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Potentiometric Titrations of Semicarbazone Derivatives 6-Keto 9-17 Mono Methyl Substituted Octadecanoic Acids in Non-Aqueous Media

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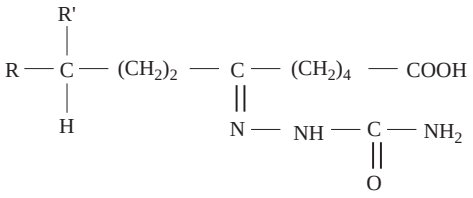
The pK_a values of 6-semicarbazone 9-17 monomethyl substituted octadecanoic acids were determined using the potentiometric titration method. 2-Propanol was used as the non-aqueous medium and tetrabutylammonium hydroxide (TBAH) as the titrant in the experiments. The contribution of semicarbazone and methyl groups to the pK_a values of octadecanoic acids was investigated and evaluated. In addition, observations were made on the IR spectra of the compounds.

Introduction

The determination of the pK_a values of organic compounds with acidity constants less than 10^{-8} can only be realised in non-aqueous media. Although water has excellent solvent properties, it is not suitable for such organic compounds since the pH jump at the equivalence point in aqueous solution cannot be evaluated with reasonable accuracy, with the result that the end point cannot be found. Moreover, most of these compounds are not soluble in water[1,2,3]. For these reasons, titration in non-aqueous media has recently acquired great importance. It is now well known that non-aqueous titrations greatly depend on the solvents used[4,5].

Since the use of fatty acids and their derivatives in drugs, detergents, cosmetics and textile auxiliaries has increased, their biochemical effectiveness and thus the determination of their acidic constants has become very important[6,7,8]. Nine different 6-keto 9-17 monomethyl substituted octadecanoic acids were synthesized[9]. The general formula of these products is shown in Figure 1.



R: Alkyl, R': methyl (R' contains 9 to 17 carbon atoms)

Figure 1. General formula of the 6-Semicarbazone 9-17 monomethyl substituted octadecanoic acids.

The potentiometric titrations of these compounds with weak-acidic properties were obtained with 0.05 M tetrabutyl ammonium hydroxide (TBAH) in 2-propanol and the pK_a values were determined in non-aqueous media.

Experimental

Reagents and Apparatus

All the reagents used in the preparation of the fatty acids and potentiometric titrations were of analytical grade. BDH TBAH (Fluka) and isopropanol (Fluka) were used. IR spectra were performed with a UNICAM-MATTSON series 1000 FTIR spectrometer. Melting points were determined using a Gallenkamp melting-point apparatus. Potentiometric titrations were carried out using a Metrohm E 349A automatic titrator equipped with a Jenway 3040 ion-analyser pH meter.

Materials and Methods

The organic compounds used in this study were prepared according to the method of Cason[10]. Some properties and characteristic IR bands of these compounds are listed in Table 1. 10^{-3} M Solutions in 2-propanol from these 6-semicarbazone 9-17 monomethyl substituted octadecanoic acids were prepared for potentiometric titration. 0.05 M Tetrabutyl ammonium hydroxide in 2-propanol was used as the titrant, and by keeping the volume of the analyte solution high, errors brought about by any changes in concentration caused by the addition of the titrant were minimized.

For the determination of pK_a values in non-aqueous media, the potentiometric titration method was chosen and the titration curves were analysed using the method proposed by Calvin-Wilson[11,12].

All the potentiometric titrations were carried out at room temperature using an automatic titrator equipped with a pH meter, a magnetic stirrer and a micro burette. After each reading of the steady-state pH and mV values, the titrations were carried out with increments of 0.05 mL 0.05 M TBAH solution. In the experiments, generally 1.20-1.50 mL of TBAH solution and 17 mL of analyte were used. In order to obtain a good steady-state reading around the inflection point of the titration curves, further time was given for the system to stabilize.

mV and pH values were plotted against the titrant volumes (mL) added, and S-shaped titration curves were obtained. From these curves, the inflection points and half-neutralisation potentials were determined and the corresponding pK_a values were calculated. Due to the stability of the compounds used in this study, was not considered necessary to carry out the experiments in an inert atmosphere.

The preparation of semicarbazone derivatives of 5-keto 9-17-monomethyl octadecanoic acids.

0.1 g Semicarbazide hydrochloride was dissolved in a solution of 1.5 g sodium acetate in 10 mL distilled water. First, 0.1 g keto fatty acid was added and later methanol was given to the reaction mixture until no turbidity is remained. It was heated slightly by stirring on a steam bath. The mixture was cooled and filtered. The crude product was purified by recrystallization from methanol and was dried over phosphore pentaoxide in a vacuum dessicator.

Results and Discussions

The melting points, elemental analysis and IR spectra of the synthesized compounds are shown in Table 1 and Table 2. As an example, only the IR spectra of 6-keto-17-methyl octadecanoic acid and 6-semicarbazone-

17-methyl octadecanoic acid are given in Figure 2.

Table 1. The melting points and elemental analysis of 6-semicarbazone 9-17 monomethyl substituted octadecanoic acids.

Compound	m.p.	Elemental Analysis, %(w/w)					
		C		H		N	
	(°C)	Found	Calcd.	Found	Calcd.	Found	Calcd.
9-Methyl-	99.5	65.35	65.04	10.35	10.57	11.26	11.37
10-Methyl-	104.0	65.41	65.04	10.37	10.57	11.31	11.37
11-Methyl-	120.0	64.95	65.04	10.09	10.57	11.31	11.37
12-Methyl-	127.0	64.98	65.04	10.71	10.57	11.33	11.37
13-Methyl-	121.0	65.48	65.04	10.85	10.57	11.46	11.37
14-Methyl-	108.5	65.09	65.04	11.02	10.57	11.53	11.37
15-Methyl-	112.0	65.70	65.04	10.90	10.57	11.44	11.37
16-Methyl-	106.0	65.78	65.04	10.87	10.57	11.50	11.37
17-Methyl-	124.5	65.12	65.04	10.65	10.57	11.40	11.37

Table 2. IR bands of 6-semicarbazone 9-17 monomethyl substituted octadecanoic acids, (in KBr pellets) in cm^{-1}.

Compound	ν(OH)	ν(COOH)	ν(C-O-H)	$\nu(CH_3)$	ν(C-O)	ν(N-CO-N)	$\delta(NH_2)$	$\nu(NH_2)$	δ(OH)
9-Methyl-	2923	1708	1469	1377	1223	1115	1492-1469	3261-3192	961
10-Methyl-	2923	1708	1469	1354	1254	1115	1492-1469	3254-3192	954
11-Methyl-	2923	1708	1477	1377	1254	1115	1492-1476	3261-3200	961
12-Methyl-	2923	1715	1500	1354	1254	1115	1500-1476	3254-3192	961
13-Methyl-	2923	1708	1500	1377	1254	1115	1500-1476	3254-3200	969
14-Methyl-	2923	1708	1500	1377	1254	1115	1500-1469	3254-3192	961
15-Methyl-	2931	1708	1469	1377	1262	1108	1500-1469	3261-3192	969
16-Methyl-	2923	1715	1469	1377	1254	1115	1500-1469	3261-3192	969
17-Methyl-	2923	17158	1469	1354	1254	1115	1500-1469	3253-3192	961

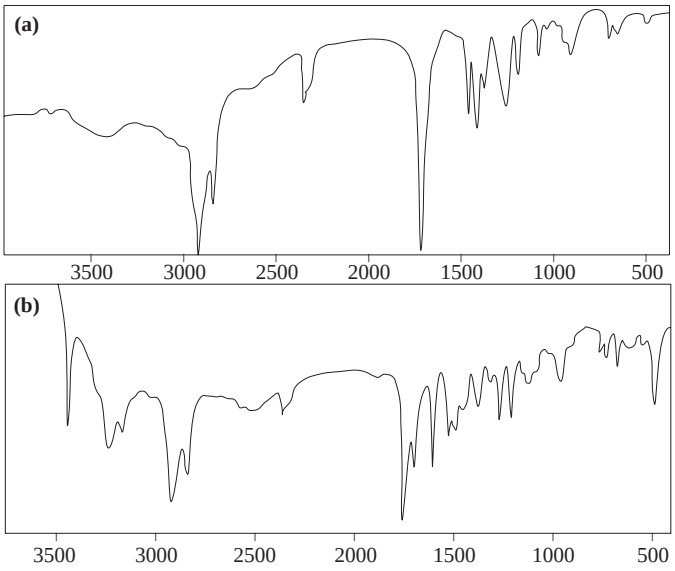


Figure 2. The spectra of 6-keto-17-methyl octadecanoic acid (a) and 6-semicarbazone-17-methyl octadecanoic acid (b) (in KBr pellets as cm^{-1}).

It can be seen that the replacement of the semicarbazone groups with keto groups causes peaks in (-NH), ($-NH_2$), (-N-CO-N-). Therefore, the peaks of other functional groups may appear at higher frequencies than they were with keto octadecanoic acids. The major characteristic peaks of these groups are at the wavenumbers -COOH (1708-1715 cm^{-1}), -OH (2923-2931 cm^{-1}), $-NH_2$ ν(3192-3253 cm^{-1}), δ(1469-1500 cm^{-1}), -NH ν(3477 cm^{-1}), (-N-CO-N-) ν(1108-1115 cm^{-1}). Thus, the spectra obtained in this study coincide with the FT-IR spectra described in the literature for similar compounds[13,14].

The potentiometric titration curves of the compounds (mV versus mL TBAH) in 2-propanol are shown in Figures 3-5. mV and mL TBAH values corresponding to the equivalence point were found from the curves. The pH value corresponding to the half-neutralization was considered to be the pK_a of the compounds.

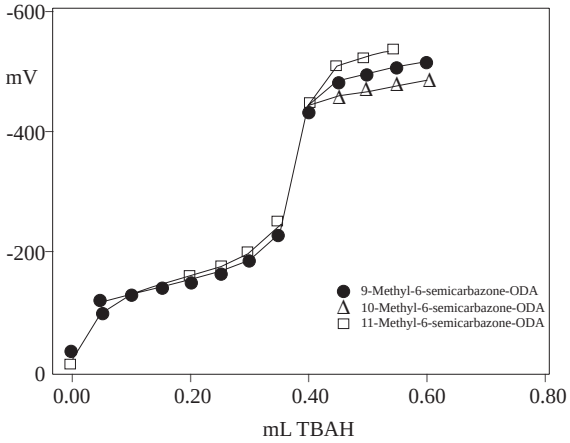


Figure 3. Potentiometric titration curves of 6-semicarbazone 9-11 monomethyl substituted octadecanoic acids with 0.05 M solution TBAH.

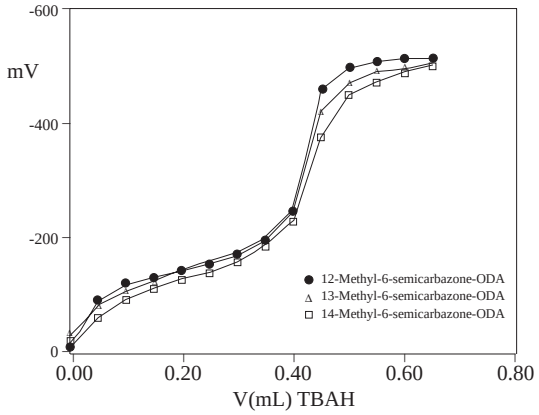


Figure 4. Potentiometric titration curves of 6-semicarbazone 12-14 monomethyl substituted octadecanoic acids with 0.05 M solution TBAH.

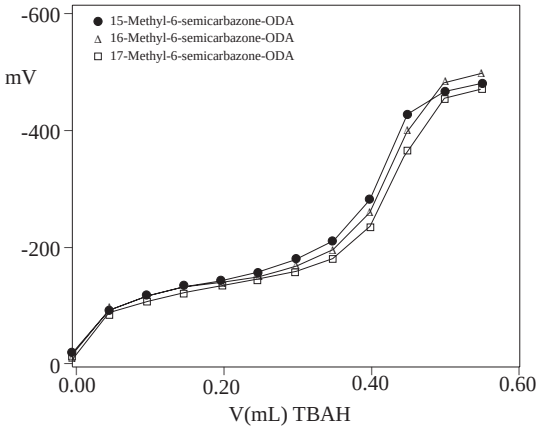


Figure 5. Potentiometric titration curves of 6-semicarbazone 15-17 monomethyl substituted octadecanoic acids with 0.05 M solution TBAH.

The pK_a values calculated in this manner for all the compounds are shown in Table 3.

Due to the inductive effects of electrophile substituent in the carboxylic acids with a high carbon content acidic strength increases. In contrast, in the presence of nucleophylic substituents, acidic strength decreases[15].

Table 3. Calculated pK_a values for 6-semicarbazone 9-17 monomethyl substituted octadecanoic acids.

Compound	pK_a	(pK_a values for corresponding 6-keto derivatives[13])
9-Methyl-6-semicarbazone-ODA	9.51	(9.56)
10-Methyl-6-semicarbazone-ODA	9.53	(9.72)
11-Methyl-6-semicarbazone-ODA	9.59	(10.09)
12-Methyl-6-semicarbazone-ODA	9.51	(9.86)
13-Methyl-6-semicarbazone-ODA	9.49	(10.08)
14-Methyl-6-semicarbazone-ODA	9.48	(10.24)
15-Methyl-6-semicarbazone-ODA	9.50	(10.74)
16-Methyl-6-semicarbazone-ODA	9.51	(11.61)
17-Methyl-6-semicarbazone-ODA	9.49	(9.97)

The pK_a values of nine different 6-semicarbazone 9-17 monomethyl substituted octadecanoic acids were determined. The pK_a values were found to be between 9.49 and 9.59. These results confirm the statement above and demonstrate that the compounds have very weak acidic properties.

The existence of highly electronegative nitrogen and oxygen atoms in the semicarbazone group, which replaced the keto groups, causes neighbouring carbon atoms to become more electropositive. However, the nucleophylic character of the methyl substituents decreases the acidic properties. Consequently, the acidic properties of the semicarbazone group are decreased by the effects of the nucleophylic groups. The pK_a values of 6-semicarbazone 9-17 monomethyl substituted octadecanoic acids are lower than those of 6-keto 9-17 monomethyl octadecanoic acids (Table 3).

Studies of the other derivatives of octadecanoic acids are continuing. Results will be reported in further publications.

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