G).

Product	Eu. Mixture		Aqueous Phase		% Salt
	ΔH (J/g)	m.p. (°C)	ΔH (J/g)	m.p. (°C)	on Label
A	22.2	-22.0	1.7	-1.5	2.8
B	11.6	-22.8	125.0	-2.2	1.5
C	N/A	-22.3	N/A	-10.3	1.8
D	N/A	N/A	17.2	-0.3	salt free
E	15.3	-22.0	13.5	-9.3	salted
F	5.50	-23.2	23.0	-5.7	semi-salted
G	7.80	-22.8	24.4	-6.1	1.0

Eu.= eutectic m.p.= melting point N/A= not available

The observed melting points of the aqueous phase of -9.3, -6.1, and -5.7°C respectively, were consistent with the salted, 1% salt, and semi-salted labels, respectively for butter samples.

IV. 4. SUMMARY

Under our experimental conditions no definite crystal transformation occurred due to the effect of lecithin on cocoa liquor. However, with addition of lecithin the melting point of cocoa liquor shifted slightly to lower temperature. The effect of lecithin was much stronger on cocoa liquor in the presence of sugar which acted as tertiary component in the lecithin-fat organization to help lecithin to alter the physical property of the system. DSC provided valuable data during crystal transformations however, this technique is limited. DSC did not offer data relating to common crystal forms of samples (α, β', and β) containing salt and water at between 0.0 and -25°C. This study showed that the fat and aqueous phase transitions occur independent of each other.

CHAPTER V

EFFECT OF HEATING AND COOLING CYCLES ON POLYMORPHIC BEHAVIOR

V. 1. MATERIALS:

Cocoa butter and cocoa liquor was obtained from Barry-Callebaut Canada, St. Hyacinthe, Quebec.

V. 2. METHODS:

V. 2. 1. Temperature Cycling

Cocoa butter samples were heated from room temperature to 70°C and held at this temperature for 10 min in DSC. The samples were cooled at a rate of 20°C/min to -25°C then reheated to 40°C at the rate of 1 °C/min. Heating and cooling cycles were performed consecutively for five times from -25°C to 40°C.

V. 2. 2. Tempering of Cocoa butter

The technique used for tempering was adapted from Talbot (1994); cocoa butter was heated to 50°C and held for 5 min, cooled to the 32°C in 5 min, then cooled to 27°C in 30 min to form both stable and unstable crystals. Following this, the sample was reheated to 35°C to remove unstable crystal fraction.

V. 2. 3. Isothermal Treatment

For isothermal treatments, samples were held at 60°C for 5 min; temperature was decreased to the required temperature at a rate of 60°C/min; samples were heated at constant temperatures of 0.0, 5.0, 10, 15, 20, and 25°C for 30 and 60 min. The samples were then heated to 60°C at 5°C/min to obtain melting thermograms.

V. 3. RESULTS AND DISCUSSIONS

V. 3. 1. Effect of Heating/Cooling Cycles on Polymorphism

V. 3. 1. 1. Cocoa Butter

Cocoa butter was shown to contain three endothermic peaks: sub-α, β′, and β (Figure 13, III. 3. 3). Figure 19 shows the effect of heating/cooling cycles on polymorphic behavior of cocoa butter; the result suggest that there was no effect on sub-α and α forms in cocoa butter which was heated from -10 to 70°C for up to five heating/cooling cycles. Melting temperature and enthalpy data in Table 12 indicated that sub-α and α polymorphs were unchanged. However, the more stable polymorphs, β′ and β forms were destroyed after the first cycle.

V. 3. 1. 2. Cocoa Liquor

Figure 20 shows the thermograms of cocoa liquor affected by heating/cooling cycles. Figure 20 and Table 13 indicate no change in melting temperature of sub-α or α forms or total enthalpy of cocoa liquor; however, as was observed with cocoa butter, traces of β

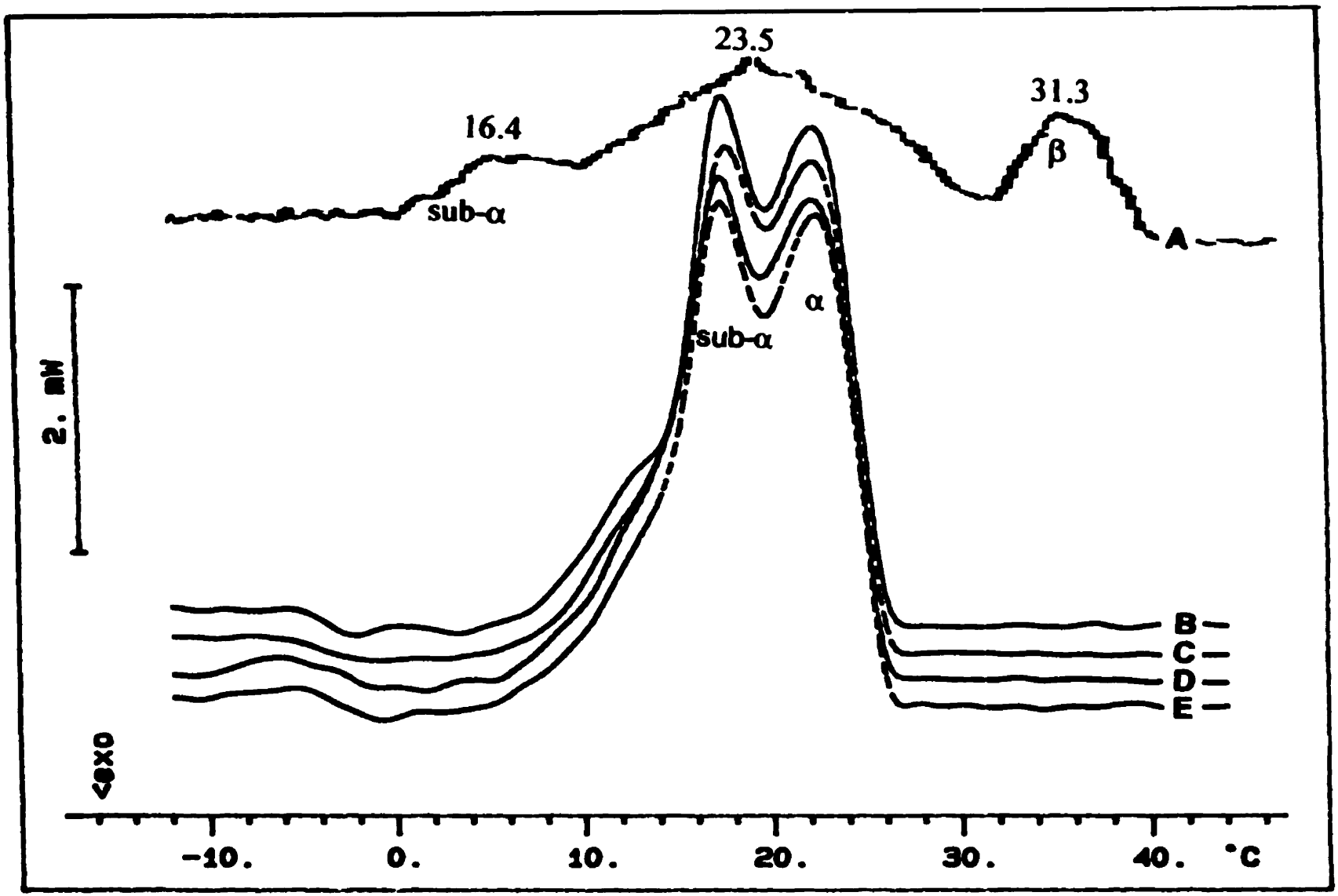


Figure 19. Effect of heating/cooling cycles on behavior of cocoa butter; A= first cycle, B= second cycle, C= third cycle, D= fourth cycle and E= fifth cycle.

Table 12. Total enthalpy values and melting temperatures of polymorphic forms of cocoa butter in heating/cooling cycles 1 to 5, (A, B, C, D, and E respectively).

Cycle	sub-α	α	β'	β	Total ΔH
	Melting Point (°C)				(J/g)
A	16.4	-	23.5	31.3	86.0
B	17.2	22.6	-	-	77.4
C	17.4	22.6	-	-	77.5
D	17.2	22.4	-	-	77.2
E	17.2	22.5	-	-	77.5

- = no crystal present.

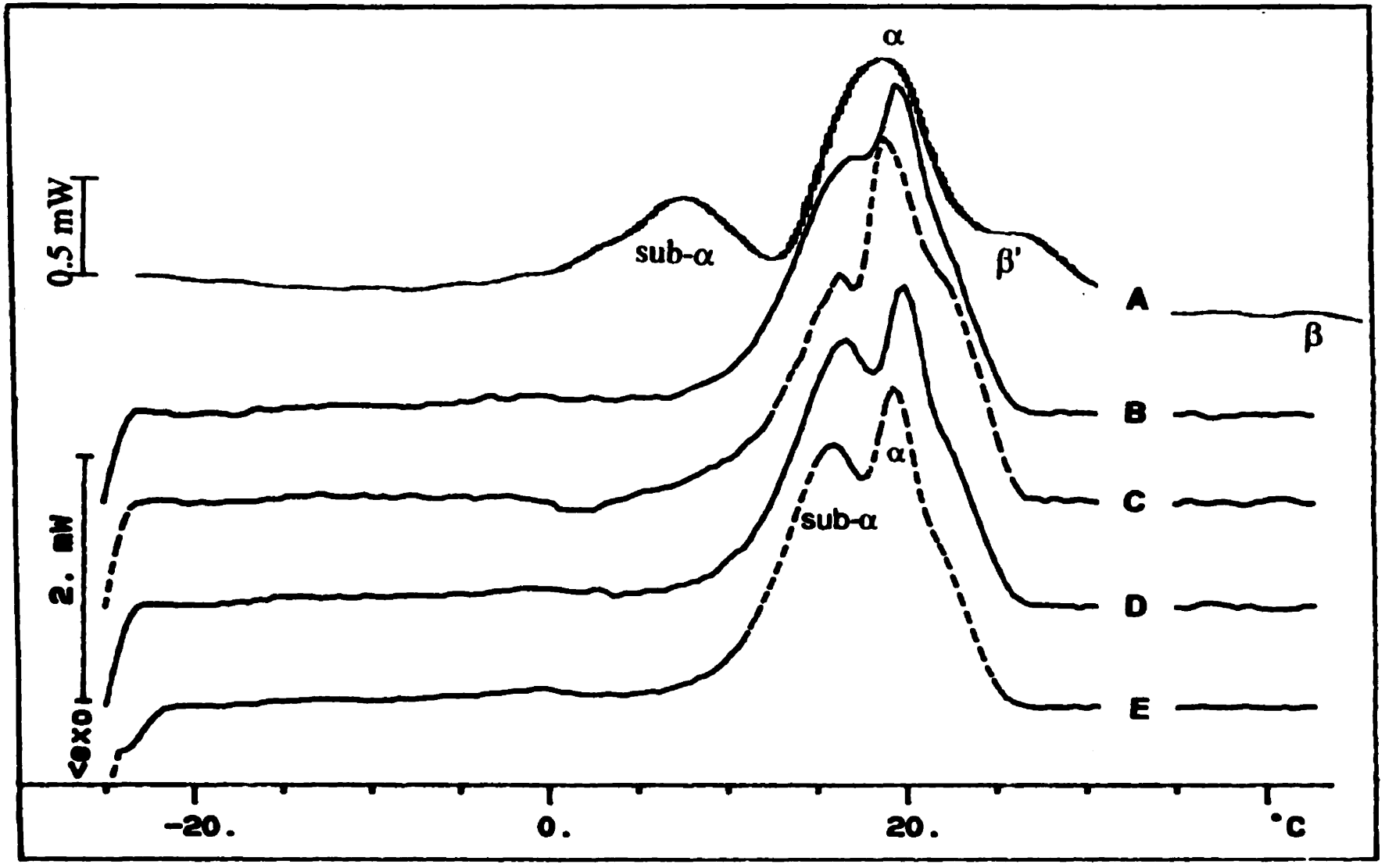


Figure 20. Effect of heating/cooling cycles on behavior of cocoa liquor; A= first cycle, B= second cycle, C= third cycle, D= fourth cycle and E= fifth cycle.

Table 13. Total enthalpy values and melting temperatures of polymorphic forms of cocoa liquor in heating/cooling cycles1 to 5, (A, B, C, D, and E respectively).

Cycle	sub-α	α	β'	β	Total ΔH
	Melting Point (°C)				(J/g)
A	15.2	20.6	24.3	32.3	46.3
B	16.8	19.3	-	-	50.2
C	16.4	19.1	-	-	50.1
D	16.7	19.7	-	-	50.0
E	16.0	19.4	-	-	50.9

-= no crystal present.

and β′ forms in the first cycle disappeared in the subsequent cycles. The result suggest that the separation of sub-α and α forms was promoted as cycles were repeated.

V. 3. 2. Effect of Tempering on the Polymorphism of Cocoa Butter

Figure 21 shows the melting curves of cocoa butter in various stages of tempering; A, B, C, and D correspond to tempering conditions at 50, 32, 27, and 35°C (Talbot 1994), respectively. Melting of the unstable β′ form was observed at 28.1°C. Sub-α form melting point at 18.5°C) appeared in all thermograms because of the low initial temperature. Sub-α form was shown to crystallize at 16°C (Wille and Lutton, 1966). Absence of β form in thermogram C (last tempering stage where for stable β forms) suggest that there was insufficient crystal seeds for the formation of the higher melting crystal, β form.

Figure 22 shows thermograms of tempered cocoa butter stored at room temperature for 90 min, 18 h, and 15 d, then examined for crystal forms. As the storing time was extended, the crystals transformed more and more to high melting fractions; after 90 min, the β′ form at 29.2°C appeared, after 18 h, β′ form at 30.7°C, and after 15 d, β form appeared at 31.5°C.

Figure 23 shows the melting thermograms of tempered cocoa butter (A) and stored cocoa butter at room temperature for seven months (B); the β form was observed at 32.9°C. Cocoa butter (A) contained sub-α and α forms melting at 15.9 and 22.9°C respectively. Transformation of low melting fractions (sub-α and α forms) to higher melting fractions (β′ and β forms) occurred after a relatively long period. Wille and

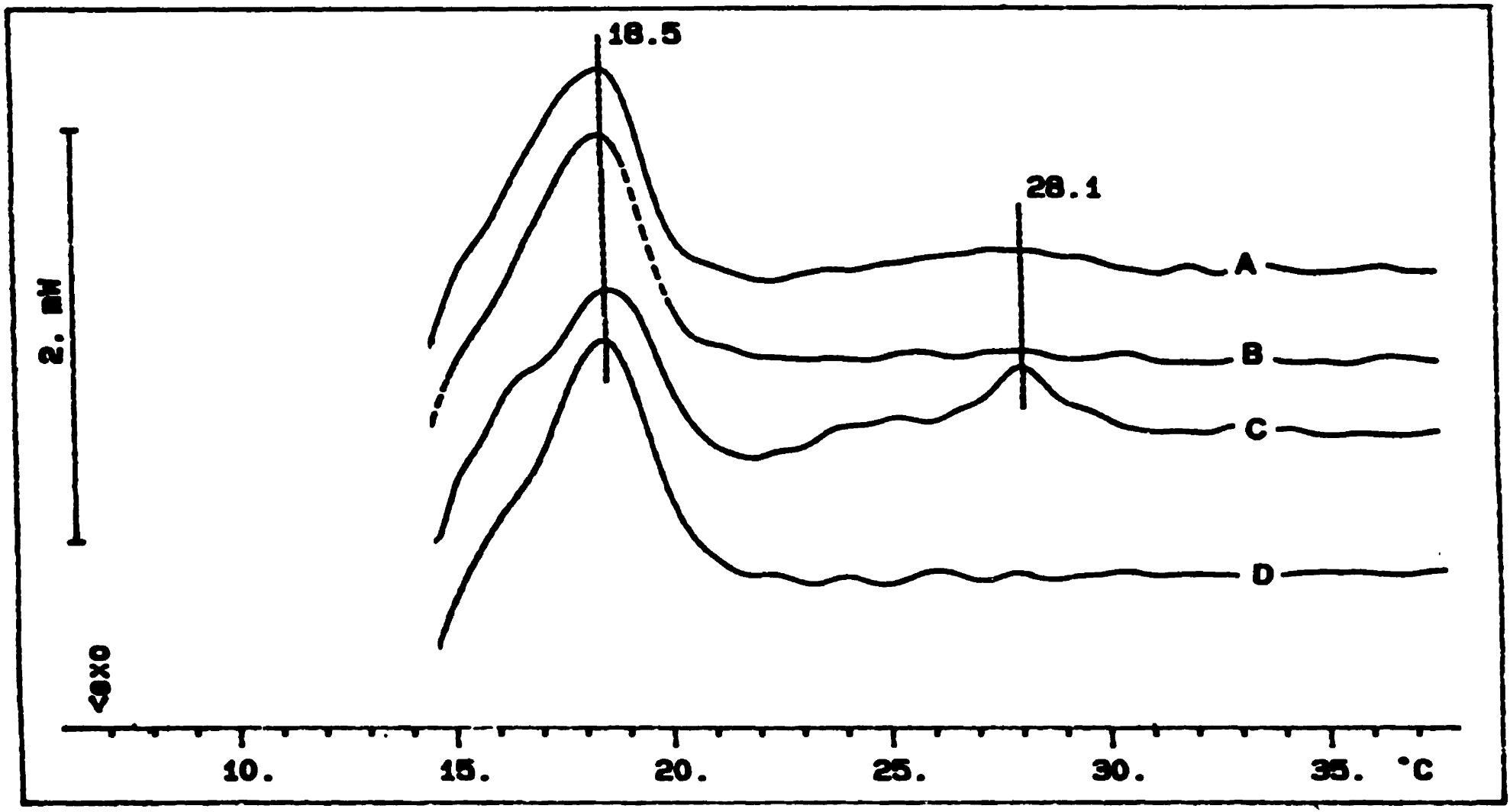


Figure 21. Effect of tempering at: 50°C (A), 32°C (B), 27°C (C), and 35°C (D) on polymorphism of cocoa butter.

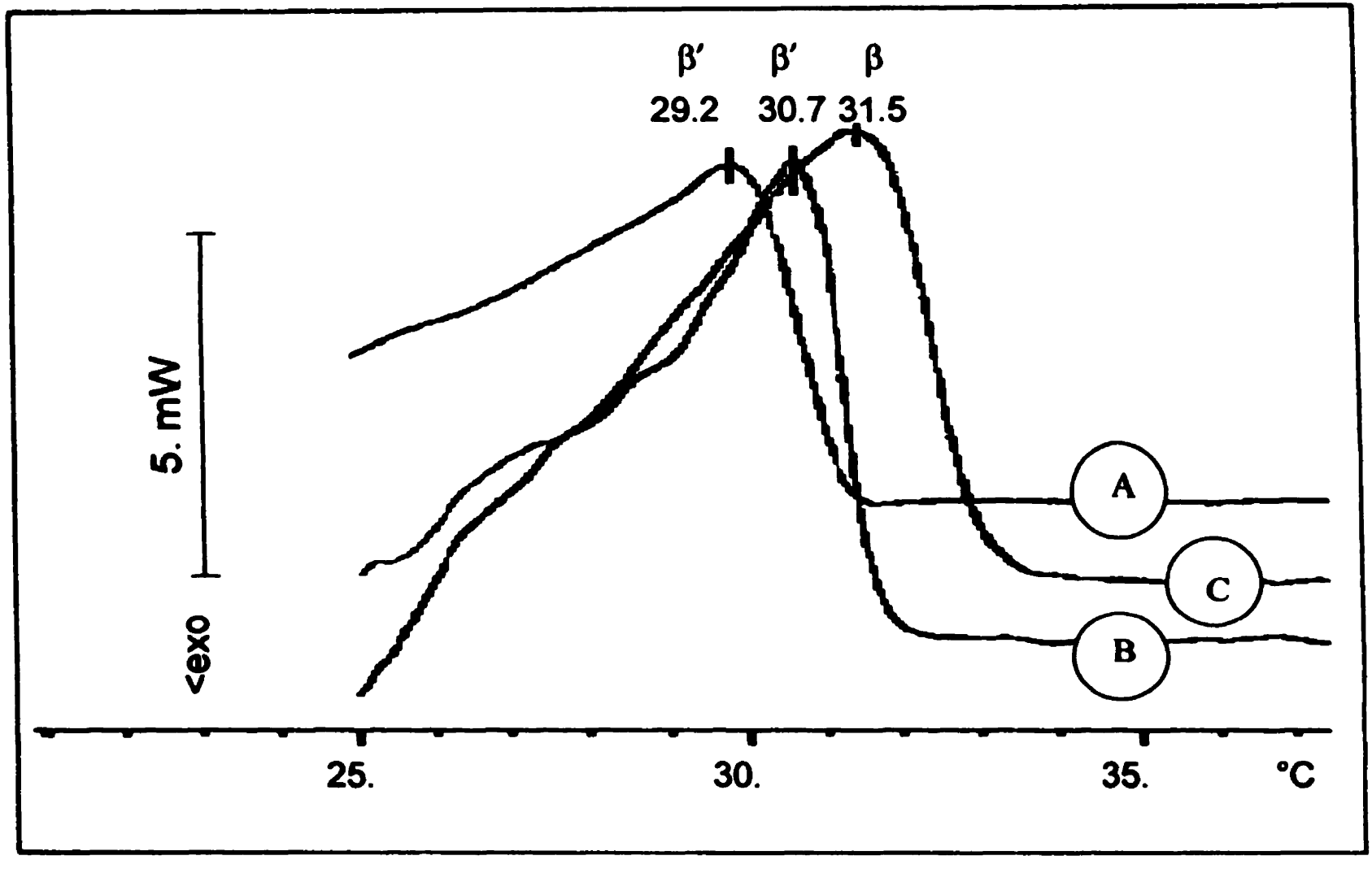


Figure 22. DSC thermograms of cocoa butter stored for 90 min (A), 18h (B), and 15d (C).

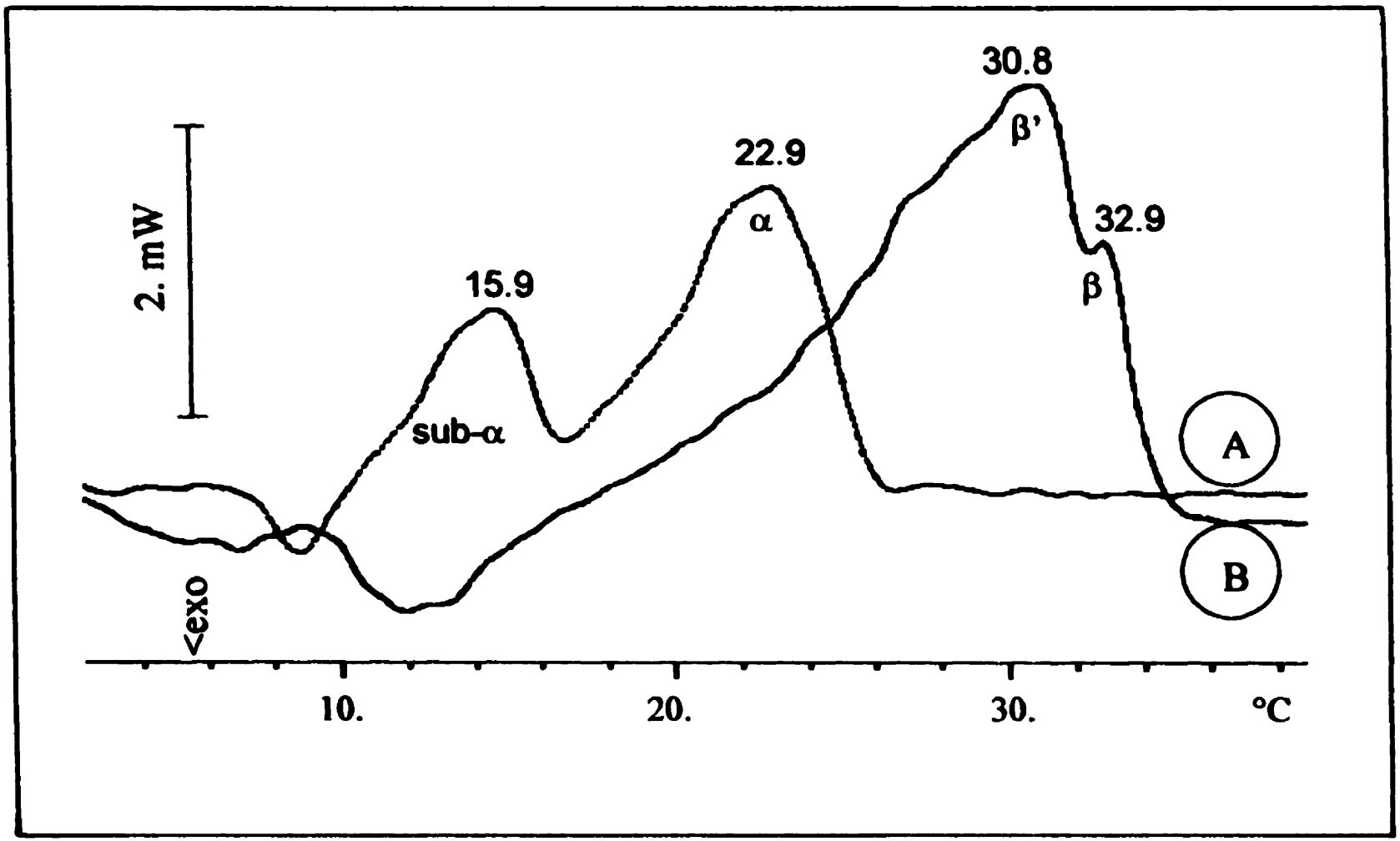


Figure 23. DSC thermograms of cocoa butter (A) and cocoa butter stored for seven months at room temperature (B).

the β form of POS (2-oleyl-palmitostearin, is the principal glyceride constituent of cocoa butter) after 6 months at room temperature.

V. 3. 3 Isothermal Treatment of Cocoa Liquor.

Figures 24 shows the thermograms of cocoa liquor held at constant temperatures then analyzed. Table 14 summarizes the temperatures of the endothermic peaks, corresponding ΔH and suggested polymorphic forms. Cocoa liquor held at 0, 5°C, and 25°C showed only one peak in the range of 18.5 to 19.7°C representing the sub-α form. Cocoa liquor held at 10°C was mixture of sub-α and α forms; at 15°C showed the β′ form at 25.1°C. At 20°C both the sub-α and β′ forms were observed. Constant temperature treatment revealed no polymorphic transformation at 0, 5, and 25°C but transformation from sub-α to β′ took place at 10°C, 15°C, and 20°C.

Table 15 shows that cocoa liquor samples held at constant temperature for 30 and 60 minutes. The results indicate that the longer the heating period, the higher the percentage of proceeding fraction; this suggest that lower melting fraction becomes part of the more stable fraction. Intermediate to high melting fractions at 15°C underwent the largest transformation; 46.5% of sub-α transformed to higher melting at longer heating time. There were no changes in fusion properties of cocoa liquor at 0 and 5°C. Aronhime et al. (1988) reported that when cocoa butter was held at 22°C for different periods of time the melting range of the low melting fraction decreased, this was not observed in our study. Wille and Lutton (1966) showed that in rapid cooling, cocoa butter polymorphs changes from sub-α and α form to β′ form; our results suggests that this transformation not only

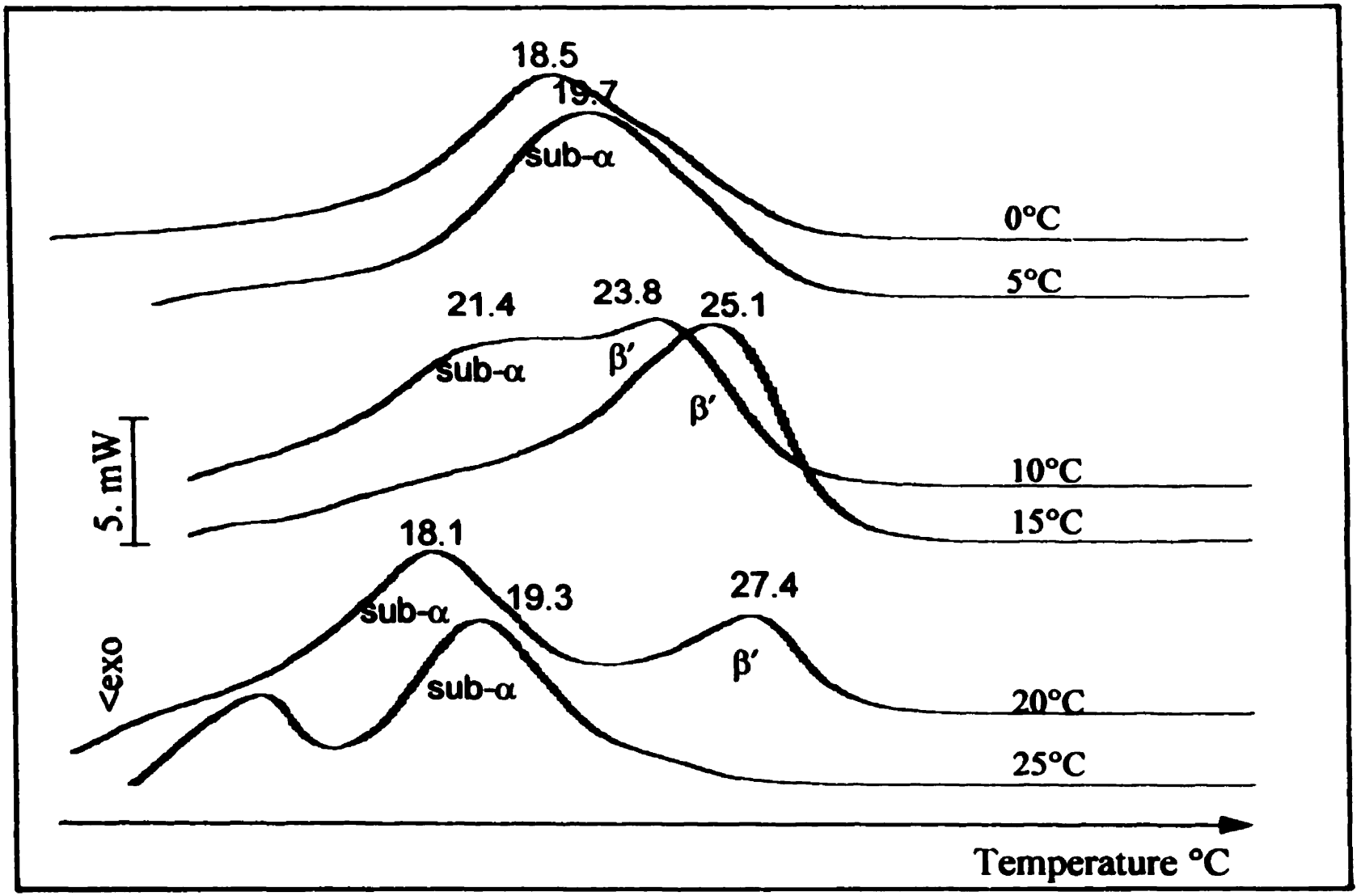


Figure 24. Thermograms of cocoa liquor heated at 0, 5, 10, 15, 20, and 25°C.

Table 14. Melting points, enthalpy, and polymorphic forms of cocoa liquor held at various temperatures.

Temperature (°C)	Melting Point (°C)	ΔH (J/g)	Systematic Nomenclature*
0	18.5	42.4	sub-α
5	19.7	44.3	sub-α
10	21.4 & 23.8	44.3	sub-α & α
15	25.1	43.8	β'
20	18.1 & 27.4	23.5 & 15.3	sub-α & β'
25	19.3	24.2	sub-α

*= Wille and Lutton (1966).

Table 15. Percent of cocoa liquor crystals at constant temperature for 30 and 60 minutes.

Temperature (°C)	sub-α	β'	sub-α	β'
	30 min	60 min	30 min	60 min
	% Crystals			
0	100	-	100	-
5	100	-	100	-
10	55.9	44.1	45.8	54.2
15	53.6	46.4	7.1	92.9
20	60.5	39.5	18.1	81.9
25	73.9	-	75.8	-

- = no crystal present.

depends upon the cooling rate but is also affected by the thermal history of the fat; different crystal forms appeared depending on whether it was stored at 0°C or 25°C.

V. 3. 4 Effect of Heating and Cooling Rates

Figure 25 shows the effect of heating rates on cocoa liquor polymorphism. Low heating rates demonstrated improved resolution and separation of the sub-α and α form fractions (C). In addition, at low heating rate of 1 and 0.6°C/min, formation of some higher melting crystals was The disadvantage of low heating and cooling is the longer time required for one measurements. Table 16 shows total melting enthalpy of cocoa liquor and its individual peak as function of heating rate. Total ΔH decreased as heating rate increased. In sub-α form, the heat of fusion decreased as the heating rate decreased while in α form the heat of fusion increased as the heating rate decreased. Progressive shifting of the peaks to a higher temperature occurred as the heating rate increased; for instance melting of sub-α form shifted from 15°C at the rate of 0.6°C/min to 16.4°C at the rate of 2°C/min.

V. 4. SUMMARY

Storing cocoa butter samples at room temperature resulted in slow transformation of crystals from sub-α → α → β′. Formation of the most stable form of crystals took place after seven months at room temperature suggesting that transformation of β′→β happens only from the solid state. Heating/cooling cycles after first cycle had no effect on behavior of sub-α or α forms of cocoa butter or cocoa liquor; however stable

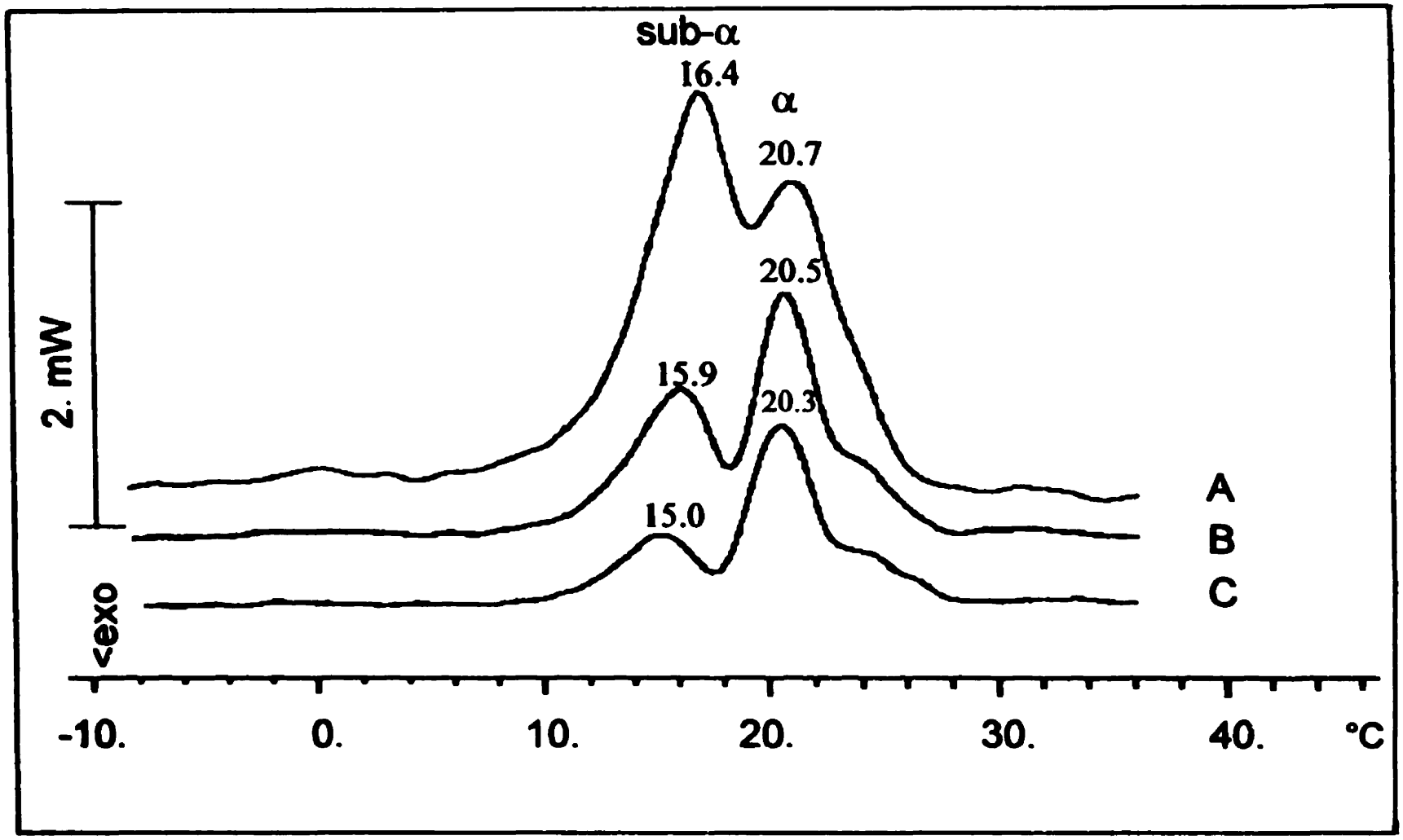


Figure 25. Effect of heating rates on polymorphism of cocoa liquor (A)= 2°C/min, (B)= 1°C/min, and (C)= 0.5°C/min.

Table 16. Effect of heating rate on melting enthalpy and peak temperatures of cocoa liquor.

	Heating Rate (°C/min)	ΔH (mJ)	Peak Tem. (°C)
Total Curve C	0.6	620.3	20.3
sub-α		188.6	15.0
α		443.0	20.3
Total Curve B	1.0	605.0	20.5
sub-α		252.0	15.9
α		363.6	20.5
Total Curve A	2.0	598.3	16.4
sub-α		353.0	16.4
α		242.7	20.7

polymorphs, β′ and β forms disappeared after first cycle. The sub-α and α forms of cocoa liquor unlike in cocoa butter were distinctively separated. Polymorphic forms of cocoa liquor at various constant temperature treatments revealed different crystal forms; at 0.0, 5.0, and 25.0°C sub- α, at 10.0 and 20.0°C mixture of sub-α and β′ at 15.0°C only the β′ form appeared. Long periods of constant heatings resulted in transformation of low melting fractions to high melting fractions.

CHAPTER VI

RHEOLOGICAL AND THERMAL CHARACTERISTICS OF FOOD FATS

VI. 1. MATERIALS:

A set of 4 commercial samples of food fats were obtained for this study. The identification of the fats are as follows: partially hydrogenated soy bean oil and cotton seed oil (#1), fractionated soy bean oil (#2), hydrogenated palm kernel oil (#3), partially hydrogenated canola oil (#4).

VI. 2. METHODS:

VI. 2. 1. Rheological Analysis:

Figure 26 illustrates the back extrusion device used for measurement of rheological parameters. Water was pumped into and out of the device; in order to have a complete temperature control, a thermocouple (type T) was located at the geometrical center of the sample. A cylindrical teflon plunger (150 mm) was mounted to the Universal Material Testing Machine (Lloyd Model LRX-2500N; Lloyd Instruments Ltd., Fareham, Hans, UK) equipped with a 50 N load cell. The system was programmed for the plunger to penetrate 10 mm at a constant speed of 100 mm/min. Measurements were taken when the temperature of the samples in the center reached the desired points from (a) 25°C to 55°C and (b) from 55°C to 25°C, at 5°C increments. The results were expressed as viscosity index. The plunger progressed 10 mm downwards into the sample; viscosity

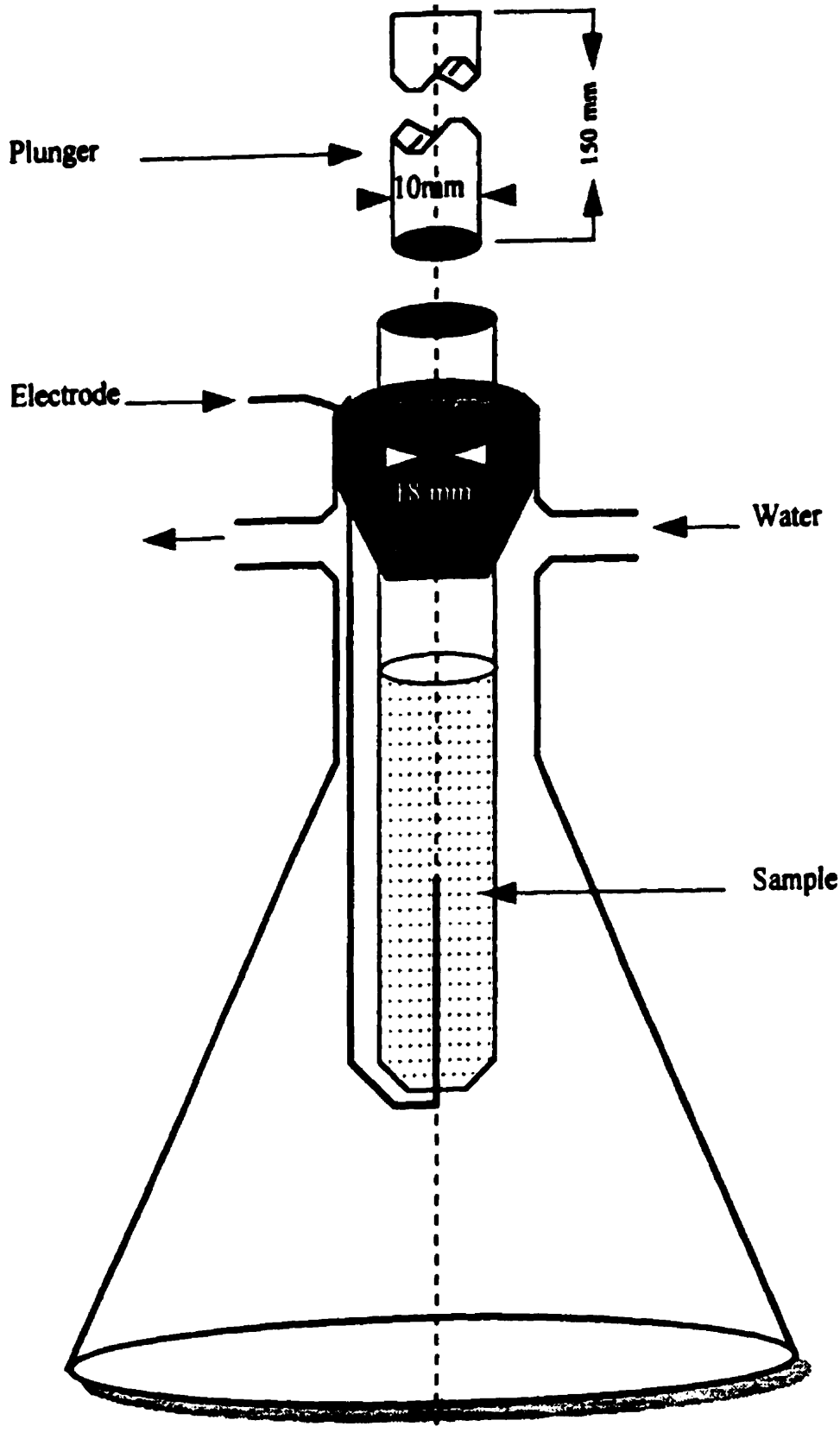


Figure 26. A back extrusion device for determination of force-deformation slope.

was measured during this time. The viscosity index (ηI) was calculated using equation (1) developed by Morgan et al. (1979).

$$\eta_I = \frac{1}{2\pi V_P}\left[\frac{F_P}{L_P}\right]\left[1 - K^2\right] \ln\left[\frac{1}{k}\right]\left[1 + \frac{\alpha}{\ln K}\right] \qquad (1)$$

where:

F_P = plunger force

L_P = plunger travel distance

V_P = plunger velocity, (mm/min.)

$K = (R_1 / R_2)$

R1 = plunger radius (mm)

R2 = inner test tube radius (mm)

$\alpha = (1-K^2) / (1+K^2)$

VI. 2. 1. 1. Hardness Evaluation

Hardness of the fat samples were measured using a Universal Testing Machine (Lloyd Model LRX-2500N; Lloyd Instruments Ltd., Fareham, Hans, UK). The samples were under constant load of 50 N as a plunger was driven 10 mm (distant) into the samples at the speed of 100 mm/min.

The maximum penetration force over maximum penetration distance was read and expressed as hardness in N/mm.

$$\textbf{Hardness} = \frac{\text{Maximum Force (N)}}{\text{Maximum Distance (mm)}}$$

VI. 2. 2. Thermal Analysis:

The samples were heated from 25°C to 70°C at the rate of 20°C/min to destroy the "memory of fat"; following a 10 min hold at 70°C, the samples were cooled to -30°C in order to solidify the liquid fraction into low melting, unstable polymorphs. The samples were then heated to 50°C at a rate of 0.625°C/min and the thermograms recorded.

VI. 2. 3. Calculation of Percent Liquid Fraction

Refer to section IV. 2. 2.

VI. 3. RESULTS AND DISCUSSIONS

VI. 3. 1. Rheological Analysis:

Figure 27 shows the relationship between viscosity index and temperature; a decrease in viscosity occurred for all fats. This decrease was much more pronounced for fats #2 and 3 over the temperature range 25 to 40°C. For fat #1 and 4 the decrease in viscosity was gradual over the entire temperature range investigated. These results suggest that the measured viscosity index is indicative of the rheological properties of the fat over a wide temperature range.

Figure 28 and Table 17 show changes of viscosity and hardness as function of temperature. The figure shows that all samples exhibited different initial viscosity index and hardness. For fats #1 and #3 the effect of temperature on viscosity and hardness were similar. Fat #2 and #4 behaved rather peculiar; there was a sudden increase in viscosity

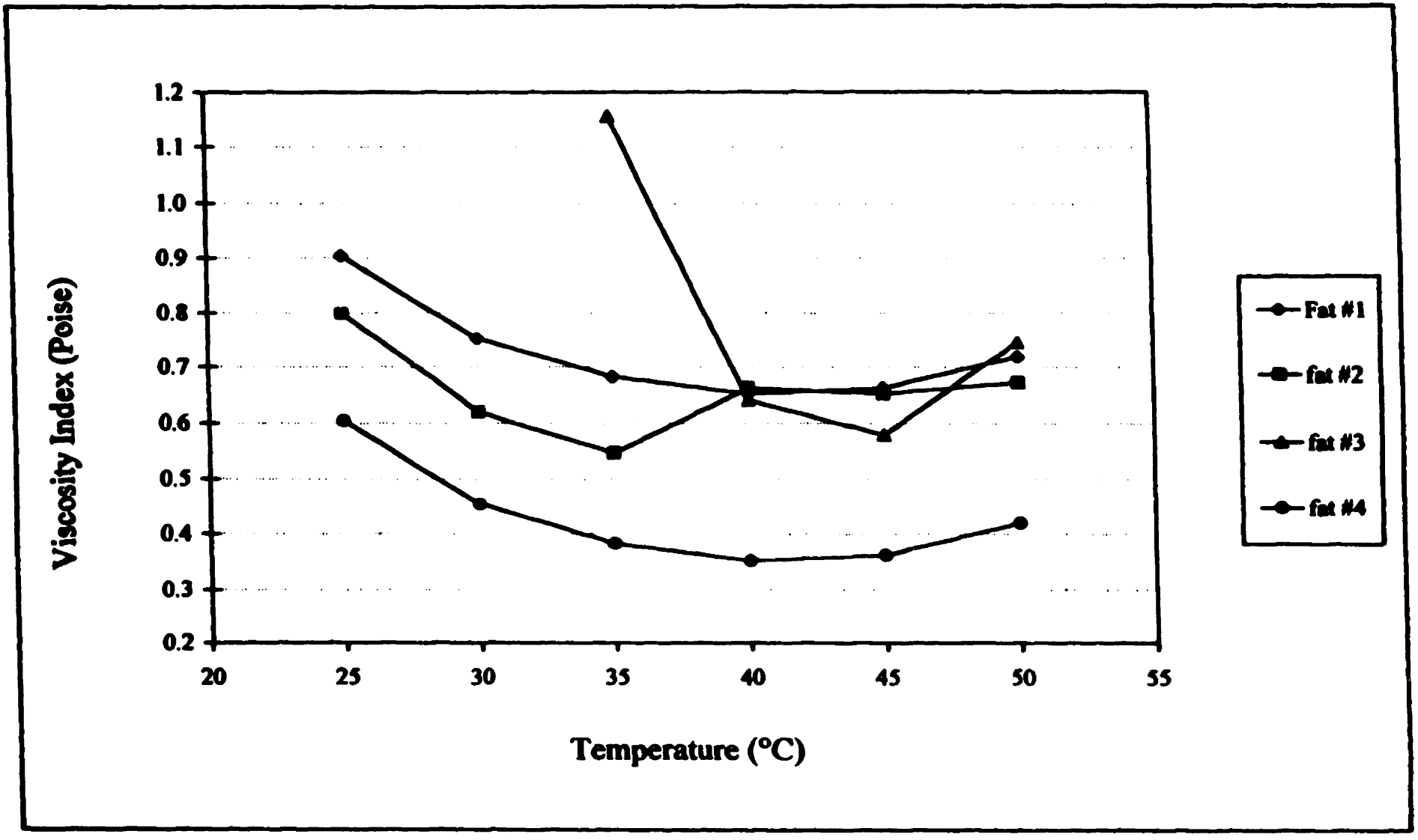


Figure 27. Relationship between viscosity index and temperature of fat blends: hydrogenated soybean oil (A), canola or sunflower oil (B), canola, linola or sunflower oil (C), canola, linola, and sunflower oil (D).

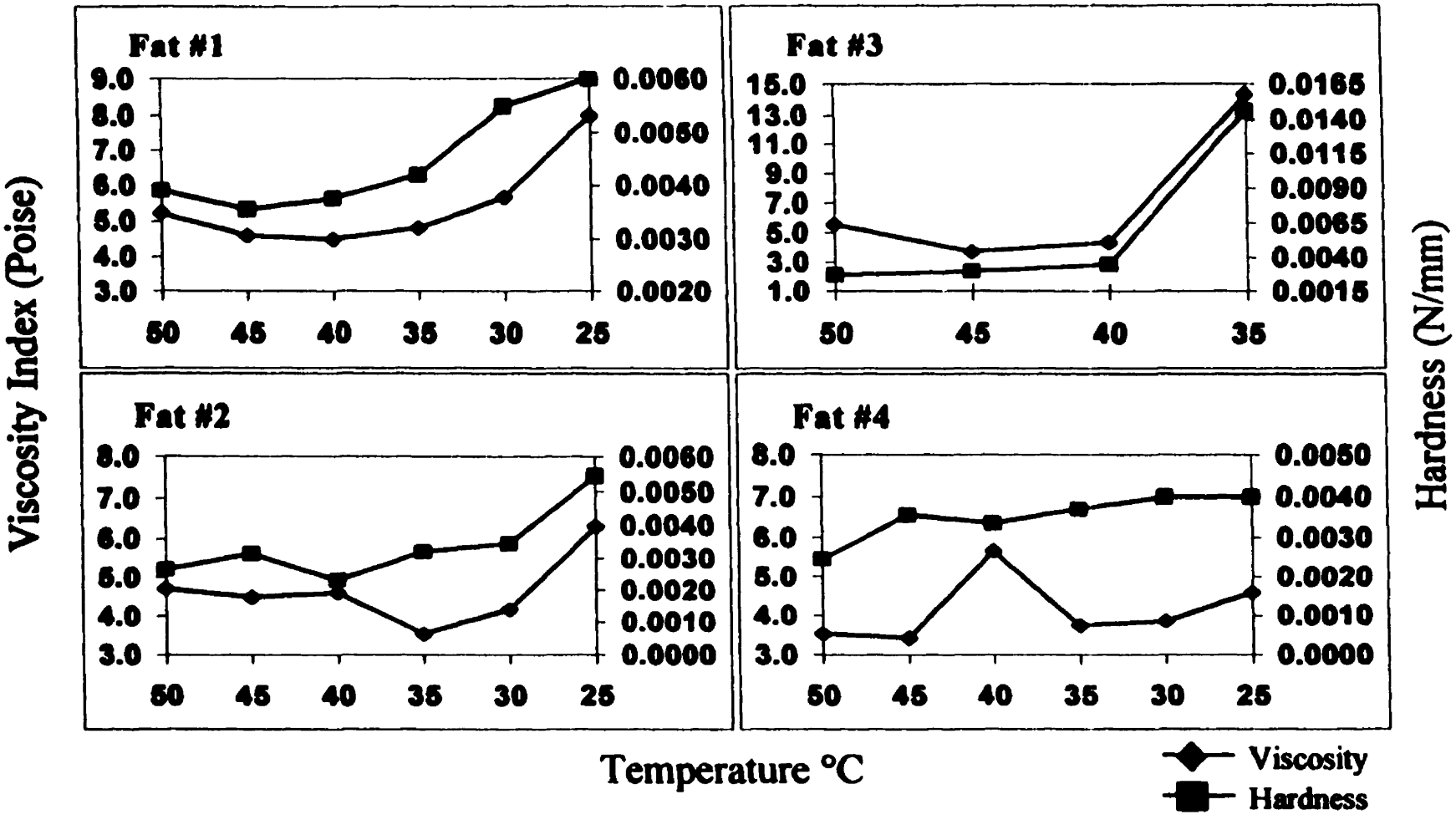


Figure 28. Effect of temperature on viscosity index and hardness of fat blends: hydrogenated soybean oil (A), canola or sunflower oil (B), canola, linola or sunflower oil (C), canola, linola, and sunflower oil (D).

Table 17. Viscosity index and hardness of commercial fat blends: hydrogenated soybean & cottonseed oil (#1), fractionated soybean oil (#2), hydrogenated palm kernel oil (#3), and hydrogenated canola oil (#4).

Temp. (°C)	Fat #1		Fat #2		Fat #3		Fat #4	
	V.I	Hardness	V.I	Hardness	V.I	Hardness	V.I	Hardness
50	5.23	0.0039	4.70	0.0027	5.56	0.0027	2.63	0.0025
45	4.59	0.0036	4.49	0.0032	3.74	0.0030	2.31	0.0036
40	4.49	0.0038	4.59	0.0023	4.38	0.0035	2.25	0.0034
35	4.81	0.0042	3.53	0.0032	14.31	0.0147	2.42	0.0037
30	5.66	0.0055	4.17	0.0035	-	-	2.85	0.0040
25	8.01	0.0060	6.30	0.0055	-	-	4.02	0.0040

V.I= viscosity index

between 45 and 35°C. At these temperature range the hardness of these fats also decreased . This phenomenon has been explained by Philipps (1962) that, in cooling fat samples, there is an increase in activation energy related to molecular aggregation that causes the discontinuity in cooling.

Figure 29 shows a typical force-distance curve. At lower temperatures there was an initial rapid rise in force over a short distance as the plunger moved into the fat. During this stage irreversible deformation of the sample under the load was observed. This stage ended with an abrupt fall of the force when plunger began to penetrate the fat. This event is represented by a sudden change in the curve called the 'yield point'. The importance of yield point has been explained by Mohsenin (1965) as the onset point of crushing or bruising point. The next phase of the curve is marked by the continues force increase after the yield point. If the force does not exceeds beyond the yield point, fats act as rigid solids (Kamel and deMan, 1975), therefore makes it possible to measure their textural properties.

VI. 3. 2. Thermal Analysis:

VI. 3. 2. 1. Percent Liquid Fraction:

Figure 30 shows the percent liquid fraction of the fat blends. For fat #1 and #2, the percent liquid fraction was distributed similarly and identified within the range of 5°C to 35°C. Table 18 shows that the percent liquid fraction of fat #2 was distributed over a much narrower temperature range (15°C to 35°C). For fat #3 at 20°C only 24% of its

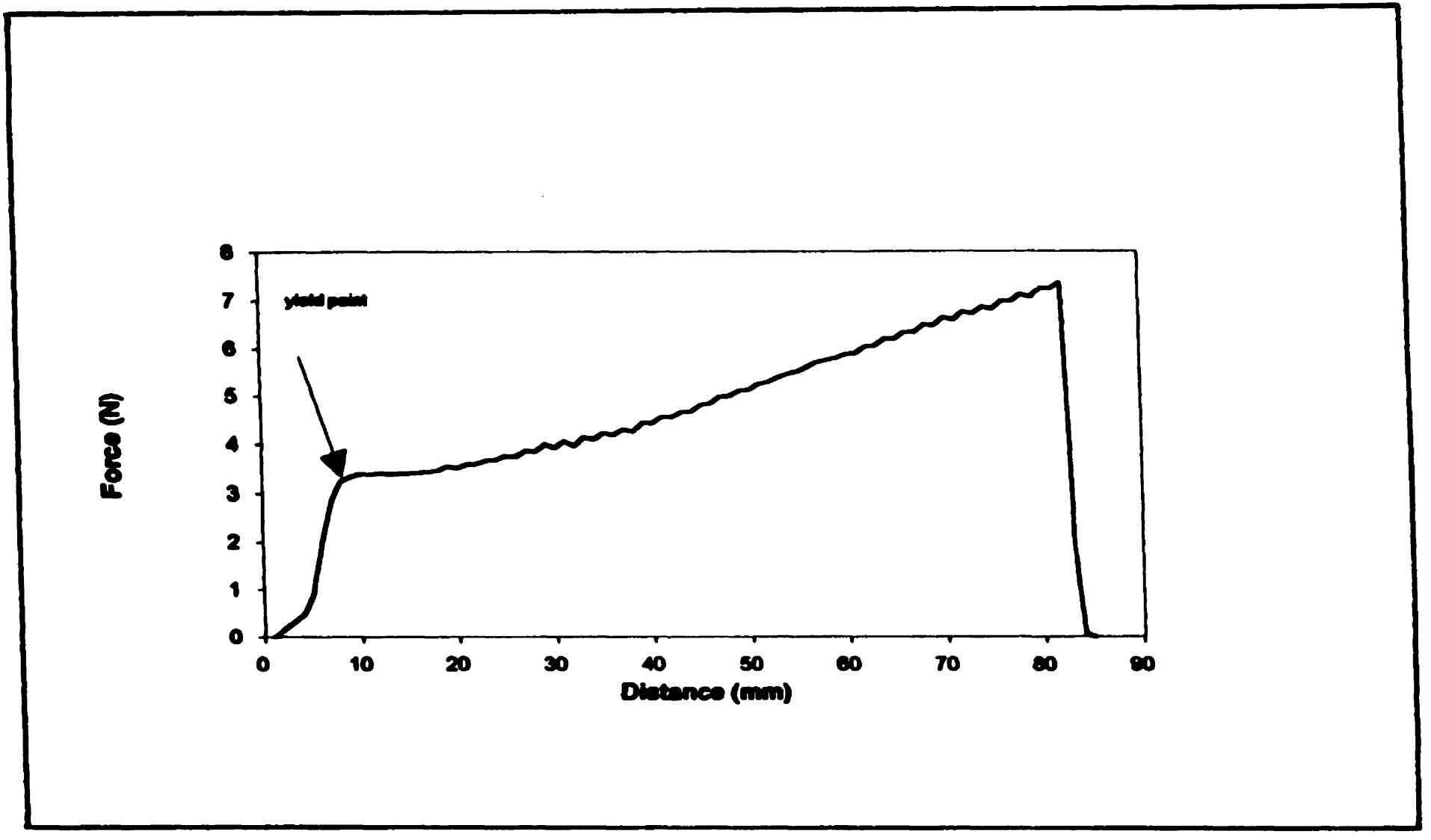


Figure 29. A typical force-distance curve of fat blends.

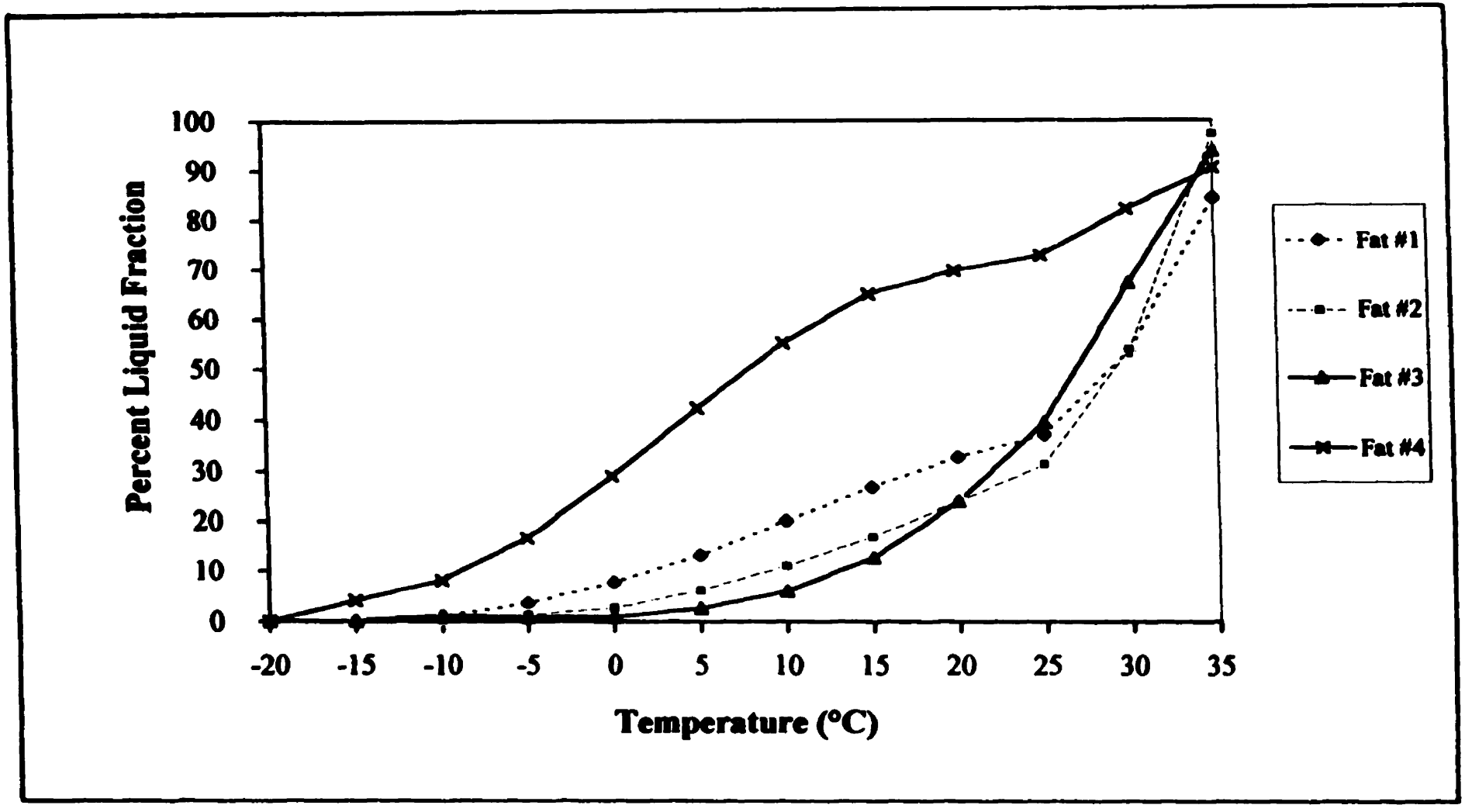


Figure 30. percent liquid fraction of commercial fat blends as function of temperature.

Table 18. Percent liquid fraction of commercial fat blends: hydrogenated soybean & cottonseed oil (#1), fractionated soybean oil (#2), hydrogenated palm kernel oil (#3), and hydrogenated canola oil (#4) and their corresponding enthalpy and melting point.

Temperature	Percent Liquid Fraction			
(°C)	Fat #1	Fat #2	Fat #3	Fat #4
-20	0.0	0.0	0.0	0.0
-15	0.1	0.0	0.2	4.1
-10	1.0	0.3	1.1	8.1
-5	3.6	1.3	0.9	16.6
0	7.7	2.7	0.9	29.0
5	13.2	6.1	2.6	42.5
10	20.1	11.0	6.0	55.5
15	26.8	16.9	12.6	65.2
20	32.8	23.9	24.0	69.9
25	37.2	31.4	39.7	73.0
30	53.8	54.2	67.4	82.5
35	84.6	97.4	94.1	90.7
Delta H (mJ)	**2021.0**	**2030.0**	**2182.0**	**1621.0**
J/g	**137.5**	**138.1**	**149.4**	**109.5**
Peak (°C)	**32.7**	**32.9**	**26.4 / 34.3**	**5.1 / 29.5**

crystals were liquidified where 70% of its fractions melted between 25°C and 35°C; this fat showed higher viscosity index, and higher hardness (Table 18 and 17 respectively).

VI. 3. 3. Relationship Between Viscosity Index and Percent Solid Fraction.

Figure 31 shows the linear regression plot of viscosity index Vs percent solid fat fraction of fats #1, #2, and #4 (Tables 17 and 18). The regression equation was:

$$Y = 0.0619\,X + 2.6137 \qquad \text{where}$$

Viscosity Index = Slope of Percent Solid Fraction + Intercept

with $R^2 = 0.6922$.

This correlation analysis was related to samples heated from 25°C to 35°C; below 25°C the samples required a force greater than 50 N while above 35°C, the samples were hundred percent liquid fraction. Values for fat #3 were eliminated because viscosity index between 25°C and 35°C produce only one measurement (Table 15). This correlation suggests that the ratio of solid to liquid fraction is a major factor that determines the hardness of fats.

VI. 3. 4. Relationship Between Viscosity Index and Hardness of Fats.

Figure 32 illustrates a high linearity between viscosity and hardness of fats #1, #2, #3, and #4 (Table 15). The regression equation calculated at:

$$Y = 902.07\,X + 1.0015 \qquad \text{where}$$

Viscosity Index = Slope of Hardness + Intercept

with $R^2 = 0.8026$

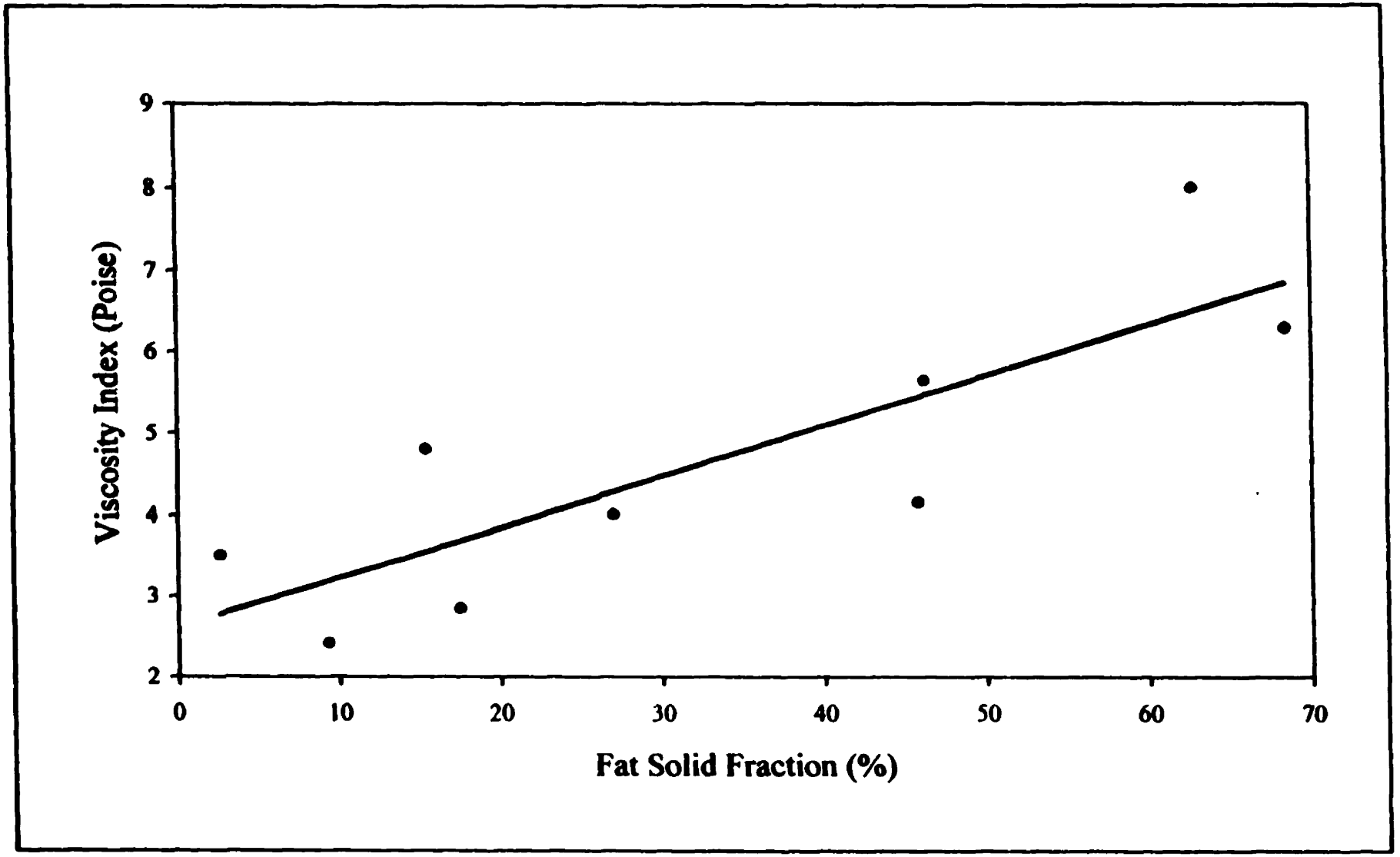


Figure 31. Relationship between viscosity index and percent solid fraction of commercial fat blends.

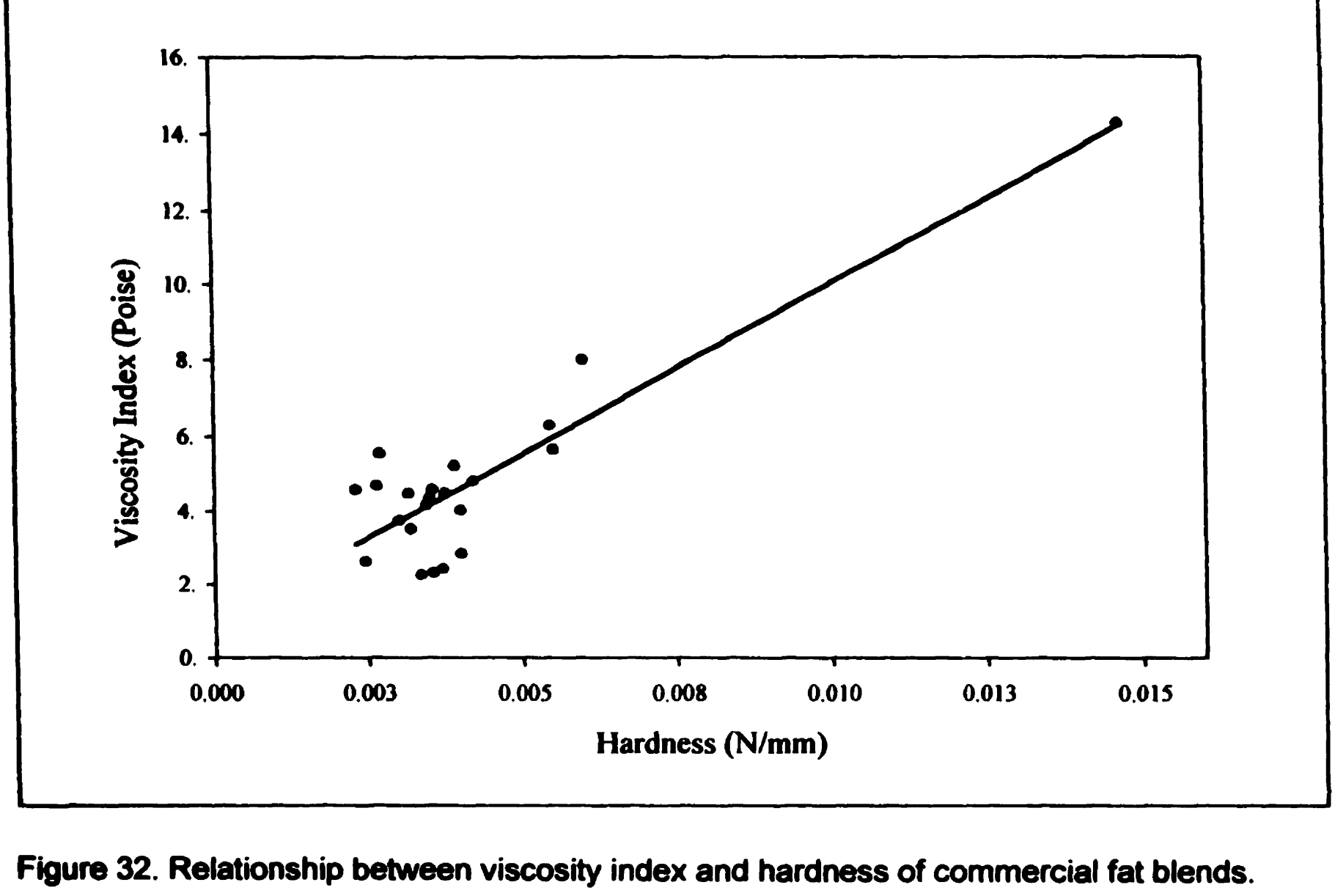


Figure 32. Relationship between viscosity index and hardness of commercial fat blends.

VI. 4. SUMMARY

The commercial fat blends had different initial viscosities which decreased as temperature increased. The viscosity index and hardness of fats determined by the force-deformation technique using the Universal Material Testing Machine (UMTM) can be correlated with the solid fat fraction of the fats. The solid/liquid ratio is an important factor in determining the hardness of edible fats. Percent liquid fraction of fat blends at any given temperature were different indicating a different composition.

GENERAL CONCLUSION

1. Various commercial fats revealed common polymorphic forms sub-α, α, β′, and β. Butters contained α, β′, and β crystal forms; margarines and commercial vegetable fat had β′ and β according to their fat constituents. Tempered cocoa butter contained sub-α, β′ and β forms; untempered cocoa butter showed sub-α and α forms while cocoa liquor revealed sub-α, α, β′ and traces of β forms. Hydrogenated rapeseed oils showed α and β forms in various amounts based on their hydrogenation level.

2. This study showed that addition of lecithin caused the melting point of cocoa liquor to shift slightly to lower temperature however, the effect of lecithin was much stronger on cocoa liquor/sugar mixture.

3. Storing cocoa butter samples at room temperature resulted in slow transformation of crystals from sub-α → α → β′. Formation of the most stable form of crystals took place after seven months at room temperature suggesting that transformation of β′→β happens only from the solid state.

4. Heating/cooling cycles after first cycle had no effect on behavior of sub-α or α forms of cocoa butter or cocoa liquor; however stable polymorphs, β′ and β forms disappeared after first cycle. The sub-α and α forms of cocoa liquor unlike in cocoa butter were distinctively separated.

5. Polymorphic forms of cocoa liquor at various constant temperature treatments revealed different crystal forms; at 0.0, 5.0, and 25.0°C sub- α, at 10.0 and 20.0°C

mixture of sub-α and β′ at 15.0°C only the β′ form appeared. Long periods of constant heatings resulted in transformation of low melting fractions to high melting fractions.

6. Commercial fat blends had different initial viscosity which decreased with temperature. The viscosity index and hardness of fats determined by the force-deformation technique using the Universal Material Testing Machine (UMTM) can be correlated with the solid fat fraction of the fats. The solid/liquid ratio is an important factor in determining the hardness of edible fats. Percent liquid fraction of fat blends at any given temperature were different indicating a different composition.

7. DSC provided valuable data physical measurements of commercial fats and oils such as melting, phase transitions, and percent liquid fraction.

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