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BRIEF COMMUNICATIONS

Dissociation Constants of Polyfluorocarboxylic Acids

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Abstract—The effect of the structure and molecular weight of fluorocarboxylic acids on their dissociation constants in acetonitrile and its mixtures with water and methanol was studied.

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It is known that, owing to the strong electron-acceptor properties of the trifluoromethyl radical, trifluoroacetic acid has a dissociation constant of 5.9×10^{-1} in water [1] and virtually does not differ from strong acids, such as hydrochloric acid. Its homologues, perfluorocarboxylic acids, are also rather strong acids. As, however, the length of the carbon chain increases, micelle formation leads to a decrease in the degree of ionization [2].

Electrochemical syntheses with anodic dimerization and cross-anodic combination of various fluorocarboxylic acids in acetonitrile mixed with water and methanol are of practical importance for preparation of new organofluoric compounds possessing various useful properties [3]. The specific role played by acetonitrile in electrolytic media, which primarily determines the efficiency of these processes, makes necessary a study of the electrochemical characteristics of fluorinated carboxylic acids in its mixtures with protonating electrolytes in order to choose the electrolysis conditions and prognosticate the results of electrosyntheses.

EXPERIMENTAL

The dissociation constants of fluorocarboxylic acids were determined by potentiometric titration [4] with a pH-673M millivoltmeter, using a glass working electrode and the standard calomel electrode. The solutions were agitated with a magnetic stirrer.

The dissociation constants of the acids were measured in individual solvents (acetonitrile, water, and methanol) and in their mixtures with relative solvent concentrations commonly used in electrochemical syntheses [3].

Depending on a medium, the following solutions were used as titrants: 0.1 M KOH for acetonitrile, 0.1M aqueous solution of NaOH for water and its mixtures with acetonitrile, and 0.1 M solution of sodium methylate in methanol for methanol and its mixture with acetonitrile.

The solvents were purified by the known procedures [5].

Titration was applied to 0.2 M solutions of the following polyfluorocarboxylic acids of reagent grade or those synthesized and purified by rectification: CF_3CF_2COOH (**I**) pentafluoropropionic acid; $CF_2ClCFClCOOH$ (**II**) 1,2-dichloroperfluoropropionic acid prepared by the method [6]; $CF_3CF_2CF_2COOH$ (**III**) heptafluoromaleic acid; $CF_3CF_2CF_2OCF(CF_3)$-COOH (**IV**) perfluoro-3-oxo-2-methylhexanoic acid; $CF_3OCF_2CF_2CF_2OCF(CF_3)COOH$ (**V**) perfluoro-3,7-dioxo-2-methyloctanoic acid [prepared by condensation of $CF_3OCF_2CF_2COF$ with hexafluoropropene oxide and subsequent hydrolysis of acylfluoride $CF_3OCF_2CF_2CF_2OCF(CF_3)COF$]; $CF_3CF_2CF_2OCF$-$(CF_3)CF_2OCF(CF_3)C$ OOH (**VI**) perfluoro-3,6-dioxo-2,5-dimethylnonanoic acid; $F(CF_2CF_2O)CF_2COOH$ (**VII**) perfluoro-3,6,9,12-tetraoxotetradecenoic acid prepared by hydrolysis of the tetrafluoroethene oxide pentamer.

The equivalence point pH_{eq} was determined by differentiating the titration curve. The determination accuracy was ±2%.

The negative logarithm of the dissociation constant, pK_{HA}, was calculated by the equation [4]:

$$pK_{HA} = 2pH_{eq} - pK_{H_2O} + \log c_{HA} = 2pH_{eq} - 13.3010.$$

Calculated dissociation constants of polyfluorocarboxylic acids in various solvents

Acid	$K_{HA} \times 10^2$							
	CH_3CN	H_2O	CH_3OH	$CH_3CN–H_2O$, vol % CH_3CN				$CH_3CN–CH_3OH$, 10 vol % CH_3CN
				90	50	40	30	
CF_3CF_2COOH (**I**)	3.66	2.50	1.58	3.55	–	–	–	1.12
$CF_2ClCFClCOOH$ (**II**)	3.12	3.98	1.26	3.16	–	–	–	1.07
$CF_3CF_2CF_2COOH$ (**III**)	1.80	1.58	–	1.25	–	–	–	–
 $CF_3CF_2CF_2O\underset{CF_3}{C}FCOOH$ (**IV**)	1.30	–	1.40	1.26	–	1.12	–	0.65
 $CF_3OCF_2CF_2CF_2O\underset{CF_3}{C}FCOOH$ (**V**)	1.17	–	0.85	1.20	–	–	1.25	0.93
 $CF_3(CF_2)_2O\underset{CF_3}{C}FCF_2O\underset{CF_3}{C}FCOOH$ (**VI**)	2.75	–	0.68	2.45	0.70	–	–	0.41
$F(CF_2CF_2O)CF_2COOH$ (**VII**)	0.88	–	–	0.79	0.45	–	–	–
$CH_3CH_2CH_2COOH$*	0.80	1.58	1.25	–	–	–	0.01	

* $K_{HA} \times 10^5$.

For comparison, the dissociation constant of normal maleic acid was determined and found to coincide with the published value [7].

Table lists the dissociation constants of the acids studied, calculated from the experimental data.

It follows from the experimental data that, in the systems studied, the dissociation constants of fluorocarboxylic acids are lower by at least an order of magnitude than the dissociation constant of trifluoroacetic acid. Therefore, they cannot be classed with strong acids. This conclusion is supported by the data of [8], according to which the K_{HA} values on the order of 10^{-2} are reported for perfluoromaleic and perfluorocaprylic acids in water. However, unsubstituted *N*-maleic acid has, similarly to most of hydrocarbon carboxylic acids [7], K_{HA} higher by three orders of magnitude (1.58×10^{-5}).

It is noteworthy that the dissociation constants of perfluorocarboxylic acids with different molecular weights and chain structures differing in substituents, oxygen heteroatoms, and pendant trifluoromethyl moieties are close in order of magnitude in water and acetonitrile. In the latter case, pentafluoropropionic acid is even stronger, as regards K_{HA}, in acetonitrile as compared with water.

The dielectric constant of a medium, to which the dissociation of a polarized O–H bond in carboxylic acid is related, is considerably higher for water, compared with acetonitrile. However, the dipole moment of the acetonitrile molecule is twice that of water and methanol [9]. Apparently, it is because of this circumstance that its capacity for solvation of fluorocarboxylic acid exceeds that of water and methanol. Presumably, the solvation-induced polarization of the O–H bond in carboxylic acid facilitates the dissociation by making the difference in their dielectric constants less pronounced.

Just this circumstance provides solvation of the carboxylate anion of fluorocarboxylic acid with acetonitrile in mixtures with water and methanol, despite the hydrophobic nature of its fluoroalkyl radical. Probably, this is a manifestation of the specific role played by acetonitrile in the reactions of anodic condensation. It is the presence of acetonitrile in an electrolyte that provides synthesis of fluoroalkyl dimers [3] in high yield because of the displacement of water and methanol from the double layer via adsorption on the anode of carboxylate anions solvated by acetonitrile.

Presumably, the dependence of the dissociation constant on the molecular weight and structure of fluorocarboxylic acids could not be observed because of the possibility of micelle formation, which creates a heterophase colloid system even at a concentration of 0.25 M. The influence of oxygen heteroatoms, which make lower the rotation barrier of the fluoroalkyl chain and create a certain steric hindrance to pendant trifluoromethyl groups, also gives no way of observing this dependence.

CONCLUSIONS

(1) It was shown that the dissociation constants of fluorocarboxylic acids are lower by at least an order of magnitude than the dissociation constant of trifluoroacetic acid. Therefore, the above compounds cannot be classed with strong acids.

(2) In water and acetonitrile, the dissociation constants of fluorocarboxylic acids of various structures and molecular weights differ only slightly, although their dielectric constants are strongly different.

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