SURFACTANTS & DETERGENTS

The Prediction of Lathering and Solubility Properties of Bar Soaps by Differential Scanning Calorimetry[1]

Shyam Gupta*
American Soap Company, Inc., Olive Branch, Mississippi 38654

The present differential scanning calorimetry (DSC) study of eight commercial bar soap products has resulted in the assignment of DSC thermal absorptions to three key polymorphic states of soap (also known as "soap phases"): Δ, β, Ω. The DSC data have also been correlated with polymorphic states of soap identified previously by x-ray diffraction (XRD) method. The correlations of quantitative DSC data with consumer-perceived lathering attributes and experimentally determined solubility properties of these bars also are discussed.

KEY WORDS: Analysis, DSC, evaluation, formulation, lathering, polymorphism, soap, soap—phases, solubility, thermal.

The predictive correlation of laboratory-generated data with consumer-perceived performance attributes of a product or experimental formulations has been a particularly desirable pursuit in the consumer products industry. In the course of our work on the development of bar soap products, we became interested in the development of a simple, rapid, and instrumentally quantitated methodology which could be predictive of the perceived lathering attributes of such products. This methodology was intended for use as a screening tool; a large number of product variables could thus be screened rapidly, resulting in the selection of a smaller number of candidates for further testing.

In search for an instrument-based methodology for the prediction of the lathering potential of bar soap products, we became cognizant of the occurrence of polymorphism in soaps from the literature. These polymorphic crystalline and liquid crystalline states of soap have been reported to be responsible for certain key functional properties of soaps, such as the amount of lather, the dissolution rate, the development of cracks in the bar during its use, and the swelling of wet soap.

The polymorphic states of soap have been studied almost exclusively by x-ray diffraction (XRD). Although a number of publications have appeared on the identification of various polymorphic states of fats and fatty acids by differential scanning calorimetry (DSC) (1-4), the corresponding studies of soaps have been very limited (5).

In the present study, DSC has been investigated as a tool alternative to XRD for the characterization of the polymorphic states of commercial bar soaps. The correlations of DSC data with consumer-perceived lathering attributes and solubility characteristics of these bars also are discussed.

EXPERIMENTAL PROCEDURES

All DSC measurements were done on a DuPont 1090 Thermal Analyzer, equipped with a pressure DSC cell (DuPont, Boston, MA). The peak areas were estimated by DuPont Advanced DSC (V.1.0) program.

For analysis, 100-200 mg samples of soap were obtained by inserting a cork borer to the center of the soap bar to be tested. The sample was then placed in a desiccator (no desiccant was used) for 12-18 hr for equilibration of the bar's moisture. A 5-10 mg sample was then weighed into an aluminum DSC pan. The pan was sealed and placed in the DSC cell. The sample was analyzed under nitrogen atmosphere at a program rate of 20°C/10°C/min/350°C. All samples were analyzed in duplicate. If the duplicate analyses showed a variance of greater than 5%, then those samples were further equilibrated in the desiccator and re-analyzed. All peak integrations were performed automatically by the computer program stated above. The starting point for peak integration was set at the bottom point of the onset of initial endotherm (the top part of the initial endotherm represented mechanical movement of pen, not thermal absorption).

RESULTS AND DISCUSSION

A preliminary evaluation of eight commercial bar soaps revealed high thermal activity, as represented by several distinct thermal absorptions. In order to develop correlations of DSC data with observed relative lathering and solubility properties of these bars, an assignment of DSC data to various polymorphic states of soap known from existing literature was attempted.

At this point, the following summary of literature on the preparation, identification, and properties of the key polymorphic states of soap should be pertinent to this discussion.

It has been known that when kettle-type soaps are cooled from the liquid to the solid state, the conditions prevailing at the time of this transition can significantly influence the final physical form of the resultant soap product. During its manufacturing process, the kettle soap goes through three key transitions: isotropic state (optically, nonrefracting translucent liquid crystalline form, as represented by neat soap, kettle soap, and middle soap), and crystalline state (optically refracting polymorphic state, which occurs in curd soap, for example).

The crystalline states of soap (soap phases) are most important, four of which (α, Δ, β, Ω) have been identified in sodium soaps by XRD. These soap phases have formation and relative abundance which are dependent upon the conditions prevailing at the time of the conversion of soap from liquid to solid state. A literature summary of the formation, XRD identification, and properties of the above soap phases is presented in Table 1 and Scheme 1 (6-10).

The properties of an 80% tallow/20% coconut oil-derived soap containing varying amounts of β and Ω polymorphs are summarized from the literature in Table 2. It is evident at this point that a correlation of the soap phases as identified by XRD and by DSC methods could be useful

---

[1] Presented at the American Oil Chemists' Society Meeting, Baltimore, April 1990.

*To whom correspondence should be addressed at American Soap Company, Inc., 11170 Green Valley Drive, Olive Branch, MS 38654.

TABLE 1

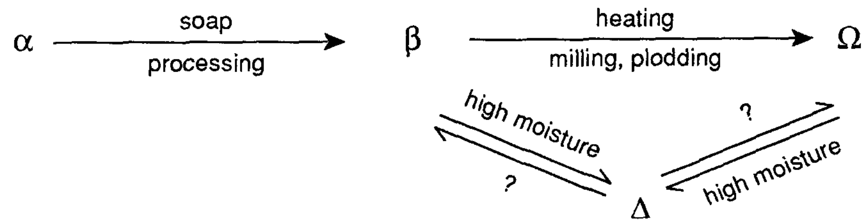
Soap Phases—Formation, Identification and Properties

	α	β	Ω	Δ
Formation	Does not exist under ordinary conditions of soap manufacturing	1. Slow cooling of neat soap. 2. By milling and plodding neat soap. 3. Stirring omega phase at a (higher) temperature where beta is stable	1. Rapid cooling of neat soap. 2. Further heating of beta phase. 3. The formation of omega is favored by higher temperatures, lower moisture and lower molecular weights of fatty acids 4. Coco and oleic acid soaps have most omega phase. 5. Omega occurs in most milled and framed soaps.	1. Formation of delta is favored by high molecular weights, high water content and lower temperatures. 2. Extrusion of high moisture soaps at above-room temperature converts beta to delta.
Identification X-Ray				
a) Ring diam (cm)	7.5, 4.5	6.35	5.85	6.05; 4.65
b) Lattice spacing, Å	2.45; 3.65	2.75	2.95	2.85; 3.55
Properties				
Firmness (arbitrary units)	—	8.0 (most firm)	7.2	3.0 (least firm)
% Rub off (in water)	—	2.4	0.5	1.7
Soaking (in water)	—	-swells and disintegrates	-no swelling or disintegration	-cracks with little swelling
Solubility	—	-rapidly soluble	-poorly soluble	-more soluble than omega
Lathering	—	-easy lathering	-poorer lathering than beta	-better lathering than omega
Translucency	—	-able to exist in a translucent form when crystals of correct size and orientation are properly pressed	-non-translucent	-(not known)
Density	—		-lower than beta	
Melting	—	-beta and omega mostly differ by 2-3°C (dilatometry)		

as a tool for the assessment of various physical property-related attributes of bar soaps: lathering and use-up rate, for example. The following assumptions are made in Table 3 in order to develop this correlation.

The DSC thermal absorptions for eight commercial bar soap products are reproduced in Figure 1.

As noted in Figure 1, all thermal absorptions are reported in °C and the corresponding integrations of peak areas in joules/gram (j/g). For the purpose of the normalization of these data, °C is multiplied by j/g value, then divided by 100 (to reduce the number thus obtained to a manageable unit) to give degree joules per gram (°j/g); degree joules per gram is our term to represent a combination of the thermal transition



SCHEME 1

TABLE 2

The Properties of an 80% Tallow/20% Coconut Oil Soap Bar Prepared with Varying Amounts of β and Ω Phases

		Phase composition (%)					Soaking at 80° F	
Sample	Processing temperature (°C)	β	Ω	Δ	Rub off (%)	Firmness (arbitrary units)	Grams lost/sq. inch	% Strength retained
1	205	0	100	0	0.8	91	0.2	40
2	194	0	100	0	0.7	106	0.3	47
3	180	25	75	0	1.0	80	0.5	43
4	165	75	15	10	1.6	84	1.3	22
5	155	85	10	5	1.9	77	1.5	6
6	140	90	5	5	1.8	60	1.3	8

TABLE 3

The Correlation of DSC Data with Polymorphic States of Soap

Soap polymorph	Assumed physical state	Thermal absorption range
Δ	Solid solution, or gelatinous	<100
β	Liquid crystalline	101-180
Ω	Crystalline	181-300

temperature and its quantity as seen in Equation 1:

$$(^\circ\mathrm{C}) \times (\mathrm{j/g})/100 = {}^\circ\mathrm{j/g} \qquad [1]$$

The prediction of bar soap lathering attributes. Lather value (LV), a dimensionless unit to represent potential lathering attributes of a bar soap, is obtained by relating the β phase (responsible for lathering) with the Ω phase (responsible for insolubility) as per Equation 2:

$$\mathrm{LV} = {}^\circ\mathrm{j/g}\ (\Omega) + {}^\circ\mathrm{j/g}\ (\beta)/{}^\circ\mathrm{j/g}\ (\Omega) \qquad [2]$$

For comparative purposes, the higher the LV of a bar soap, the greater its overall preference as shown by a consumer panel test. (A difference of +0.3 LV units generally shows a 90% statistical significance among bars when compared by a consumer panel.)

Table 4 lists thermal absorption, calculated °j/g, and LV data of eight commercial bar soap products studied by us.

The data on lather comparisons of bar soap pairs by consumer panels and their correlation with results predicted by LV data are summarized in Table 5. It is worthy of note that an increase in the coconut moiety of tallow/coconut oil-derived soap bars showed a parallel increase in the β polymorph: this is contrary to the literature (6,8), which stipulates an increase in the Ω phase content instead, for this change.

The prediction of bar soap solubility. A solubility index (SI) for bar soap solubility is obtained by combining all solubility-related polymorphic states (Δ,β) and relating that value to insolubility-related Ω polymorph, as per Equation 3:

$$\mathrm{SI} = [{}^\circ\mathrm{j/g}\ (\beta) + {}^\circ\mathrm{j/g}\ (\Delta)\ /\ {}^\circ\mathrm{j/g}\ (\Omega)] \times 10 + \mathrm{CF} \qquad [3]$$

The correction factor, CF, is obtained from SI (calculated from DSC data, per Table 4) of a 100% coconut oil-based bar (Kirk's Castille bar) and that bar's actual solubility, as determined by the laboratory tests (11). (Kirk's bar was determined to have 94% solubility by this test), as per Equation 4:

$$\mathrm{CF} = \text{experimental solubility} - \text{DSC solubility index} \qquad [4]$$

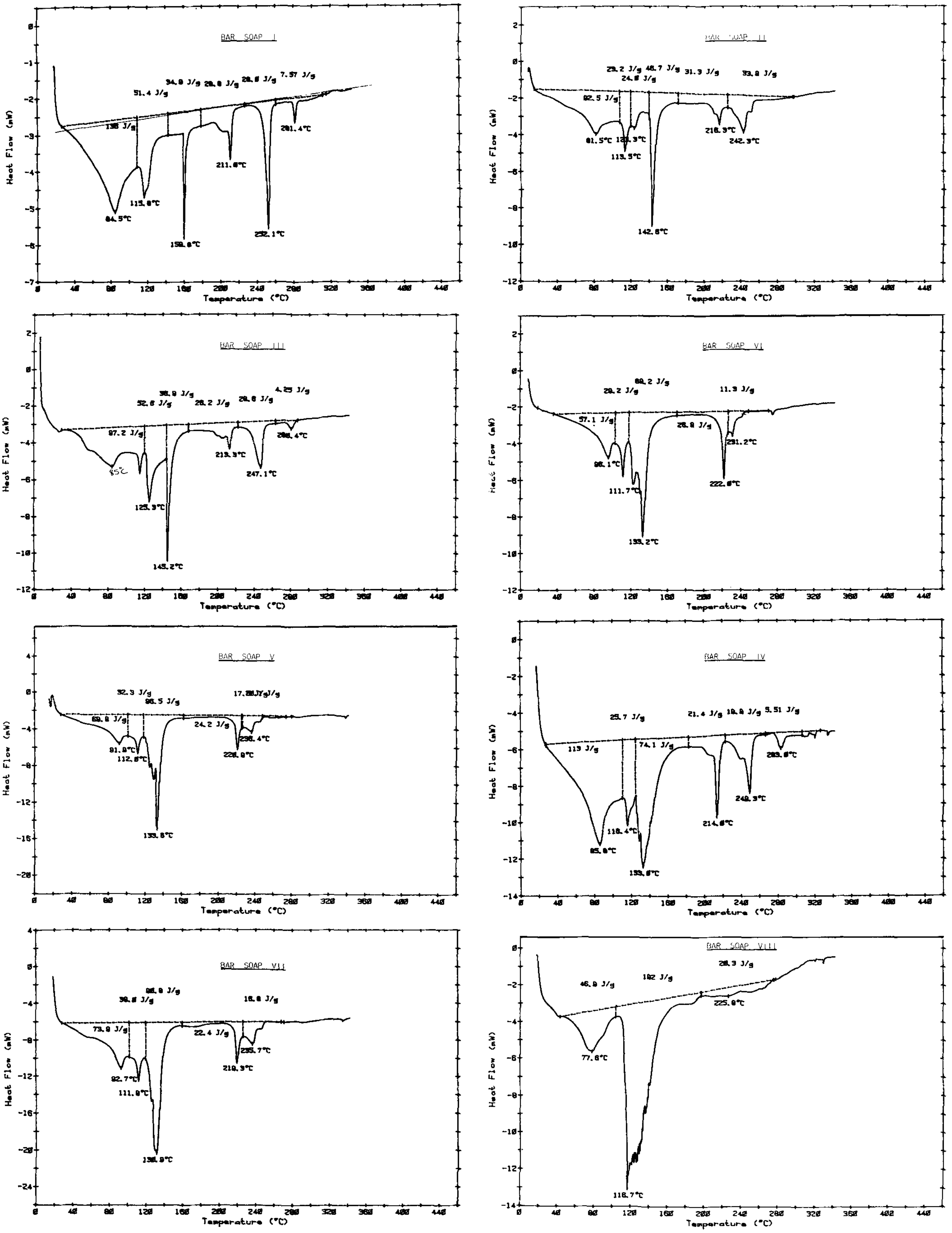


FIG. 1. DSC analysis of commercial bar soaps—bar soap I-bar soap VIII.

TABLE 4

Differential Scanning Calorimetry (DSC) and Lather Value (LV) Data of Commercial Bar Soaps

		Δ-Phase				β-Phase				Ω-Phase				
Bar soap	T/C[a] ratio	°C	(J/g)	°J/g	Total °J/g	°C	(J/g)	°J/g	Total °J/g	°C	(J/g)	°J/g	Total °J/g	Lather value
I	85/15	85	(136)	116	116	116	(51)	59	115	211	(29)	61	154	1.7
						160	(35)	56		252	(28)	71		
										281	(8)	22		
II	80/20	85	(97)	82	82	115		66	120	213	(26)	55	138	1.8
						125	(53)	54		247	(29)	72		
						145	(37)			280	(4)	11		
III	80/20	82	(93)	76	76	114	(23)	26	123	216	(31)	67	149	1.8
						123	(24)	30		242	(34)	82		
						143	(47)	67						
IV	70/30	86	(113)	97	97	116	(26)	30	128	214	(21)	45	112	2.1
						133	(74)	98		249	(20)	50		
										283	(6)	17		
V	50/50	92	(70)	64	64	112	(32)	36	166	221	(24)	53	93	2.8
						134	(97)	130		236	(17)	40		
VI	50/50	96	(57)	55	55	112	(29)	32	150	222	(27)	60	85	2.8
						133	(89)	118		231	(11)	25		
VII	55/45	93	(74)	69	69	112	(38)	43	162	219	(22)	48	88	2.8
						131	(91)	119		236	(17)	40		
VIII	0/100	78	(47)	37	37	117	(192)	225	225	226	(20)	45	45	6.0

[a] Tallow/coconut.

TABLE 5

Lather Value (LV) Data and Lather Panel Results Comparison

Bars compared	LV prediction (LV bar pairs)	Lather panel results
I, VI	I < VI (1.7/2.8)	I < VI
I,II	I = II (1.7/1.8)	I = II
I, III	I = III (1.7/1.8)	I = III
I, V	I < V (1.7/2.8)	I < V
IV, VII	IV < VII (2.1/2.8)	IV < VII

TABLE 6

The Comparison of Bar Soap Solubility with SI Data

Bar soap	% Loss (by solubility test)	Solubility index, SI (calculated from DSC data)
I	48–51	51
II	49–52	49
III	47–49	50
IV	53–56	56
V	62–65	61
VI	61–63	60
VII	60–63	62
VIII	94 (tentative)	94

The DSC solubility (Kirk's bar) $= [°\text{j/g}\,(\beta) + °\text{j/g}\,(\Delta)/°\text{j/g}\,(\Omega)] \times 10$

$$= [225 + 37 / 45] \times 10$$
$$= 58$$

From Equation 4, CF $= 94 - 58 = 36$

Table 6 lists the results of a laboratory-determined bar solubility test (11) and its correlation with solubility index (SI) estimated from DSC data.

This study has shown that DSC can be utilized as a screen tool for the determination of the lathering and solubility properties of bar soap products and developmental bar soap formulations.

REFERENCES

1. Hageman, J.W., in *Crystallization and Polymorphism of Fats and Fatty Acids,* edited by N. Garti, and K. Sato, Marcel Dekker, New York, NY (1988).
2. Guth, O.J., J. Arohime and N. Garti, *J. Am. Oil Chem. Soc. 66*:1606 (1989).
3. Arishima, T., and K. Sato, *Ibid. 66*:1614 (1989).
4. Busfield, W.K., and P.N. Proschogo, *Ibid. 67*:171, 176 (1990).
5. Cingolani, A., G. Spinolo, M. Sanesi and P. Franzosini, *Z. Naturforsch. 35A*:757 (1980).
6. Davidsohn, J., and E.J. Better, *Fats and Oils Soap Manufacturing,* Interscience, New York, NY (1953).
7. Pryde, E. (editor), *Fatty Acids,* American Oil Chemists' Society, Champaign, IL, 1979.
8. Ferguson, R., F. Rosevear and R. Stillman, *Ind. Eng. Chem. 35*:1005 (1943).
9. Ferguson, R., *Oil and Soap 6,*(1944).
10. U.S. patent 2686716 (1954).
11. Gupta, S., in *Soap Technology for the 1990's,* edited by L. Spitz, American Oil Chemists' Society, Champaign, IL, 1990.

[Received June 26, 1990; accepted March 1, 1991]