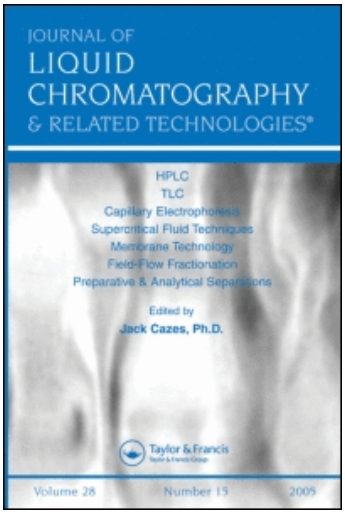

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

R_M Values Application for Calculation and Prediction of Selected Physicochemical Properties of Homologous Series of Saturated Fatty Acids

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To cite this Article Bober, K.(2008) 'R_M Values Application for Calculation and Prediction of Selected Physicochemical Properties of Homologous Series of Saturated Fatty Acids', Journal of Liquid Chromatography & Related Technologies, 31: 4, 567 — 577
To link to this Article: DOI: 10.1080/10826070701812798
URL: http://dx.doi.org/10.1080/10826070701812798

Journal of Liquid Chromatography & Related Technologies®, 31: 567–577, 2008

ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070701812798

R_M Values Application for Calculation and Prediction of Selected Physicochemical Properties of Homologous Series of Saturated Fatty Acids

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Abstract: Acids from pentanoic to tricosanoic have been separated using RP-HPTLC, on RP-18 plates with and without a concentrating zone, using methanol–water, ethanol–water and *n*-propanol–water (90:10, 95:5, and 100:0, v/v) as mobile phases. R_F values obtained have been converted into R_M values. R_M values have been used to calculate and predict the neutralization value, boiling point, melting point, and heat of crystallization of fatty acids investigated. Relationships between selected physiochemical properties of fatty acids and R_M values obtained using RP-HPTLC have been described by polynomials of the second degree or linear functions. All described relationships have been characterized by high values of determination coefficients, which were in the range of 93.32 ÷ 99.94%. It suggests the possibility of using them to calculate and predict the values of neutralization value, boiling point, melting point, and heat of crystallization of acids investigated.

Keywords: Fatty acids, RP-HPTLC, Neutralization value, Boiling point, Melting point, Heat of crystallization

INTRODUCTION

The problem of prediction of the physicochemical properties of organic compounds has been of interest for over one hundred years and still is up to

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date. There are some monographs[1–5] and many reviews concerning this problem.

Many chemists also take into consideration the problem of prediction of the physicochemical properties on the base of value of R_M parameter. The relationships between R_M parameter and logP values of polycyclic hydrocarbons,[6] long-chain fatty acids, hydroxyacids, and their esters[7] were analyzed in such a way.

This work is a continuation of fatty acid investigations. Previous research concerned chromatographic separation using TLC, elaboration of new visualizing agents, and application of selected structural descriptors in QSRR and QSPR analysis of acids investigated.[8–15]

The aim of this work was to use the R_M parameter to calculate and predict the values of neutralization value, boiling point, melting point, and heat of crystallization of selected fatty acids.

EXPERIMENTAL

Acids Investigated

The subject of the research were the following acids: pentanoic (C5), hexanoic (C6), heptanoic (C7), octanoic (C8), nonanoic (C9), decanoic (C10), undecanoic (C11), dodecanoic (C12), tridecanoic (C13), tetradecanoic (14), pentadecanoic (C15), hexadecanoic (C16), heptadecanoic (C17), octadecanoic (C18), nonadecanoic (C19), eicosanoic (C20), uncosanoic (C21), docosanoic (C22), tricosanoic (C23).

Partition Thin Layer Chromatography

Solutions of the acids were prepared from chemicals (99% pure) supplied by Larodan Chemicals, Sweden. Methanol, ethanol, and *n*-propanol (analytical grade) were obtained from POCh (Gliwice, Poland).

Partition TLC was performed on 10 × 20 cm glass backed RP-18 HPTLC plates with and without a concentrating zone (Merck #15498 and 1.05914, respectively). Solutions of the acids, 20 μg acid in 5 μL chloroform, were spotted on the plates and the plates were developed at room temperature in a chamber for 20 × 20 cm plates (Camag, Switzerland), previously saturated for 30 min with the mobile phase. The mobile phases were: methanol–water, 90:10 (v/v); methanol–water, 95:5 (v/v); 100% methanol; ethanol–water, 90:10 (v/v); ethanol–water, 95:5 (v/v); 100% ethanol; or *n*-propanol–water, 90:10 (v/v); *n*-propanol–water, 95:5 (v/v) and 100% *n*-propanol. The development distance was 7 or 7.5 cm, respectively, for plates with or without a concentrating zone. The substances analyzed were visualized in iodine vapor.

R_F values were measured and converted to R_M values according to the equation:

$$R_M = \log\left(\frac{1}{R_F} - 1\right) \quad (1)$$

Regression Analysis

The regression equations, describing relationships between values of selected physicochemical properties of fatty acids investigated and values of R_M parameter obtained by RP-HPTLC were obtained, using the computer program STATISTICA 7.1.

RESULTS AND DISCUSSION

The values of selected physicochemical properties investigated, neutralization value, boiling point, melting point, and heat of crystallization, obtained from literature are presented in Table 1.[16] The experimental values of R_M obtained by using RP-HPTLC are found in Table 2.

Table 1. Values of selected physicochemical properties of fatty acids investigated [16]

Symbol of acid	Neutralization value (mg KOH/g)	Boiling point (°C)	Melting point (°C)	Heat of crystallization (kg cal/mol)
C5	549.34	187.0	−59.00	—
C6	483.00	205.8	−3.40	3.60
C7	430.96	223.0	−10.50	3.58
C8	389.05	239.7	16.70	5.11
C9	354.56	255.6	12.50	4.85
C10	325.69	270.0	31.60	6.69
C11	301.17	284.0	29.30	5.99
C12	280.08	298.9	44.20	8.75
C13	261.75	312.4	41.50	8.02
C14	245.68	326.2	53.90	10.74
C15	231.46	339.1	52.30	10.30
C16	218.80	351.5	63.10	12.98
C17	207.45	363.8	61.30	12.22
C18	197.23	376.1	69.60	—
C19	187.96	—	68.60	—
C20	179.52	328.0	75.30	16.95
C21	171.81	—	74.30	—
C22	164.73	—	79.90	18.75
C23	158.22	—	79.10	17.60

Table 2. R_M values obtained using RP-HPTLC for acids investigated

	Mobile phase: methanol–water			Mobile phase: ethanol–water			Mobile phase: *n*-propanol–water		
Symbol of acid	90:10, v/v	95:5, v/v	100:0, v/v	90:10, v/v	95:5, v/v	100:0, v/v	90:10, v/v	95:5, v/v	100:0, v/v
RP-18 plates without concentrating zone									
C5	−0.664	−0.81							
C6	−0.454	−0.686							
C7	−0.356	−0.550	−0.602	−0.500	−0.650	−0.714			
C8	−0.231	−0.436	−0.500	−0.500	−0.550	−0.635	−0.814	−0.921	−0.921
C9	−0.108	−0.310	−0.438	−0.382	−0.491	−0.57	−0.764	−0.865	−0.865
C10	0.036	−0.194	−0.327	−0.274	−0.382	−0.522	−0.679	−0.814	−0.865
C11	0.182	−0.063	−0.226	−0.176	−0.310	−0.477	−0.602	−0.764	−0.814
C12	0.337	0.064	−0.176	−0.035	−0.194	−0.393	−0.568	−0.679	−0.764
C13	0.486	0.194	−0.066	0.035	−0.106	−0.343	−0.501	−0.602	−0.720
C14	0.664	0.358	0.087	0.153	−0.021	−0.269	−0.438	−0.568	−0.679
C15	0.908	0.491	0.222	0.274	0.064	−0.176	−0.382	−0.532	−0.638
C16	1.049	0.650	0.368	0.438	0.172	−0.108	−0.302	−0.438	−0.638
C17	1.369	0.857	0.537	0.532	0.239	0.000	−0.250	−0.410	−0.568
C18	1.557	0.964	0.635	0.602	0.358	0.087	−0.200	−0.327	−0.501
C19		1.187	0.753		0.436	0.154	−0.105	−0.274	−0.47
C20		1.288	0.899		0.550	0.222	−0.057	−0.226	
C21			1.016				0.035		
C22			1.091						
C23			1.180						

RP-18 plates with concentrating zone

C5									
C6									
C7									
C8	−0.227	−0.339	−0.493	−0.461	−0.954		−0.890	−1.110	−1.110
C9	−0.124	−0.282	−0.428	−0.339	−0.890	−1.219	−0.778	−1.026	−1.110
C10	0.000	−0.151	−0.339	−0.227	−0.730	−1.026	−0.73	−1.026	−1.026
C11	0.151	−0.049	−0.256	−0.124	−0.602	−0.954	−0.682	−0.954	−1.026
C12	0.282	0.075	−0.176	−0.024	−0.461	−0.778	−0.641	−0.890	−0.954
C13	0.430	0.176	−0.099	0.075	−0.339	−0.682	−0.565	−0.829	−0.954
C14	0.565	0.311	0.000	0.202	−0.227	−0.527	−0.527	−0.730	−0.890
C15	0.778	0.461	0.099	0.311	−0.099	−0.428	−0.428	−0.730	−0.829
C16	0.954	0.641	0.229	0.430	0.000	−0.310	−0.368	−0.641	−0.778
C17	1.219	0.833	0.368	0.565	0.126	−0.202	−0.310	−0.565	−0.778
C18	1.540	1.026	0.493	0.778	0.229	−0.099	−0.256	−0.493	−0.730
C19		1.219	0.650	0.833	0.339	0.000	−0.176	−0.428	−0.641
C20		1.347	0.890	1.026	0.461		−0.124	−0.386	−0.565
C21			1.026	1.117	0.493		−0.049	−0.282	−0.527
C22								−0.202	−0.493
C23									

Table 3. Selected regression equations describing the relationships between values of selected physicochemical properties and R_M values of acids investigated

Physicochemical property	Range of acids	Regression equation[a]	n	R^2 (%)	F	s	Eq. no
RP-18 plates without concentrating zone, mobile phase: methanol – water (100:0, v/v)							
Neutralization value	C7÷C23	n.v. = 265.3370(±4.6517) − 182.1070(±9.0018)R_M + 88.2355(±12.1524)R_M^2	17	97.76	305	13.19	2
Boiling point	C7÷C20 (without C19)	b.p. = 322.6410(±3.9726) + 115.3590(±6.9094)R_M – 101.7530(±14.4857)R_M^2	13	96.56	140	9.8	3
Melting point							
O[b]	C7÷C23	m.p. = 40.9462(±2.1562) + 60.1397(±3.8351)R_M – 26.1508(±5.1199)R_M^2	9	98.42	187	4.38	4
E[c]		m.p. = 49.1983(±1.4305) + 48.8075(±3.1021)R_M – 20.6845(±4.2911)R_M^2	8	98.86	217	2.80	5
Heat of crystallization							
O[b]	C7÷C23 (without C18. C19, C21)	h.c. = 8.2536(±0.1188) + 7.8831(±0.2055)R_M	7	99.66	1471	0.31	6
E[c]		h.c. = 9.7034(±0.1538) + 8.3540(±0.2559)R_M	7	99.53	1066	0.38	7
RP-18 plates without concentrating zone, mobile phase: ethanol–water (95:5, v/v)							
Neutralization value	C7÷C20	n.v. = 239.5600(±2.5127) – 181.1410(±4.8058)R_M +150.9460(±13.8149)R_M^2	14	99.46	1008	6.29	8

Boiling point	C7÷C20 (without C19)	b.p. = 322.6870(±5.0492) + 100.7130(±10.7050)R_M − 125.6900(±28.6963)R_M^2	13	94.31	82	12.6	9
Melting point							
O[b]	C7÷C20	m.p. = 50.0624(±0.1.4018) + 59. 8593(±3.1840)R_M − 45.4611(±8.3072)R_M^2	7	99.48	383	2.49	10
E[c]		m.p. = 55.2009(±0.3612) + 52.3442(±0.6411)R_M − 30.1020(±2.0233)R_M^2	7	99.94	3457	0.62	11
Heat of crystallization							
O[b]	C7÷C20	h.c. = 9.5322(±0.2216) + 9.7554(±0.5950)R_M	6	98.54	267	0.45	12
E[c]	(without C18, C19)	h.c. = 10.9761(±0.0514) + 10.9100(±0.1392)R_M	6	99.94	6146	0.12	13
RP-18 plates with concentrating zone, mobile phase: *n*-propanol–water (95:5, v/v)							
Neutralization value	C8÷C22	n.v. =185.1080(±13.9939) + 117.3630(±46.5502)R_M + 261.5680(±34.4510)R_M^2	15	98.51	396	9.18	14
Boiling point	C8÷C20 (without C19)	b.p. = 262.1320(±41.1001) − 356.3260(±115.1040)R_M − 346.2990(±75.8426)R_M^2	12	93.32	63	12.4	15
Melting point							
O[b]	C8÷C22	m.p. = 80.7605(±2.3760) − 59.9021(±3.7339)R_M^2	7	98.09	859	3.36	16
E[c]		m.p. = 82.4944(±1.2429) − 50.8241(±1.8068)R_M^2	8	99.25	3128	2.08	17
Heat of crystallization							
O[b]	C8÷C22 (without C18, C19, C21)	h.c. = 21.8066(±0.8117) + 16.4847(±0.9698)R_M	5	98.97	289	0.35	18
E[c]		h.c. = 22.3540(±0.4184) + 15.3476(±0.5395)R_M	7	99.39	809	0.44	19

[a]For all regression equations $p < 0.001$.
[b]Concerning acids with odd number of carbon atoms.
[c]Concerning acids with even number of carbon atoms.

Table 4. Regression equations describing the relationships between values of selected physicochemical properties and R_M values of acids investigated with one acid omitted as well as experimental and predicted values of those properties

Physicochemical property	Acid omitted	Regression equation[a]	n	R^2 (%)	F	s	Eq. no	Experim. value	Predicted value
RP-18 plates without concentrating zone, mobile phase: methanol–water (100:0, v/v)									
Neutralization value	C16	n.v. = 264.0830(±5.0792) −183.9490(±9.5564)R_M + 91.0639(±13.0485)R_M^2	16	97.81	291	13.45	20	218.80	208.72
Boiling point	C8	b.p. = 322.6390(±4.1890) + 115.4260(±8.0390)R_M − 101.8390(±15.8864)R_M^2	12	95.88	105	10.3	21	239.7	239.5
Melting point									
O[b]	C15	m.p. = 41.2019(±2.7669) + 60.4168(±4.4746)R_M − 26.6480(±6.2647)R_M^2	8	98.42	155	4.79	22	52.30	53.30
E[c]	C14	m.p. = 48.9617(±1.8830) + 48.5626(±3.6002)R_M − 20.1608(±5.2642)R_M^2	7	98.87	176	3.11	23	53.90	53.03
Heat of crystallization									
O[b]	C15	h.c. = 8.2055(±0.1265) + 7.8624(±0.2047)R_M	6	99.73	1476	0.31	24	10.30	9.95
E[c]	C14	h.c. = 9.6473(±0.1712) + 8.3734(±0.2641)R_M	6	99.60	1005	0.39	25	10.74	10.38
RP-18 plates without concentrating zone, mobile phase: ethanol–water (95:5, v/v)									
Neutralization value	C15	n.v. = 239.0370(±2.8258)−181.1420(±4.9837)R_M + 152.9440(±14.9225)R_M^2	13	99.46	916	6.52	26	231.46	228.07
Boiling point	C10	b.p. = 333.2260(±5.3746) + 99.3976(±11.4756)R_M − 126.8090(±29.9608)R_M^2	12	94.17	73	13.1	27	270.0	276.8

Melting point									
O[b]	C15	m.p. = 50.6621(±1.8060) + 59.7426(±3.4672)R_M − 47.7143(±9.7384)R_M^2	6	99.51	304	2.70	28	52.30	54.29
E[c]	C8	m.p. = 54.9718(±0.1337) + 51.0262(±0.3312)R_M − 26.0408(±1.0322)R_M^2	6	99.99	14037	0.22	29	16.70	19.03
Heat of crystallization									
O[b]	C9	h.c. = 9.6146(±0.2051) + 9.6428(±0.5345)R_M	5	99.09	325	0.40	30	5.99	6.62
E[c]	C10	h.c. = 10.9993(±0.0525) + 10.8442(±0.1413)R_M	5	99.95	5739	0.12	31	6.69	6.86
RP-18 plates with concentrating zone, mobile phase: *n*-propanol − water (95:5, v/v)									
Neutralization value	C19	n.v. = 184.4980(±14.4299) + 118.5530 (±47.9190)R_M + 263.4480(±35.5767)R_M^2	14	98.46	353	9.44	32	187.96	182.02
Boiling point	C9	b.p. = 264.4240(±42.5728) − 346.9140 (± 119.6760)R_M − 337.4160(±79.4313)R_M^2	11	92.38	48	12.8	33	255.6	265.2
Melting point									
O[b]	C11	m.p. = 81.2260(±2.3502) − 61.9515(±4.0643)R_M^2	6	98.31	867	3.27	34	29.30	24.84
E[c]	C12	m.p. = 82.4345(±1.2351) − 51.2473(±1.8388)R_M^2	7	99.36	2946	2.06	35	44.20	41.84
Heat of crystallization									
O[b]	C15	h.c. = 21.2654(±0.0390) + 15.9993(±0.4520)R_M	4	99.99	125250	0.02	36	10.30	9.58
E[c]	C14	h.c. = 22.4132(±0.4213) + 15.3347(±0.5381)R_M	6	99.51	812	0.44	37	10.74	11.22

[a]For all regression equations $p < 0.001$.
[b]Concerning acids with odd number of carbon atoms.
[c]Concerning acids with even number of carbon atoms.

The relationships between values of neutralization value, boiling point, melting point, and heat of crystallization of fatty acids investigated and R_M values, obtained using RP-HPTLC, on plates RP-18 without and with concentrating zones, using methanol–water, ethanol–water and *n*-propanol–water as mobile phases were settled. In the case of the melting point and heat of crystallization the relationships were settled separately for acids with odd and even numbers of carbon atoms in the chain of acid.

Some regression equations describing the relationships between the values of physicochemical properties and values of R_M parameters do not take into consideration all acids chromatographed because of no literature data of values of these acids properties.

The selected regression equations describing the relationships between values of physicochemical properties of fatty acids and values of R_M parameters obtained, using RP-HPTLC on plates RP-18 without and with concentrating zones, using methanol–water, ethanol–water and *n*-propanol–water as mobile phases are presented in Table 3.

The values of selected physicochemical properties that include neutralization value, boiling point, melting point, and heat of crystallization can be calculated using equations (2)÷(19) in Table 3, on the basis of R_M values obtained by RP-HPTLC method for acids investigated. On the basis of these equations, the physicochemical properties can be also predicted, by omitting one of the acid in the regression equation, using known values of R_M parameter.

New regression equations obtained by omitting one of the acids, as well as the predicted and experimental values of neutralization value, boiling point, melting point, and heat of crystallization are presented in Table 4 (equations (20)÷(37)).

On the basis of above mentioned examples, the possibility of the prediction of the values of physicochemical properties of fatty acids on the basis of relationships investigated, using values of the R_M parameter coming from a particular experiment is shown.

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Received August 22, 2007
Accepted September 7, 2007
Manuscript 6202