



Prediction of the melting points of fatty acids from computed molecular descriptors: A quantitative structure–property relationship study

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ABSTRACT

The aim of these works present in this paper consisted in the development and evaluation of quantitative structure property models (QSPR) for the prediction of the melting points of a series constituted by 62 fatty acids. The best multilinear regressions method (MLR) is used to develop models for the prediction of the melting points. The descriptors of the model are selected among an extended set of more than 500 descriptors (constitutional, topological, geometric, quantum chemical and thermodynamic descriptors). Applicability domains were defined and the predictive power was determined using a set of validations. The QSPR models are established using the BMLR method implemented in CODESSA software. It turns out that the best QSPR model ($R^2 = 0.948$, $R^2_{adj} = 0.936$, $SD = 0.940$ and $F\text{-test} = 190.90$) is obtained with five molecular descriptors.

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1. Introduction

The economic importance of the distinctive melting and solidification behavior of fatty acids and their esters was well described by Bailey (1950). Fatty acids and their derivatives constitute an almost infinite variety of long-chain compounds differing in carbon chain length, unsaturation, and isomerism, resulting in a complex and fascinating gamut of physical properties. The transformation from the liquid to the solid state is accompanied by release of heat (latent heat of crystallization signifying an exothermic reaction); the reverse, transformation from solid to liquid, is accompanied by a negative heat effect (endothermic reaction). This forms the basis for the widely used technique of differential scanning calorimetry. Another important phenomenon is melting expansion. Conversion from the solid state to the liquid state results in a melting expansion that is added to the normal thermal expansion. This phenomenon constitutes the basis for the determination of the solid fat index by dilatometry. Protons in the solid state of a fat behave differently from those in the liquid state when subjected to radiofrequency energy when the sample is contained in a magnetic field. This serves as the basis for the determination of the solid fat content in a product by wide-line or pulsed-nuclear magnetic resonance (Harold et al., 2002).

Melting of a fat is an instantaneous reaction, whereas crystallization is usually a slow process. The driving force in crystallization is the degree of supercooling phases: nucleation and crystal growth. A high degree of supercooling will be conducive to nucleation, and many small crystals will be formed. At temperatures closer to the crystallization point, crystal growth will be favored and large crystals will be formed. Another result of a high degree of supercooling is the formation of mixed crystals, also known as solid solutions. Molecules with a range of melting points may crystallize together. As a result, rapidly cooled fats may have higher solid fat content than the same fats that cooled more gradually. These mixed crystals will partially melt when the fat is subjected to temperature variations below its melting point, a phenomenon known as tempering (Moziar et al., 1989).

Svenstrup et al. (2005) have shown that the number of melting points and the melting temperature are correlated with the cooling rate for pork fat, lard, and leaf fat in three different products: extracted fat, raw fat, and fat as an ingredient in liver pate, a rapid cooling leads to lowering of the melting point, assigned to the presence of unstable β' crystals, and that the melting points vary with the treatment of the fat. The findings suggest that the fraction of unsaturated fatty acids present in the fat is important for both crystallization rate and melting points of α and β crystals in extracted lard, and is less pronounced in liver pate because of the presence of diverse components such as proteins. The identification of the various levels of structure present in fat crystal networks, and the development of analytical techniques to quantify these levels have

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Table 1
Experimental and calculated values of Mp of fatty acids A, B, and C correspond to the subsets used in cross validation procedure.

		Structure names	Cal. Mp	Exp. Mp	Residual
1	A	3-7-11-15-Tetramethylhexadecanoic acid	-58.5	-65.0	6.5
2	B	cis-cis-cis-cis-6-9-12-15-Octadecatetraenoic acid	-30.6	-57.0	26.4
3	C	cis-cis-cis-cis-5-8-11-14-Eicosatetraenoic acid	-46.8	-49.0	2.2
4	A	cis-cis-cis-cis-cis-cis-4-7-10-13-16-19-Docosahexaenoic acid	-48.6	-45.0	-3.6
5	B	Pentanoic acid	-23.2	-33.0	9.8
6	C	3-Methylbutanoic acid	-32.9	-29.0	-3.9
7	A	cis-cis-cis-9-12-15-Octadecatrienoic acid	-27.6	-11.0	-16.6
8	B	cis-cis-9-12-Octadecadienoic acid	-15.5	-7.0	-8.5
9	C	Heptanoic acid	2.8	-7.0	9.8
10	A	Butanoic acid	-5.9	-5.0	-0.9
11	B	cis-9-Tetradecenoic acid	7.3	-4.0	11.3
12	C	cis-cis-5-13-Docosadienoic acid	23.1	-4.0	27.1
13	A	Hexanoic acid	-9.3	-3.0	-6.3
14	B	cis-9-Hexadecenoic acid	13.2	0.0	13.2
15	C	12-Hydroxy-cis-9-octadecenoic acid	17.7	5.0	12.7
16	A	Nonanoic acid	19.6	12.0	7.6
17	B	cis-9-Octadecenoic acid	17.0	13.0	4.0
18	C	cis-11-Octadecenoic acid	18.6	15.0	3.6
19	A	Octanoic acid	9.2	16.0	-6.8
20	B	cis-trans-9-11-Octadecadienoic acid	2.0	20.0	-18.0
21	C	trans-cis-10-12-Octadecadienoic acid	11.4	23.0	-11.6
22	A	cis-11-Eicosenoic acid	23.0	24.0	-1.0
23	B	cis-9-Eicosenoic acid	26.0	24.0	2.0
24	C	9-Decenoic acid	-1.3	26.0	-27.3
25	A	cis-5-Eicosenoic acid	28.7	27.0	1.7
26	B	Undecanoic acid	32.2	28.0	4.2
27	C	cis-6-Octadecenoic acid	18.3	29.0	-10.7
28	A	Decanoic acid	27.8	31.0	-3.2
29	B	cis-12-13-Epoxy-cis-9-octadecenoic acid	25.5	32.0	-6.5
30	C	trans-trans-cis-9-11-13-Octadecatrienoic acid	53.3	32.0	21.3
31	A	cis-11-Docosenoic acid	26.2	33.0	-6.8
32	B	cis-13-Docosenoic acid	28.1	34.0	-5.9
33	C	trans-trans-cis-8-10-12-Octadecatrienoic acid	51.1	40.0	11.1
34	A	Tridecanoic acid	45.6	41.0	4.6
35	B	cis-15-Tetracosenoic acid	34.4	43.0	-8.6
36	C	Dodecanoic acid	39.6	43.0	-3.4
37	A	trans-11-Octadecenoic acid	43.1	44.0	-0.9
38	B	cis-trans-cis-9-11-13-Octadecatrienoic acid	51.3	45.0	6.3
39	C	trans-9-Octadecenoic acid	43.1	45.0	-1.9
40	A	cis-trans-trans-9-11-13-Octadecatrienoic acid	41.2	49.0	-7.8
41	B	Pentadecanoic acid	56.5	52.0	4.5
42	C	Tetradecanoic acid	51.1	54.0	-2.9
43	A	Heptadecanoic acid	63.7	61.0	2.7
44	B	trans-13-Docosenoic acid	58.9	61.0	-2.1
45	C	Hexadecanoic acid	57.7	62.0	-4.3
46	A	Nonadecanoic acid	67.8	69.0	-1.2
47	B	Octadecanoic acid	64.3	69.0	-4.7
48	C	trans-trans-trans-9-11-13-Octadecatrienoic acid	69.9	71.0	-1.1
49	A	Eicosanoic acid	70.7	76.0	-5.3
50	B	Pentacosanoic acid	83.9	77.0	6.9
51	C	Tricosanoic acid	79.3	79.0	0.3
52	A	Docosanoic acid	77.1	81.0	-3.9
53	B	Heneicosanoic acid	73.8	82.0	-8.2
54	C	cis-trans-trans-cis-9-11-13-15-Octadecatetraenoic acid	74.1	86.0	-11.9
55	A	Heptacosanoic acid	88.5	87.0	1.5
56	B	Tetracosanoic acid	81.0	87.0	-6.0
57	C	Hexacosanoic acid	85.7	88.0	-2.3
58	A	Nonacosanoic acid	93.0	90.0	3.0
59	B	Octacosanoic acid	90.4	90.0	0.4
60	C	Hentriacontanoic acid	97.6	93.0	4.6
61	A	Triacantanoic acid	94.8	93.0	1.8
62	B	Dotriacontanoic acid	102.8	96.0	3.1
		Minimum	-58.5	-65.0	-
		Maximum	102.8	96.0	-
		Mean	34.9	34.8	0.0
		Median	33.3	33.5	-0.9

been reviewed by Narine and Marangoni (1999, 2002). The types, formulations, functionality, and processing required for the production of lipid-shortening systems, as well as their crystallization, structural elucidation, and mechanical modeling of fat crystal networks have been reviewed by Ghotra et al. (2002). Also, Humphrey et al. (2004) have compared the lipid-shortening functionality as

a function of molecular ensemble and shear: crystallization and melting.

Alternatively, the quantitative structure–property relationship (QSPR) provides a promising method for estimating the melting point of fatty acids based on descriptors derived solely from the molecular structure to fit experimental data. The QSPR is based

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