

Determination of Acidity Constants of Perfluoroalkanoic Acids

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Acidity constants (K_a) of perfluoroalkanoic acids were determined by pH titration and by electric conductivity for shorter alkanolic acids (C1 to C5) with 1 to 5 carbon atoms in the alkyl chain. The acidity constants obtained by the two methods are in good agreement. They increase from C1 (ethanoic) to C3 (butanoic acid) and then decrease from C3 to C5 (hexanoic acid) with increasing alkyl chain length. An abrupt decrease in the K_a value for the C5 acid occurred; the attempt to explain this in terms of viscosity of the solutions did not succeed. The decrease in the K_a values with increasing alkyl chain length was substantiated by the values for C9 (decanoic) to C11 (dodecanoic) acids, which were determined from the solubility change with the solution pH. For the intermediate alkanolic acids (C6 to C8), the K_a values could not be determined precisely by these methods due to the extreme difficulty in separating the colloidal acid particles from the aqueous phase, because the particles have an emulsifying action of their own.

Fluorocarbon substances are quite different in physicochemical properties from their hydrocarbon analogues. Many kinds of researches have been made to exploit the properties of fluorocarbons and to access their interesting functions.¹ For example, fluorinated surfactants are more surface active than their corresponding hydrogenated surfactants in such respects as critical micelle concentration and interfacial tension. Thus, their solution properties have long been a matter of interest from several practical viewpoints. Many colloid chemists have been studying the micellar properties of both pure and mixed surfactants,^{2–10} predominantly the perfluoroalkanoic acids and their corresponding alkali metal salts. In these studies, the acids have been assumed to dissociate completely due to their strong acidity. Indeed, trifluoroacetic acid is a strong acid, with the reported acidity constant of 0.53–0.59 at 25 °C, although the value is almost twice as large as those obtained in this study. Therefore, the acid is not completely dissociated,¹¹ which was made clear a half century ago.¹² Since then, no one has tried to determine any acidity constant of longer alkyl chain homologues, although pK_a values in 50% aqueous ethanol are available.¹³ In other words, the acidity constants of longer chain perfluorinated acids have not been determined yet. Nevertheless, many investigators have employed the above value, assuming their complete dissociation below the cmc in aqueous solution.

The aim of this paper is, therefore, to determine accurately the acidity constants of perfluoro-1-alkanoic acids whose alkyl chain length ranges from 1 to 11 carbons. The methods used are acid–base titration, electric conductivity, and solubility change with pH.

Experimental

Chemicals. The perfluorinated acids are all obtained from Daikin Chemical Co. Ltd. They were purified by the following two methods, depending on perfluoroalkyl chain length. The low

molecular weight perfluorinated acids (C1 to C5) were purified by distillation, since they had a correspondingly higher vapor pressure. The purity was checked by elemental analysis. The analysis was not satisfactory due to the difficulties originating in their volatility and the presence of fluorine atoms in the chemical composition. Then, the purity was checked by NMR spectroscopy on the liquid samples with a JEOL Lambda-400 p-FT NMR spectrometer. The NMR peaks indicated a purity of more than 99%.

The higher molecular weight homologues (C9 to C11) were purified by repeated recrystallizations from aqueous solution. A solid suspension of the acid in water was solubilized by adding an excess of LiOH solution. Insoluble materials and dust were removed by filtration. The acid was reprecipitated from the solution by adding an excess amount of HCl solution. Finally, the acid crystals were washed by a large amount of water to remove the residual HCl. The above procedure was repeated at least three times, and then the purified acid in solid state was dried in a desiccator under reduced pressure over P_2O_5 . In the above procedure, the C9 and C10 acids became gelatinous and filtration was quite difficult. This is due to formation of a liquid crystalline phase by fluorinated acid and water.¹¹ In this case, the acid was separated out by centrifugation. The aqueous solubility of these C9–C11 acids is too low for the NMR technique to be used for the purity check. Elemental analysis was employed for the purity check only by the weight percentage of carbon atoms, in spite of the difficulties mentioned above. The observed and calculated values (in parentheses) were in satisfactory agreement; $C_9F_{19}COOH$ 23.05 (23.34), $C_{10}F_{21}COOH$ 23.14 (23.40), $C_{11}F_{23}COOH$ 23.19 (23.45)%. In spite of the satisfactory agreement between the two, the purity cannot be assessed only by the elemental analysis. This is because the differences in the numerical values among the three are within error limits of elemental analysis. The above purification procedure has led to satisfactory cmc values in the previous studies,^{10,14,15} so the materials should be considered highly purified. This point will be discussed later. The water used was distilled twice from alkaline permanganate solution, with a final specific conductivity of less than 10^{-6} S cm^{-1} .

Titration. The pH was measured with a pH meter (TOA Electronics Ltd., HM-60V) equipped with an electrode of type GST-5421C. The electrode was standardized at three different pHs of 1.680, 4.010, and 6.860 at (298.15 ± 0.01) K. The pH electrode demonstrated a good linearity between electric potential and pH values from 1 to 13. The meter display shows three decimal points. A 15 mL acid solution of known concentration was neutralized stepwise by introducing aliquots of a standardized NaOH solution. The titration was carried out under an inert atmosphere in order to protect it from atmospheric CO_2 .

Conductivity. A glass tube containing 15 mL of purified water for conductivity measurement was set in a thermostat at (298.15 ± 0.01) K. The concentration of the acid or its lithium salt solution was increased stepwise by introducing aliquots of stock solution of the acid or salt to the water. The conductivity of the solution was measured after each introduction. During this operation too, the solution was isolated from atmospheric CO_2 . The lithium salt solution used was the end-point solution neutralized by LiOH.

Solubility Change with pH. An experimental procedure similar to that used for the titration was adopted at (298.15 ± 0.01) K, where an acid phase coexisted with aqueous solution. In this case, however, the concentration of the saturated acid solution was first determined as follows. After reaching the solubility equilibrium, the solution pH was measured and the solid acid phase was separated out by centrifugation. The supernatant solution was further filtrated through a filter of 0.23 μm pore size (Millipore FGLP01300) in order to remove unsettled acid particles at 298 K. The acid concentration of the filtrate was determined by titration using a standardized LiOH solution. This step is necessary for the determination of the first point of the total acid concentration vs $1/a_{\text{H}^+} \gamma_{\pm}$ plots. The second step involves titration of the acid by LiOH solution and measurements of the solution pH after equilibration and settlement of dispersed acid particles after each titration.

Solution Viscosity. The viscosity for each of the acid solutions was examined at (298.15 ± 0.01) K, because the equivalent conductivity of ionic species is controlled by the viscosity of the medium through their mobility. At the same time, the equivalent conductivity is directly related with the specific conductivity. The solution was filtered through a Millipore filter prior to measurement. An Ubbelohde viscometer was used for the measurement, where purified water was used to calibrate the viscosity (0.8903 mP at 298.15K).¹⁶ The flow rate was repeatedly measured until it became constant within 0.1 second (88.6 seconds for water).

Analytical Procedures

Titration. The dissociation of monobasic acid (AH) is expressed as



where AH, A^- , and K_a are undissociated acid, dissociated anion, and the dissociation constant or the acidity constant, respectively. The dissociation constant is defined by the following equation:

$$K_a = \frac{[\text{A}^-] \gamma_{\pm} a_{\text{H}^+}}{[\text{AH}]}, \quad (2)$$

where brackets, a , and γ_{\pm} are the corresponding concentration, activity, and activity coefficient, respectively, and the activity

coefficient of AH is assumed to be 1 due to the extremely low concentration. When acid is titrated with sodium hydroxide, the following electroneutrality condition holds for the titration solution:

$$[\text{H}^+] + [\text{Na}^+] = [\text{A}^-] + [\text{OH}^-]. \quad (3)$$

Within the present pH range of the solution, 1–3, $[\text{OH}^-]$ is much smaller than $[\text{H}^+]$ and can be neglected in Eq. 3. As the first approximation, the activity coefficients are set to be 1. Thus, $[\text{H}^+] = 10^{-\text{pH}}$, and $[\text{Na}^+]$ is evaluated from the amount of added NaOH solution. Then, the ionic strength I is the sum of $[\text{H}^+]$ and $[\text{Na}^+]$ due to Eq. 3, and the activity coefficient can be evaluated from the following Debye–Hückel equation:

$$\log \gamma_{\pm} = -\frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}}, \quad (4)$$

where the radius of ions is assumed to be 0.45 nm. A more accurate $[\text{H}^+]$ is recalculated from the a_{H^+} and γ_{\pm} values as $a_{\text{H}^+}/\gamma_{\pm}$ using the improved ionic strength. This procedure is iterated until $[\text{H}^+]$ becomes constant, improving the reliability in $[\text{H}^+]$, $[\text{Na}^+]$, and $[\text{A}^-]$ as well as the activity coefficient. The total acid concentration (C_t) is given by

$$C_t = [\text{AH}] + [\text{A}^-]. \quad (5)$$

The C_t concentration can be determined from the neutrality end-point of the titration curve, and the final requisite concentration $[\text{AH}]$ for Eq. 2 can thus be determined from Eq. 5.

Electric Conductivity. For a strong acid that completely dissociates at finite concentration, the limiting equivalent conductivity ($\lambda_0(\text{acid})$) can be determined by 1) plotting the equivalent conductivity (λ) against the square root of the concentration and 2) subsequent extrapolation of the plots to the concentration zero. For the acids in this study, the above condition is not guaranteed. Therefore, the following procedure is taken to obtain the $\lambda_0(\text{acid})$ value:

$$\lambda_0(\text{acid}) = \lambda_0(\text{Li salt}) + \lambda_0(\text{H}^+) - \lambda_0(\text{Li}^+). \quad (6)$$

It is quite important for the present conductivity method to determine the λ_0 values in Eq. 6 with the conductivity cell used. This is because several values of $\lambda_0(\text{H}^+)$ are available from the literature; 349.93,¹⁷ 347.2,¹⁸ 349.8,¹⁹ and 349.65 $\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$ ²⁰ and because the value used becomes a crucial parameter for K_a determination. In this study, therefore, $\lambda_0(\text{Li salt})$ was obtained by the cell as the limiting equivalent conductivity of the Li salt, while both $\lambda_0(\text{H}^+)$ and $\lambda_0(\text{Li}^+)$ values were evaluated from solutions of HCl and LiCl, respectively. The reference value of 76.35 $\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$ was used for $\lambda_0(\text{Cl}^-)$ at 298.15 K. If the degree of dissociation of acid is α in Eq. 1, the dissociation constant or the acidity constant becomes

$$K_a = \frac{C_t \alpha^2 \gamma_{\pm}^2}{1 - \alpha} \quad (7)$$

where C_t is the total concentration of the acid and α is defined as $\alpha = \lambda/\lambda_0$. The activity coefficient was evaluated by the above the Debye–Hückel equation, where the ionic strength was set equal to $C_t \alpha$.

Solubility Change with pH. When a solid acid phase coexists with the aqueous phase, aqueous solubility or solution pH becomes definite for a given temperature under atmospheric pressure. Therefore, if the total acid concentration (C_t , undissociated acid plus dissociated anion) is to be changed, addition of some extra acid or base into the system is required. This is a requisite condition for the determination of the acidity constant by the solubility method.^{21–23} Combination of Eqs. 2 and 5 leads to the following relation:

$$C_t = [\text{AH}] + [\text{A}^-] = [\text{AH}] + K_a [\text{AH}] / a_{\text{H}^+} \gamma_{\pm}, \quad (8)$$

where the activity of AH is assumed equal to the concentration because of its low concentration, say less than 1×10^{-4} mol dm^{-3} in the present case. As long as a solid phase of AH coexists in the system, the chemical potential of undissociated acid AH remains constant at constant temperature and pressure. In other words, the concentration [AH] in the solution phase remains constant irrespective of the solution pH. On the other hand, pH and $[\text{A}^-]$ can be changed stepwise by repetitive addition of LiOH solutions of known concentration. Then, if the total concentration is plotted against $1/a_{\text{H}^+} \gamma_{\pm}$, a linear relation must hold between them. The K_a value can be obtained by dividing the slope of the plot by its intercept on the ordinate axis and with Eq. 4. When $[\text{A}^-]$ is quite low as in the present case ($< 2.5 \times 10^{-3}$), the activity coefficient can be set as 1 with more than 95% confidence.

Results and Discussion

The titration curve of CH_3COOH by NaOH solution was analyzed to see if the acidity constant found by the titration method is equal to the literature value. The variation in the acidity constant was $1.70\text{--}1.76 \times 10^{-5}$ over the neutralization range of 0.2–0.7 for a total acid at the acid concentrations of 0.031 and 0.147 mol dm^{-3} . These values are very close to the literature value of $1.73\text{--}1.77 \times 10^{-5}$.²⁴ The neutralization titration curves of the present perfluorinated acids by NaOH solution are a typical one of a strong acid by a strong base. The initial pH of the acid solutions is around 1.2 for both total acid concentrations of 0.1 and 0.05 mol dm^{-3} . It gradually increases up to 3 with addition of NaOH, and then steeply increases up to 11 with further addition of NaOH. At the same time, the pH range used for the acidity constants is just around a half of the neu-

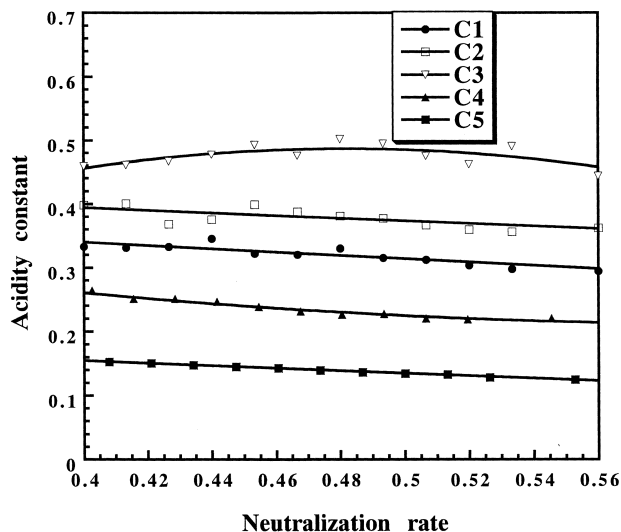


Fig. 1. Change of acidity constant against neutralization rate by 1.0 mol dm^{-3} NaOH solution for C1 to C5 acids: the acid concentration is ca. 0.05 mol dm^{-3} .

trality end-point, and the range was selected for increasing reliability of the concentration for both denominator and numerator of Eq. 2. The acidity constants thus obtained are shown in Table 1 and Fig. 1, where slight changes of the K_a values with the neutralization rate can be seen. The differences in the K_a value between two acid concentrations are within the error limits, except for C3 acid. A further important point in the figure is that the K_a values increase with alkyl chain length from C1 (ethanoic acid) to C3 (butanoic acid), and then decreases from C3 to C5 (hexanoic acid). The abrupt decrease in K_a value for hexanoic acid is likely due to commencement of aggregation as pre-micelle, which might be possible because hydrophobicity of C5 fluorocarbon corresponds to that of C7–C8 hydrocarbon.²⁵ An alternate reason which will be examined later is the fact that the aqueous solution of C5 acid becomes quite viscous with increasing concentration, although the solution has a viscosity similar to water at lower concentrations of 0.1 and 0.05 mol dm^{-3} . Another point to be mentioned here is that sodium *n*-perfluoroalkanoates have higher micellization temperatures²⁶ or conventional Krafft points than corresponding lithium salts. For example, the micellization temperature is 24.5

Table 1. Experimentally Determined Parameters and the Acidity Constant (K_a) at 298.15 K

acids	K_a (Titration 1)	K_a (Titration 2)	$\lambda_0(\text{Li salt})$ $\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$	$\lambda_0(\text{acid})$ $\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$	$K_a(\text{conductivity})$	$K_a(\text{solubility})$
C1	0.32 ± 0.02	0.26 ± 0.04	79.98 ± 0.10	382.90 ± 2.49	0.24 ± 0.05	
C2	0.38 ± 0.01	0.34 ± 0.02	73.14 ± 0.01	376.06 ± 2.40	0.29 ± 0.03	
C3	0.48 ± 0.02	0.36 ± 0.06	69.61 ± 0.06	372.55 ± 2.45	0.38 ± 0.02	
C4	0.23 ± 0.02	0.23 ± 0.03	67.82 ± 0.10	370.74 ± 2.49	0.37 ± 0.02	
C5	0.14 ± 0.01	0.12 ± 0.01	67.10 ± 0.03	370.18 ± 2.42	0.18 ± 0.04	
C9						2.66×10^{-3}
C10						2.48×10^{-3}
C11						$7.44 \times 10^{-4 \text{ a}}$

$\lambda_0(\text{HCl}) = 420.83 \pm 2.39 \text{ cm}^2 \Omega^{-1} \text{equiv}^{-1}$ and $\lambda_0(\text{LiCl}) = 116.21 \pm 0.06 \text{ cm}^2 \Omega^{-1} \text{equiv}^{-1}$ at 298.15 K.

Titration 1 and 2 are total concentration = 0.05 and 0.1 mol dm^{-3} , respectively.

a) This value was evaluated at 303.2 K.

°C and below 0 °C for $n\text{-C}_8\text{F}_{17}\text{COONa}$ and $n\text{-C}_8\text{F}_{17}\text{COOLi}$, respectively.⁴ Therefore, LiOH is safer to use instead of NaOH for longer homologues.

The electrical conductivity method was used for determining K_a in order to increase the reliability in the acidity constants. If the perfluorinated acids are strong and perfectly dissociated at a definite concentration, the limiting equivalent conductivity ($\lambda_0(\text{acid})$) can be determined by extrapolation of equivalent conductivity to zero acid concentration. However, this criterion is not guaranteed for the present acids. So the procedure mentioned above was carried out. In order to confirm the validity of the present method, the K_a value of ethanoic acid was evaluated by the method and found to be 1.60×10^{-5} , which is very close to the reference value as given above. In Fig. 2 are shown the linear relationships between the equivalent conductivity and the square root of concentration of the lithium salts. The limiting equivalent conductivities $\lambda_0(\text{Li salt})$ could be accurately determined from the intercept on the ordinate axis (see the values in Table 1). Identical procedures are followed for obtaining both $\lambda_0(\text{H}^+)$ and $\lambda_0(\text{Li}^+)$ values from HCl and LiCl solutions, where the reference value of $76.35 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$ for $\lambda_0(\text{Cl}^-)$ at 298.15 K ²⁷ was used as mentioned above. The $\lambda_0(\text{acid})$ values can now be determined (see Table 1). If the equivalent conductivity change with concentration is known for the acids, the acidity constants can be evaluated from Eq. 7. Plots of the specific conductivity vs concentration are almost the same for the C1 to C5 acids due to the extremely high conductivity of H^+ ion. Despite the dominating conductivity of the proton, a definite decrease with increasing alkyl chain can be observed. The change in acidity constant with concentration is plotted in Fig. 3. In this case too, a concentration dependence is observed, and the acidity constants increase with increasing concentration, which is contrary to the theoretical expectation. It can be seen that the $\lambda_0(\text{H}^+)$ value has a critical effect on the concentration dependence; the higher the value, the less independent on the concentration the K_a values become. The results in Fig. 3 are the optimum ones resulting from the $\lambda_0(\text{H}^+)$ value obtained by the present cell, the error limits being taken into account. Using the conductometric method too, one finds that the acidity constant increases from C1 to C3 and then decreases from C3 to C5 with increasing the alkyl chain length. In addition, the values from the two methods are in good agreement within the error limits except for C4 acid, where the extent of the error in Table 1 is the standard deviation.

As mentioned above, the aqueous solution of C5 becomes very viscous at higher concentrations, which means that some structure is formed among the monomers in the solution. Hydrogen bonding is a highly possible cause for the structure formation, leading to a lower dissociation constant of the carboxylic group, as is observed for acetic acid in the aqueous solution. In order to ascertain this effect, the viscosity of aqueous solutions for C1 to C5 acids was measured over the concentration range from 0 to 0.09 mol dm^{-3} . The viscosities were found to be approximately equal to one another for the above concentration range. The rate of increase in viscosity becomes larger for the longer alkyl chain acids, where the viscosity is made to be the mean value of two measurements. However, the difference in solution viscosity among the acids

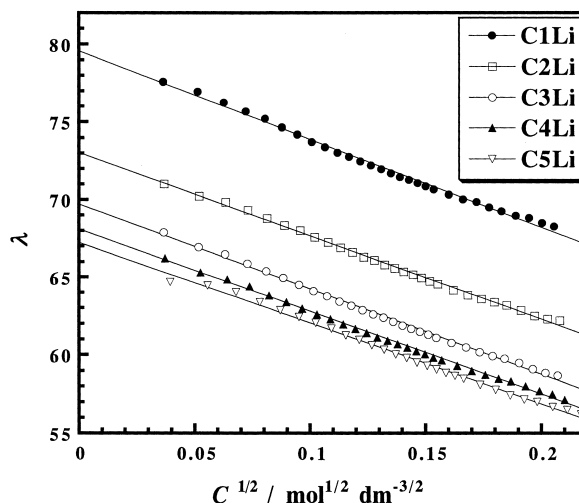


Fig. 2. Specific conductance (λ) vs. square root of concentration plots for lithium salts of shorter homologous acids.

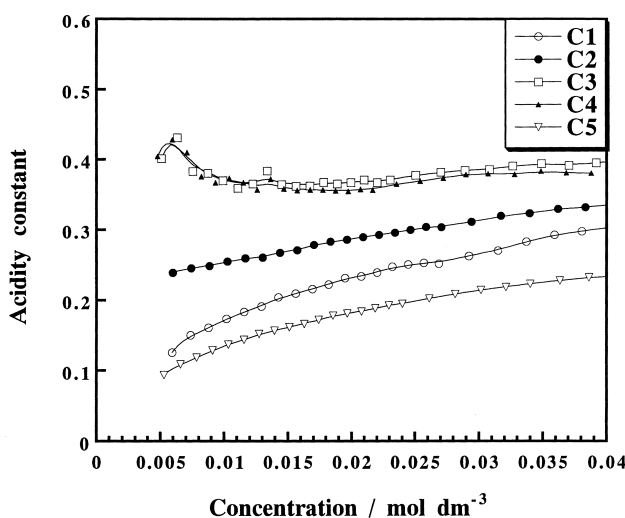


Fig. 3. Acidity constant vs. concentration plots for C1 to C5 acids at 298.15 K by conductivity measurement.

remained within 2% of the average values for the five acids at the concentration of 0.05 mol dm^{-3} . Such a small change in viscosity could not explain the large difference in K_a values of more than 100%. The above results strongly suggest the formation of some oligomer, dimer or trimer, by hydrogen bonding between carboxylic groups. The oligomers in dilute solutions are not large enough to produce long-range structure. Another possibility is that hydrophobic interaction among perfluorinated alkyl chains would play a very important role in the oligomer formation. In other words, the longer the alkyl chain, the easier becomes oligomer formation. The ease of aggregation for longer fluorinated alkyl chain has been observed in our previous work.²⁸ Hence, the oligomer formation is much easier for undissociated longer acids. These two must be manifested in the lower acidity constant of the longer homologues. In order to further substantiate the above fact, the dissociation constant for the longer chain acids, C9 to C11 acids, was determined by the solubility method.

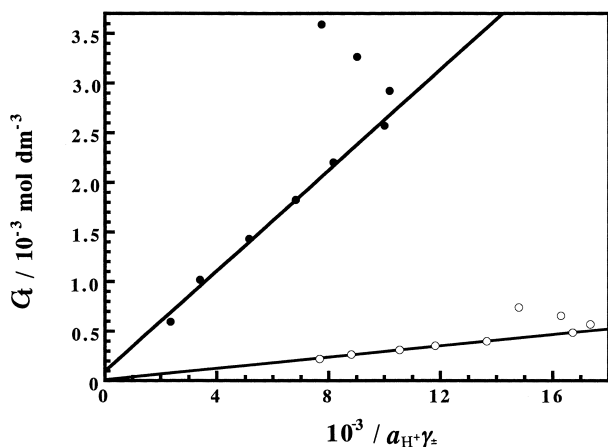


Fig. 4. Total acid concentration vs. $1/a_{\text{H}^+} \gamma_{\pm}$ plots for C9(●) and C10(○) acids at 298.15 K.

The solubility as a function of pH is shown in Fig. 4, where a linear relationship can be observed at lower concentrations. The acidity constant can be evaluated from the slope and the intercept as mentioned above.²¹ The intercept on the ordinate may not be clear from Fig. 4, but a certain positive value can be interpreted by an expanded ordinate scale. All the results are summarized in Fig. 5. As is clear from a regular decrease in K_a value, the acidity constants of the homologues longer than the C3 or C4 acid clearly decrease with increasing carbon number of the acids. However, the decrease can not be verified from other direct experimental evidence at present, as mentioned above. The titration method is quite difficult for longer homologues because of lower monomer concentration of undissociated acid, say less than 1×10^{-4} mol dm⁻³ for the decanoic acid. The conductivity method is also inappropriate because of much uncertainty of conductivity values originating in lower concentration. However, it becomes quite certain that the acidity constant truly decreases with increasing alkyl chain length for the perfluoroalkanoic acids. In addition, these acids are much weaker than expected. The important point is that

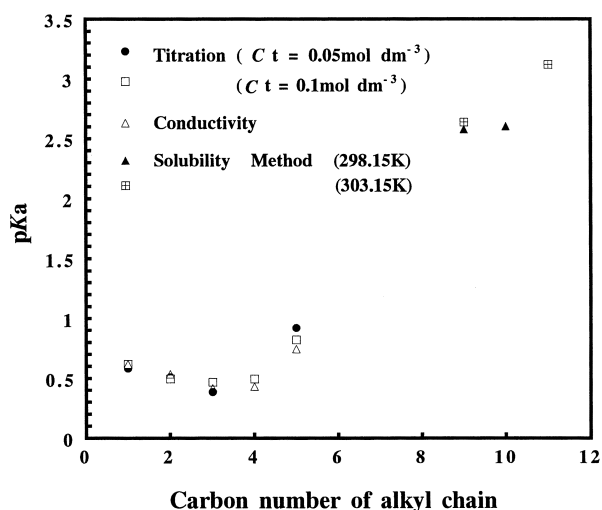
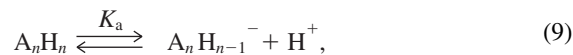


Fig. 5. Change of pK_a with the number of carbon atom in alkyl chain of the perfluoroalkanoic acids.

the measured acidity constants are not for the monomeric acid AH but for some oligomeric acid A_nH_n at a given concentration for the longer homologues. This is analogous to dimerization of acetic acids in an aqueous solution. In other words, the acidity constants for C5–C11 acids might not be directly compared with those for C1–C4 acids.

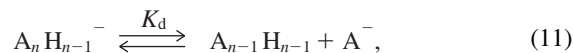
As for some oligomer A_nH_n , the following dissociation is possible:



Then, the total acid concentration C_t becomes

$$C_t = n\{[A_nH_n] + K_a [A_nH_n]/a_{\text{H}^+} \gamma_{\pm}\} \quad (10)$$

and a linear relationship holds between C_t and $1/a_{\text{H}^+} \gamma_{\pm}$. Both slope and intercept values can give the K_a value as mentioned above. However, if the above dissociation is only the case, aggregation of the species $A_nH_{n-1}^-$ leads to micelle formation, which seems unreasonable judging from Fig. 4. Another possibility is the following additional equilibrium:



which is a dissociation of A^- from $A_nH_{n-1}^-$. From Eqs. 9 and 11, the total acid concentration becomes:

$$C_t = n\{[A_nH_n] + K_a [A_nH_n]/a_{\text{H}^+} \gamma_{\pm}\} + (n-1)[A_{n-1}H_{n-1}] + \frac{K_a K_d [A_nH_n]}{[A_{n-1}H_{n-1}]} / a_{\text{H}^+} \gamma_{\pm} \quad (12)$$

As far as an excess solid phase of AH coexists in the system, both $[A_nH_n]$ and $[A_{n-1}H_{n-1}]$ remain constant at constant temperature and pressure. This can be the reason that there exists a linear relationship between C_t and $1/a_{\text{H}^+} \gamma_{\pm}$. However, the slope and the intercept values do not lead to the K_a value as above. In conclusion, the K_a values obtained for the C5 to C11 acids are not for monomeric AH but for some oligomeric A_nH_n . Indeed they might be an apparent K_a value, but the observed values are real ones. It is almost impossible to determine the K_a value of monomeric AH at a definite concentration range, because the monomeric concentration is extremely low.

The pH values decreased after passing a maximum with increasing concentration (Fig. 4), which is a clear indication of the aggregation or micellization of acid anions,^{15,29} the Li^+ counterions being bound to the micellar surface. In this case, mixed micelles are formed between the acid and the corresponding lithium salt, because the aqueous solubility of the acid is kept constant, as far as an excess acid phase coexists in the system. The lower cmc values are easily predictable from the mixed micellization with solubilized acid. In addition, a sharp change in pH at the cmc qualitatively indicates the high purity of these acids.²⁹

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