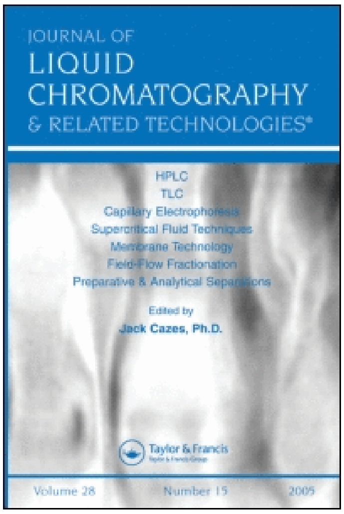

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RP-HPTLC Application in the Investigation of Solubility in Water of Long-Chain Fatty Acids

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RP-HPTLC Application in the Investigation of Solubility in Water of Long-Chain Fatty Acids

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Abstract: Acids, from octanoic to octadecanoic, have been separated using RP-HPTLC, on RP-18 plates without and with a concentrating zone, using methanol-water and ethanol-water (90 : 10 and 95 : 5, v/v) as mobile phases. R_F values obtained have been converted to R_M values. R_M values have been used to calculate the solubilities in water of fatty acids investigated at different temperatures. Relationships between solubility in water of fatty acids at different temperatures and R_M values obtained using RP-HPTLC have been described by polynomials of third degree or expotential functions. All described relationships have been characterized by high values of determination coefficients, which were in the range of 96.65 ÷ 99.97%. This suggests the possibility of using them to calculate and predict the values of solubilities in water of acids investigated.

Keywords: RP-HPTLC, Fatty acids, Solubility in water

INTRODUCTION

Fatty acids are characterized by many physicochemical properties, among others, solubility. Estimation of physicochemical properties of chemical compounds, including fatty acids, is one of the many tasks of contemporary chemistry. Many chemical, as well as physical, properties of fatty acids depend on their structures.[1] Molecules of fatty acids are polar and can form hydrogen bonds between themselves or other molecules.[2] The first four

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acids from their homologous series are soluble in water, the fifth one is partially soluble, and higher components of the homologous series are practically insoluble. Solubility in water is caused by the p-resence of hydrogen bonds and dipole-dipole interactions between polar fragments of organic molecules and water. Acids' solubility in water decreases with increasing length of their hydrocarbon chain and degree of branching.[3] Acids with long hydrocarbon chains are not soluble in water. The energy input needed for hydrogen bond cleavage is higher than the gain in energy coming from hydration of the hydrophilic carboxylic group. A hydrocarbon radical, which is hydrophobic, does not show water affinity[3] and, because of this, long-chain fatty acids are characterized mostly by hydrophobic properties. When a hydrocarbon radical is large, the strength of the carboxyl group is not enough to bring the molecule of acid into solution. The presence of molecules with large hydrophobic groups in water solution is energetically unfavourable, because those groups separate the molecules of water from themselves and reduce the number of hydrogen bonds between them.[3] The higher carboxylic acids are soluble in the same solutions as their analogous hydrocarbons.[4] These acids, even though they have a hydrophilic part, are not soluble in water.[5] They are soluble in ethanol, benzene, chloroform, propylene glycol, hexane, etc.

This work is a continuation of our fatty acid investigations. Previous research concerning chromatographic separation using TLC, elaboration of new visualizing agents, and application of selected structural descriptors in QSRR and QSPR analysis of acids has been investigated.[6–12]

The aim of this work was to use the R_M parameter to calculate and predict the solubilities of selected fatty acids in water.

EXPERIMENTAL

Chemicals

Solutions of the acids (octanoic, nonanoic, decanoic, undecanoic, dodecanoic, tridecanoic, tetradecanoic, pentadecanoic, hexadecanoic, heptadecanoic, and octadecanoic) were prepared from chemicals (99% pure) supplied by Larodan Chemicals, Sweden.

Partition TLC was performed on 10 cm × 20 cm glass-backed RP-18 HPTLC plates, with and without a concentrating zone, (Merck #15498 and 1.05914, respectively). Chloroform, methanol, and ethanol (analytical grade) were obtained from POCh (Gliwice, Poland).

Thin Layer Chromatography

Solutions of the acids, 20 μg acid in 5 μL chloroform, were spotted onto the plates; the plates were developed at room temperature in a twin-trough chamber (Camag, Switzerland) which had been previously saturated for 30 min with the mobile phase. The investigated mobile phases were: methanol-water, 90 : 10 (v/v), methanol-water, 95 : 5 (v/v), ethanol-water, 90 : 10 (v/v), and ethanol-water, 95 : 5 (v/v). 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.

Chromatographic Parameters

R_F values were measured and converted to R_M values by use of the formula:

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

Regression Analysis

The regression equations describing the relationships between values of solubility of fatty acids investigated and values of the R_M parameters obtained by RP-HPTLC were determined, using the computer program Statistica 7.1.

RESULTS AND DISCUSSION

Values of solubility of saturated fatty acids, from octanoic to octadecanoic, in water in different temperatures[13] are presented in Table 1. Values of R_F and R_M parameters, obtained by RP-HPTLC, are presented in Table 2. Chromatographic separation carried out served to develop the regression equations

Table 1. Solubility in water of fatty acids in different temperatures expressed in g/100 g H_2O[13]

Acid	Acid symbol	Solubility of fatty acids in g/100 g H_2O in temperature				
		0.0°C	20.0°C	30.0°C	45.0°C	60.0°C
Octanoic	C8	0.044	0.068	0.079	0.095	0.113
Nonanoic	C9	0.014	0.026	0.032	0.041	0.051
Decanoic	C10	0.0095	0.015	0.018	0.023	0.027
Undecanoic	C11	0.0063	0.0093	0.011	0.013	0.015
Dodecanoic	C12	0.0037	0.0055	0.0063	0.0075	0.0087
Tridecanoic	C13	0.0021	0.0033	0.0038	0.0044	0.0054
Tetradecanoic	C14	0.0013	0.0020	0.0024	0.0029	0.0034
Pentadecanoic	C15	0.00076	0.0012	0.0014	0.0017	0.0020
Hexadecanoic	C16	0.00046	0.00072	0.00083	0.0010	0.0012
Heptadecanoic	C17	0.00028	0.00042	0.00055	0.00069	0.00081
Octadecanoic	C18	0.00018	0.00029	0.00034	0.00042	0.0005

Table 2. R_F and R_M values obtained using RP-HPTLC

Acid symbol	Mobile phase: methanol–water				Mobile phase: ethanol–water			
	90 : 10, v/v		95 : 5, v/v		90 : 10, v/v		95 : 5, v/v	
	R_F	R_M	R_F	R_M	R_F	R_M	R_F	R_M
RP-18 plates without concentrating zone								
C8	0.653	−0.274	0.732	−0.436	0.760	−0.500	0.780	−0.550
C9	0.560	−0.105	0.671	−0.310	0.707	−0.382	0.756	−0.491
C10	0.533	−0.057	0.610	−0.194	0.653	−0.274	0.707	−0.382
C11	0.387	0.200	0.536	−0.063	0.600	−0.176	0.671	−0.310
C12	0.360	0.250	0.463	0.064	0.520	−0.035	0.609	−0.194
C13	0.253	0.470	0.390	0.194	0.480	0.035	0.561	−0.106
C14	0.187	0.638	0.305	0.358	0.413	0.153	0.512	−0.021
C15	0.160	0.720	0.244	0.491	0.347	0.274	0.463	0.064
C16	0.120	0.865	0.183	0.650	0.267	0.438	0.402	0.172
C17	0.093	0.989	0.122	0.857	0.227	0.532	0.366	0.239
C18	0.080	1.061	0.098	0.964	0.200	0.602	0.305	0.358
RP-18 plates with concentrating zone								
C8	0.628	−0.227	0.686	−0.339	0.743	−0.461	0.900	−0.954
C9	0.571	−0.124	0.657	−0.282	0.686	−0.339	0.886	−0.890
C10	0.500	0.000	0.586	−0.151	0.628	−0.227	0.843	−0.730
C11	0.414	0.151	0.528	−0.049	0.571	−0.124	0.800	−0.602
C12	0.343	0.282	0.457	0.075	0.514	−0.024	0.743	−0.461
C13	0.271	0.430	0.400	0.176	0.457	0.075	0.686	−0.339
C14	0.214	0.565	0.328	0.311	0.386	0.202	0.628	−0.227
C15	0.143	0.778	0.257	0.461	0.328	0.311	0.557	−0.099
C16	0.100	0.954	0.186	0.641	0.271	0.430	0.500	0.000
C17	0.057	1.219	0.128	0.833	0.214	0.565	0.428	0.126
C18	0.028	1.540	0.086	1.026	0.143	0.778	0.371	0.229

describing the relationships between solubilities of acids from octanoic to octadecanoic in water, at different temperatures and values of R_M parameters obtained during separations on RP-18 plates without and with a concentrating zone, using methanol-water and ethanol-water (90 : 10 and 95 : 5, v/v) as mobile phases. From data presented, there arises the concept that R_F values decrease in all cases with increasing of length of hydrocarbon chain of the acid, as well as with increasing water contents in mobile phase alcohol-water. The relationships between solubilities of fatty acids in water, at different temperatures, and R_M values obtained by RP-HPTLC, are described by polynomials of third degree or exponential functions. All described relationships are characterized by high values of determination coefficients, which are in the range of 96.65 ÷ 99.97%. The acids from octanoic to octadecanoic or from nonanoic to octadecanoic were taken into consideration in these relationships in order to obtain the highest values of determination coefficients.

Table 3. Selected regression equations that can be used to calculate the solubility of fatty acids in water in different temperatures

Chromatographic conditions	Temperature (°C)	Range of acids investigated	Regression equation	n	R^2 (%)	s	F	Equation number
RP-18 plates with concentrating zone, mobile phase: ethanol-water (95 : 5, v/v)	0	C9 ÷ C18	$s = -0.0076\ (\pm 0.0016)\ R_M^3 + 0.0084\ (\pm 0.0016)\ R_M^2 - 0.0020\ (\pm 0.0004)\ R_M + 0.0004\ (\pm 0.0001)$	10	99.91	0.00017	3089	2
RP-18 plates without concentrating zone, mobile phase: ethanol-water (95 : 5, v/v)	20	C9 ÷ C18	$s = 0.0185\ (\pm 0.0001) e^{-5.3874(\pm 0.0958) R_M}$	10	99.90	0.00028	6585	3
RP-18 plates with concentrating zone, mobile phase: methanol -water (95 : 5, v/v)	30	C9 ÷ C18	$s = -0.0463\ (\pm 0.0062)\ R_M^3 + 0.0854\ (\pm 0.0071)\ R_M^2 - 0.0484\ (\pm 0.0019)\ R_M + 0.0095\ (\pm 0.0005)$	10	99.29	0.00106	342	4
RP-18 plates without concentrating zone, mobile phase: ethanol-water (90 : 10, v/v)	45	C8 ÷ C18	$s = 0.0039\ (\pm 0.0004) e^{-6.3558(\pm 0.2167) R_M}$	11	99.68	0.00171	1951	5
RP-18 plates with concentrating zone, mobile phase: etanol-water (95 : 5, v/v)	60	C9 ÷ C18	$s = 0.00013\ (\pm 0.00004) e^{-4.1199(\pm 0.0409) R_M}$	10	99.97	0.00030	20273	6

$p \leq 0.001$.

Table 4. Regression equation that can be used to predict the solubility of fatty acids in water in different temperatures as well as experimental and predicted solubility values

Chromatographic conditions	Omitted acid	Regression equation	n	R^2 (%)	s	F	Equation number	Experimental value	Predicted value
RP-18 plates without concentrating zone, mobile phase: ethanol-water (95 : 5, v/v)	C14	$s = 0.0019\ (\pm 0.0001)e^{-5.3792(\pm 0.1066)R_M}$	9	99.90	0.00030	5797	7	0.0020 g/ 100 g H_2O in temperature 20 °C	0.0021 g/ 100 g H_2O
RP-18 plates with concentrating zone, mobile phase: methanol- water (95 : 5, v/v)	C12	$s = -0.0462\ (\pm\ 0.0073)R_M^3 + 0.0852(\pm 0.0085)\ R_M^2 - 0.0484\ (\pm 0.0021)\ R_M + 0.0095\ (\pm 0.0007)$	9	99.29	0.00116	277	8	0.0063 g/ 100 g H_2O in temperature 30°C	0.0063 g/ 100 g H_2O
RP-18 plates with concentrating zone, mobile phase: ethanol-water (95 : 5, v/v)	C12	$s = 0.0078\ (\pm 0.0003)e^{-5.5220(\pm 0.1182)R_M}$	9	99.91	0.00032	5911	9	0.0087 g/ 100 g H_2O in temperature 60°C	0.0089 g/ 100 g H_2O

$p \leq 0{,}001$

For example, some regression equations that can be used to calculate values of solubilities of fatty acids (Equations (2)–(6) are presented in Table 3. Using the regression equations' described relationships studied, the values of solubility in water of investigated fatty acids can be calculated on the basis of known R_M values obtained by RP-HPTLC.

Many chemists are interested in the problems of prediction of values of physicochemical properties.[14,15] Some of the works are devoted to the prediction of values of physicochemical properties of organic compounds on the basis of known R_M values. In such a way, the relationships between values of R_M parameter and logP values of polycyclic hydrocarbons,[16] as well as long-chain fatty acids, hydroxy acids, and their esters[17] were analyzed. It was stated that, on the basis of those relationships, the value of partition coefficients of investigated compounds can be predicted. Values of molar volumes of homologous series of saturated fatty acids were calculated and predicted on the basis of known values of R_M parameters, as well.[7]

In this work, an attempt was made to predict the values of solubility in water, at different temperatures, of fatty acids from octanoic to octadecanoic, on the basis of known values of R_M parameters obtained by RP-HPTLC. For this purpose, new regression equations were determined by omitting the solubility value of one of the acids in selected regression equations. On the basis of the new equations, the solubility values of the omitted acids can be predicted. Regression equations obtained from Equations (3), (4), and (6), in which one of acids was omitted (Equations (7)–(9)), as well as experimental and predicted values of solubilities of omitted acids, are presented in Table 4.

As a result of the calculations carried out, we can state that the new regression equations can serve to predict the values of solubility in water of fatty acids from octanoic to octadecanoic. This shows the similar experimental and predicted values of solubility in water of fatty acids (Table 4).

CONCLUSIONS

Regression equations describing relationships between solubilities of fatty acids in water at different temperatures, and R_M values obtained by RP-HPTLC are characterized by high values of determination coefficients, which are in the range of 96.65 ÷ 99.97%. It was shown that these equations can serve, both to calculate, and predict the values of solubilities in water of investigated fatty acids.

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