Hydrolysis of Dimethyltin(IV)Dichloride in Different Ionic Media

Farrokh Gharib*, Mostafa Mohammadpour Amini, Afshin Haghgou

Chemistry Department, Shahid Beheshti University, Tehran, Evin, Iran
gharibf@hotmail.com

ABSTRACT

The hydrolysis of dimethyltin(IV)dichloride was studied spectrophotometrically in different aqueous media of sodium chloride and sodium perchlorate in a wide range of ionic strength, 0.1-1.0 mol dm^{-3} and pH range of 1-11, at 25 °C. Least squares calculations are consistent with the formation of $M(OH)^{+}$, $M(OH)_2$, $M(OH)_3^{-}$, $M_2(OH)_2^{+2}$, and $M_2(OH)_3^{+}$ species, where M is $(CH_3)_2Sn^{+2}$. The dependency on ionic strength for different electrolyte solutions was taken into account by using a Debye-Huckel type equation, and finally the results have been compared with data previously reported and interpreted.

INTRODUCTION

The first data on antitumour activities of organotins were published by Crowe /1/, and subsequently a series of investigations has been carried out in this field. In fact, organotins in cell membranes /2-3/ and walls /4/, bound to hemoglobin /5-7/ and possibly to native DNA /8-10/, and in addition to organotin compounds in aqueous systems, were tested as antitumour drugs /11/ and their activity has been investigated by different techniques. Among organotins, dialkyl derivatives exhibit greater antitumour activity than the corresponding mono-, tri-, and tetraalkyl derivatives /12/. The activity of the tri- or tetra-alkyl derivatives may be explained by dealkylation *in vivo*, which yields the corresponding active dialkyl derivatives. If one ranks specific alkyl organotins in terms of antitumour activity of the parent compounds, the diethyl and diphenyl derivatives have the highest activity *in vivo*, provided that one takes no cognizance of their toxicity /13/.

Accepting the hypothesis that R_2Sn^{+2} are the usual active species for the antitumour action of organotins /14/, a good antitumour agent should be easily dissociable following administration to animals. This requires weak bonds between tin and the donor atom of the coordinated ligands, which are readily hydrolysable. If the compound is hydrolytically unstable, the R_2Sn moiety will be released too soon, and if it is too stable, it may

* To whom correspondence should be addressed.

be released too slowly and consequently lower activity will be observed. Therefore, there is a relationship between the stability of the organotin compounds and their antitumour activity.

Organotins cations are considered to be acids, in the Lewis scale, of different hardness, depending on the groups bonded to the tin(IV). Consequently, they show a strong tendency to hydrolysis in aqueous solution, as demonstrated by Tobias and Friedline /15/. Other studies on the interactions of dimethyltin(IV) cation with O-donor ligands /16-18/ have recently been reported, confirming the results previously obtained in the hydrolysis investigations. Unfortunately, thermodynamic parameters reported in all these studies refer to a single ionic medium and a single value of ionic strength, except the work reported by De Stefano *et al.* /19/. From these data, therefore, it is impossible to know the behavior of organotin compounds in a multicomponent solution and to describe the chemical speciation of these compounds in natural fluids. However, it is generally recognized that there is a correlation between the biological activity and the chemical form of metal ion (free, complexed, and hydrolyzed) present in the environment.

Studies on hydrolysis of organotin compounds in aqueous solution have generally been limited to methyltin derivatives, since other organotins do not have sufficient solubility in water to permit spectrophotometric investigation /20/. This work deals with the study of hydrolysis of $(CH_3)_2Sn^{+2}$ in aqueous solution at 25 °C and different ionic media, 0.1 to 1.0 mol dm^{-3}, of sodium perchlorate and sodium chloride, using a combination of potentiometric and spectrophotometric techniques. The parameters which define this dependency were analyzed with the aim of obtaining further information with regard to their variation as a function of charges involved in the hydrolysis reaction. Moreover, a general equation was established for the dependence of hydrolysis constant on ionic strength. This equation gives the possibility of estimating a hydrolysis constant at a fixed ionic strength when its value is known at another ionic strength in the range 0.1 < ionic strength < 1.0 mol dm^{-3}, and therefore may make a significant contribution to solving many analytical and speciation problems.

EXPERIMENTAL SECTION

Chemicals

The sodium perchlorate and sodium chloride were obtained from Merck as analytical reagent grade material and were dried under vacuum at room temperature for at least 48 hours before use. The NaOH solution was prepared from a titrisol solution (Merck) and its concentration was determined by several titrations with standard HCl solution. Perchloric and hydrochloric acids were obtained from Merck as analytical reagent grade materials and were used as supplied. Dilute acid solutions were standardized against standard NaOH solution. Dimethyltin(IV) dichloride was obtained from Merck as analytical reagent grade material and was used without further purification. All dilute solutions were prepared from double-distilled water with specific conductance equal to $(1.3 \pm 0.1)\ \mu\Omega^{-1}cm^{-1}$.

Apparatus

An Eyela pH-meter, PHM 2000, was used for pH measurements. The hydrogen ion concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. Spectrophotometric titrations were performed on a UV-vis Shimadzu 2100 spectrophotometer with a GDU-20 computer and using thermostated matched 10 mm quartz cells.

Measurements

All measurements were carried out at 25 °C. The ionic strength was maintained at fixed values from 0.1 to 1.0 mol dm^{-3} with each supporting electrolyte. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol dm^{-3} of HCl or $HClO_4$, containing 0.09 mol dm^{-3} sodium salt of the proposed electrolyte (for adjusting the ionic strength to 0.1 mol dm^{-3}). The same procedure was performed for the other ionic strengths. For these standard solutions, we set $-\log[H^+] = 2.0$ /21/. Junction potential corrections have been calculated from Eq 1

$$-\log[H^+]_{real} = -\log[H^+]_{measured} + a + b[H^+]_{measured} \quad (1)$$

a and b were determined by measuring of hydrogen ion concentration for two different solutions of each acid with sufficient sodium salt of the proposed electrolyte to adjust the ionic media.

Procedure

50 cm^3 acidic solution of dimethyltin(IV)dichloride, 4.0×10^{-3} mol dm^{-3} was titrated with an alkali solution, 0.1 mol dm^{-3} NaOH, both in the same ionic strength. The $-\log[H^+]$ and absorbance were measured after the addition of a few drops of titrant, and this procedure extended up to the required $-\log[H^+]$. A purified nitrogen atmosphere was maintained in the vessel during the titrations. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations are shown in the text and Tables.

Results and Discussion

On the basis of literature data /16, 22/ the formation of the following hydrolytic species have been hypothesized: $[(CH_3)_2Sn]OH^+$, $[(CH_3)_2Sn](OH)_2$, $[(CH_3)_2Sn](OH)_3^-$, $[(CH_3)_2Sn]_2(OH)_2^{+2}$, $[(CH_3)_2Sn]_2(OH)_3^+$, $[(CH_3)_2Sn]_3(OH)_4^{+2}$, $[(CH_3)_2Sn]_2(OH)_4$, $[(CH_3)_2Sn]_3(OH)_4^{+2}$, $[(CH_3)_2Sn]_3(OH)_2^{+4}$, $[(CH_3)_2Sn]_4(OH)_5^{+3}$, and $[(CH_3)_2Sn]_4(OH)_6^{+2}$. Our results in this work are consistent with the formation of three mononuclear, $[(CH_3)_2]Sn(OH)_q^{2-q}$ (q = 1, 2, 3), and two binuclear, $[(CH_3)_2Sn]_2(OH)_q^{4-q}$ (q = 2, 3) species. Mononuclear species are formed in high percentages (> 80 %), while binuclear species do not exceed 5-10 %, in our experimental conditions. Hydrolysis reactions and their formation constants are (where $M^{+2} = [(CH_3)_2Sn^{+2}]$):

$$M^{+2} + OH^- \rightleftharpoons M(OH)^+ \quad (2)$$

$$M^{+2} + 2OH^- \rightleftharpoons M(OH)_2 \quad (3)$$

$$M^{+2} + 3OH^- \rightleftharpoons M(OH)_3^- \quad (4)$$

$$2M^{+2} + 2OH^- \rightleftharpoons M_2(OH)_2^{+2} \quad (5)$$

$$2M^{+2} + 3OH^- \rightleftharpoons M_2(OH)_3^+ \quad (6)$$

or, generally:

$$pM^{+2} + qOH^- \rightleftharpoons M_p(OH)_q^{(2p-q)+} \quad (7)$$

According to equation 7, the hydrolysis constant, β_{pq}, is expressed as:

$$\beta_{pq} = [M_p(OH)_q^{(2p-q)+}] / [M^{+2}]^p[OH^-]^q \quad (8)$$

The method of determination of β_{pq} is based on the relation A = f (pH) /23/. Absorbance, A, and $-\log[H^+]$ were measured for a solution containing $(CH_3)_2Sn^{+2}$ with sufficient NaOH solution, as described before. Treatment of the spectrophotometric data (each 1 nm) obtained during the titrations as a function of the H^+ concentration was submitted to the computer program. The program allows calculation of hydrolysis constant for different stoichiometry models. The degree of refinement then guides to choice between the models. Using a suitable computer program /24/ the data were fitted to the final equation for estimating the hydrolysis constant of eq 7. We used the Gauss-Newton nonlinear least-squares method in the computer program to refine the absorbance by minimizing the error squares sum from Eq 10

$$U = \sum(a_i - b_i)^2 \quad (i = 1, 2, 3, \ldots) \quad (10)$$

where a_i is a quasi-experimental value and b_i is a calculated one. The computer program consisted of two different kinds of fitting, (a) graphical, (b) numerical. The final selection of the species was based on both graphical and numerical methods, considering in addition the various statistical criteria, i. e. sums of squared residuals and the differences of total concentration of M^{+2} used from those of calculated ones. Figure 1 is shown as an example of graphical fitting for the observed and calculated absorbances from the computer program, by the fitting method.

Different models including polynuclear species with various hydroxyl groups were tested by the program. The models finally chosen, formed by $M(OH)^+$, $M(OH)_2$, $M(OH)_3^-$, $M_2(OH)_2^{+2}$, and $M_2(OH)_3^+$ resulted in a satisfactory numerical and graphical fitting. The average values for various wavelengths calculated for the hydrolysis constant of the species at different background salts are listed in Table1 and are shown in Figure 2 as a function of ionic strength.

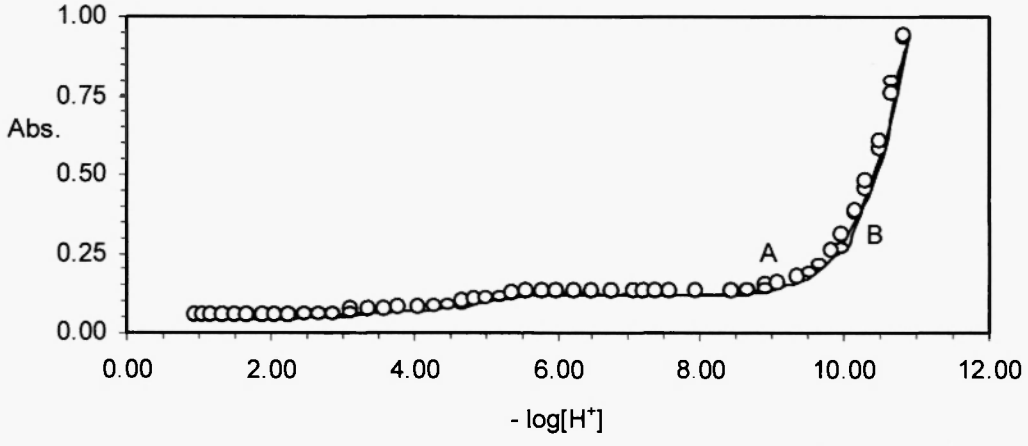

Fig. 1: A typical graphical fitting for the hydrolysis of dimethyltin(IV)dichloride system at 25 °C, 215 nm, and ionic strength 0.1 mol dm^{-3} sodium perchlorate, (A) experimental absorbance, (B) calculated absorbance from the computer program by fitting method.

Table 1

Average values of hydrolysis constants for dimethyltin(IV)dichloride species in aqueous solution at 25 °C and different ionic strengths of $NaClO_4$ and NaCl together with the values reported in the literature

ionic strength / mol dm^{-3}	$-\log\beta_{11}$	$-\log\beta_{12}$	$-\log\beta_{13}$	$-\log\beta_{22}$	$-\log\beta_{23}$
	$NaClO_4$				
0.1	3.12 ± 0.03	8.43 ± 0.04	19.45 ± 0.09	4.86 ± 0.05	9.74 ± 0.08
0.3	3.18 ± 0.02	8.50 ± 0.05	19.49 ± 0.11	4.90 ± 0.06	9.80 ± 0.10
0.5	3.22 ± 0.01	8.55 ± 0.06	19.55 ± 0.10	4.96 ± 0.05	9.85 ± 0.11
0.7	3.31 ± 0.04	8.61 ± 0.04	19.66 ± 0.11	5.06 ± 0.07	9.95 ± 0.09
1.0	3.40 ± 0.03	8.75 ± 0.03	19.79 ± 0.12	5.24 ± 0.06	10.10 ± 0.10
0.1	3.54[a]	8.98[a]	-	4.6[a]	9.76[a]
0.1	3.30[b]	9.05[b]	20.3[b]	5.1[b]	9.7[b]
	NaCl				
0.1	3.16 ± 0.05	8.48 ± 0.06	19.48 ± 0.12	4.89 ± 0.05	9.75 ± 0.09
0.3	3.26 ± 0.06	8.69 ± 0.07	19.62 ± 0.15	4.99 ± 0.06	9.91 ± 0.10
0.5	3.32 ± 0.04	8.89 ± 0.09	19.73 ± 0.11	5.10± 0.04	10.09 ± 0.11
0.7	3.45 ± 0.05	9.08 ± 0.08	19.84 ± 0.13	5.26 ± 0.08	10.25 ±0.08
1.0	3.58 ± 0.04	9.35± 0.05	20.02 ± 0.14	5.45 ± 0.06	10.49 ± 0.09
0.1	3.25[a]	8.54[a]	-	5.05[a]	9.81[a]
0.1	3.12[b]	8.45[b]	19.48[b]	5.2[b]	9.7[b]

[a] obtained from reference 15, and [b] from reference 19.

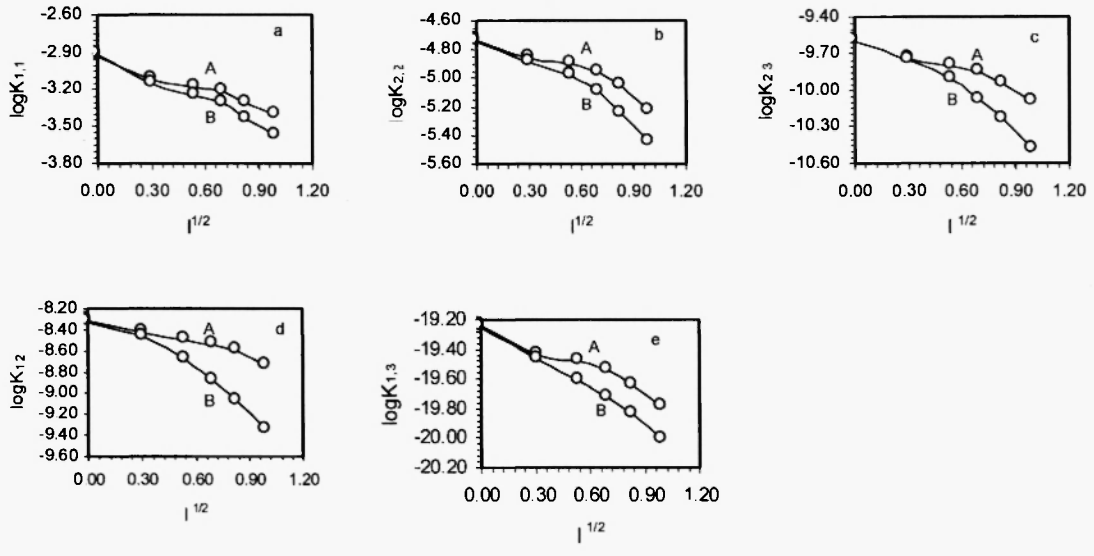

Fig. 2: Dependence on ionic strength in $NaClO_4$, A, and NaCl, B, medias at 25 °C of (a) $(CH_3)_2Sn(OH)^+$, (b) $[(CH_3)_2Sn]_2(OH)_2^{+2}$, (c) $[(CH_3)_2Sn]_2(OH)_3^+$, (d) $(CH_3)Sn(OH)_2$, (e) $(CH_3)_2Sn(OH)_3^-$.

Figure 2 shows a convergence to a single value of $\log\beta_{pq}$ at I = 0 mol dm^{-3}, i.e. the thermodynamic constant, which was calculated by the fitting method. The thermodynamic hydrolysis constants for all species are listed in Table 2, together with the values reported in the literature.

Table 2.

Average values of thermodynamic hydrolysis constants for dimethyltin(IV)-dichloride species in aqueous solution at 25 °C and different ionic strengths of $NaClO_4$ and NaCl together with the values reported in the literature

$-\log\beta_{11}$	$-\log\beta_{12}$	$-\log\beta_{13}$	$-\log\beta_{22}$	$-\log\beta_{23}$
$NaClO_4$				
2.93 ± 0.04	8.31 ± 0.09	19.24 ± 0.12	4.75 ± 0.06	9.59 ± 0.08
2.86[a]	8.16[a]	19.35[a]	4.99[a]	9.06[a]
NaCl				
2.92 ±0.03	8.33 ±0.08	19.25 ± 0.13	4.75 ± 0.05	9.6 ± 0.07

[a] Obtained from reference 19.

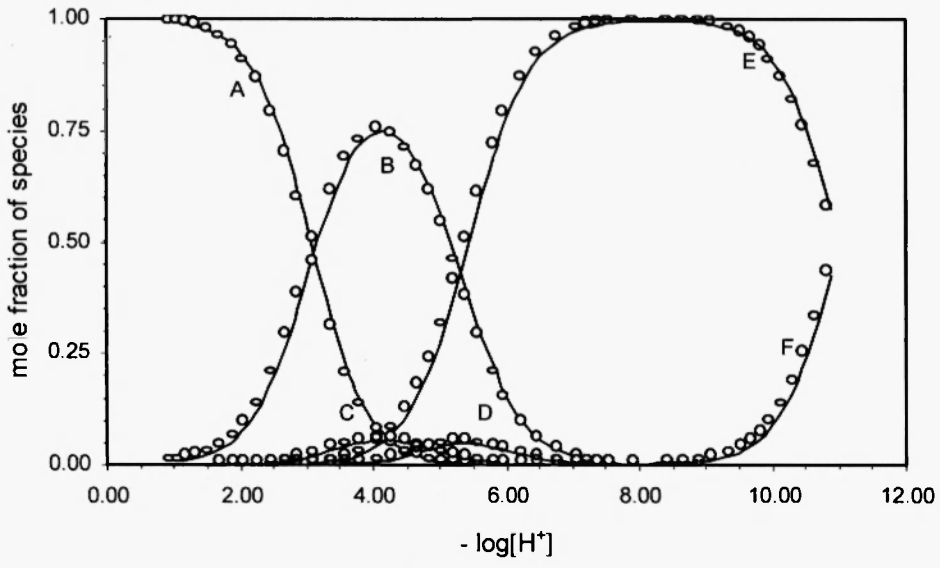

Fig. 3: Distribution diagram of $(CH_3)_2Sn^{+2}$, M^{+2},hydrolytic species versus hydrogen ion concentration at 25 °C and ionic strength 0.1 mol dm^{-3} sodium perchlorate, (A) M^{+2}, (B) $M(OH)^+$, (C) $M_2(OH)_2^{+2}$, (D) $M_2(OH)_3^+$, (E) $M(OH)_2$, (F) $M(OH)_3^-$.

In Figure 3, the equilibrium distribution of various hydrolytic species of $(CH_3)_2Sn^{+2}$ is reported versus $-\log[H^+]$, where the ionic strength is 0.1 mol dm^{-3} $NaClO_4$. The mononuclear complex, $(CH_3)_2Sn(OH)^+$, is the predominant species in acidic pH range (at $-\log[H^+] = 4.2$, ~ 74 %), and the complex $(CH_3)_2Sn(OH)_2$ shows ~ 100 % formation in the pH range 7.5-9.5. The species $(CH_3)_2Sn(OH)_3^-$ becomes predominant at $-\log[H^+] >$ 10.5. Binuclear species are formed in fairly low percentages; in the conditions of Figure 3, the species $[(CH_3)_2Sn]_2(OH)_2^{+2}$ and $[(CH_3)_2Sn]_2(OH)_3^+$ show a maximum formation percentage at $-\log[H^+] = 4.3$ (~ 6 %) and at $-\log[H^+] = 5.5$ (~ 5 %), respectively.

Dependence on ionic strength.

The dependence of the hydrolysis constants on ionic strength for the hydrolytic species can be described by a semi-empirical equation /25-26/:

$$\log K(I) = \log K(I^*) - f(I) + CI \qquad (9)$$

where $f(I) = Z^*AI^{1/2}/(1 + BI^{1/2})$, K(I) and K(I*) are the hydrolysis constants of the actual and the reference ionic media, respectively. A is the parameter of Debye-Hückel equation, (A = 0.5115 at 25 °C), $Z^* = \Sigma(\text{charges})^2_{\text{reactants}} - \Sigma(\text{charges})^2_{\text{products}}$, C is an empirical parameter to be determined, and B is set equal to 1.5 /27/ (a small error in fixing B is absorbed in the linear term C /27/). Results of a series of investigations done by Daniele *et al* /25,26/, De Stefano *et al* /28,29/, and Gharib *et al* /27,30-38/ showed that, when all the interactions occurring in the solution are considered, in the range 0 < ionic strength ≤ I, the empirical

parameters are dependent on the stoichiometry of the formation reaction. If an approximate value of C is known, the hydrolysis constant can be determined for the variation of ionic strength from I* to I by the equation

$$\log K(I) = \log K(I^*) - f(I,I^*) + C(I - I^*) \quad (10)$$

where

$$f(I,I^*) = Z^*A[I^{1/2}/(1 + 1.5I^{1/2}) - I^{*1/2}/(1 + 1.5I^{*1/2})] \quad (11)$$

I and I* are the ionic strength of the solution by appropriate electrolyte. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with Eq 10 is not always good over the whole range of ionic strength from 0.1 to 1.0 mol dm^{-3}. This equation may be useful for small changes of ionic strength, but a better fit is obtained by adding a further term of the from $DI^{3/2}$ and EI^2 (D and E are the other adjustable parameters). Therefore the data were fitted to Eq 12:

$$\log K(I) = \log K(I^*) - F(I,I^*) + C(I - I^*) + D(I^{3/2} - I^{*3/2}) + E(I^2 - I^{*2}) \quad (12)$$

It is noticeable that the introduction of the term $D(I^{3/2} - I^{*3/2})$ or $E(I^2 - I^{*2})$ very often improves the quality of the fit. For example, for the hydrolysis constant of $(CH_3)_2Sn(OH)^+$ in sodium perchlorate media, from eq 12 we obtained three sets of values depending on whether or not we take into account the term in D and E:

$C = -6.45$, $D = 0.0$, $E = 0.0$, $U = 5.85 \times 10^{-4}$
$C = 0.49$, $D = -0.55$, $E = 0.0$, $U = 5.13 \times 10^{-4}$
$C = 1.27$, $D = -2.21$, $E = 0.91$, $U = 3.05 \times 10^{-6}$

The squares sum, U, shows that there is a significant improvement in the fit when D and E terms are introduced.

The parameters for the dependence on ionic strength (C, D, and E) are calculated by the fitting method and reported in Table 3. The empirical parameters obtained for NaCl media, Table 3, are different with respect to those in $NaClO_4$, indicating that some interactions occur between dimethyltin(IV) and Cl^-. Hydrolysis constants in NaCl media are lower from those determined in $NaClO_4$, see Table 1, and suggest that hydrolytic species of $(CH_3)_2Sn^{+2}$ are less stable in chloride than in perchlorate media. This behavior can be explained by assuming that chloride complexes are formed with both free and hydrolyzed dimethyltin cations and was well described by De Stefano *et al.* /19/ and Natsume *et al.* /22/ by assuming of formation two complex species $(CH_3)_2SnCl^+$ and $(CH_3)_2Sn(OH)_2Cl^-$ depending on pH. Apparently, increasing pH facilitates the formation of hydrolytic species; also, the concentration of hydrolytic species depends on the concentration of supporting electrolyte, Figure 2. At NaCl media, hydrolysis of dimethyltin(IV) becomes

more arduous but in contrast, $NaClO_4$ is less influential on the hydrolysis constant due to the bulky nature of ClO_4^-, which has no tendency to coordinate to tin as Lewis base. This speculation is in good agreement with the hydrolysis constant values obtained in this work.

Table 3

Parameters for the dependence on ionic strength of hydrolysis constants for all species in different background electrolytes.

Empirical parameters	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}
	$NaClO_4$				
C	1.27	7.18×10^{-4}	0.83	1.36	2.28
D	-2.21	0.48	-2.05	-1.99	-3.18
E	0.91	-0.61	0.91	0.52	1.05
	NaCl				
C	0.95	-1.06	-1.51	1.77	4.32
D	-1.92	0.40	1.76	-3.71	-9.56
E	0.77	-0.16	-0.90	1.64	5.25

REFERENCES

1. A. J. Crowe, P. J. Smith and G. Atassi, *Chem. Biol. Interact.*, **32**, 171, (1980).
2. A. J. Crowe, *Metal Based Antitumour Drugs*, Freund Publishing House, London, 1988.
3. R. Barbieri and A. Silvestri, *Inorg. Chim. Acta*, **188**, 95, (1991).
4. L. May, G. Eng, S. P. Goddington and L. L. Stockton, *Hyperfine Interact.*, **42**, 909, (1988).
5. B. M. Elliott, W. N. Aldridge and J. W. Bridges, *Biochem. J.*, **177**, 461, (17979).
6. R. Barbieri and M. T. Musmeci, *J. Inorg. Biochem.*, **32**, 89, (1988).
7. R. Barbieri, A. Silvestri, G. Ruisi and M. T. Musmeci, *J. Chem. Soc. Dalton Trans.*, 519, (1989).
8. R. Barbieri, A. Silvestri and V. Piro, *J. Chem. Soc. Dalton Trans.*, 3605, (1990).
9. 9.R. Barbieri, A Silvestri and V. Piro, *Organotins and DNA, Abstr., Mossbauer Spectroscopy Discussion Group, 31st Meet, University of Sheffield, U.K., July 2-4*, 1990.
10. R. Barbieri and A. Silvestri, *J. Inorg. Biochem.*, **41**, 31, (1991).
11. R. Barbieri, A. Silvestri, S. Filippeschi, M. Magistrelli and F. Huber, *Inorg. Chim. Acta*, **177**, 141, (1990).
12. A. H. Penninks, M. Bol-Schoenmakers and W. Seinen, *Cellular Interaction of Organotin Compounds in Relation to Their Antitumour Activity*, Springer Verlag, Berlin,1990.
13. A. J. Crowe, *Tin Compounds and Their Potential as Pharmaceutical Agents*, Springer Verlag, Berlin,1990.

14. J. M. Tsangaris and D. R. Williams, *App. Organometallic Chem.*, 6, 3, (1992).
15. R. S. Tobias and C. E. Friedline, *Inorg. Chem.*,**4**, 215, (1965).
16. G. Arena, A. Gianguzza, L. Pellerito, R. Purrello and E. Rizzarelli, *J. Chem. Soc. Dalton Trans.*, 773, 1989.
17. G. Arena, A. Gianguzza, S. Musumeci, L. Pellerito and R. Rizzarelli, *J. Chem. Soc. Dalton Trans.*, 2603, (1990).
18. V. Cucinotta, A. Gianguzza, G. Maccarrone, L. Pellerito, R. Purrello and E. Rizzarelli, *J. Chem. Soc. Dalton Trans.*, 2299, (1992).
19. C. De Stefano, C. Foti, A. Gianguzza, M. Martino, L. Pellerito and S. Sammartano, *J. Chem. Eng. Data*, **41**, 511, (1996).
20. S. J. Blunden and P. J. Smith, *Inorg. Chim. Acta*, **60**, 105, (1982).
21. P. Lagrange, K. Schneider, K. Zare and J. Lagrange, *Polyhedron*, **13**, 861, (1994).
22. T. Natsume, S. Aizawa, K. Hatano and S. Funahashi, *J. Chem. Soc. Dalton Trans.*, 2749, (1994).
23. M. T. Beck and I Nagypal, *Chemistry of Complex Equilibria*, Ellis Harwood, New york, 1990.
24. D. C. Harris, *J. Chem. Educ.*, **75**, 119, (1998).
25. P. G. Daniele, C. Rigano and S. Sammartano, *Talanta*, **30**, 81, (1983).
26. P. G. Daniele, C. Rigano and S. Sammartano, *Anal. Chem.*, **57**, 2956, (1986).
27. F. Gharib, K. Zare, A. Taghvamanesh and M. Monajjemi, *J. Chem. Eng. Data*, **46**, 1140, (2001).
28. C. De Stefano, C. Foti and A. Gianguzza, *J. Chem. Res.*, 464, (1994).
29. A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, *Talanta*, **34**, 933, (1987).
30. F. Gharib, K. Zare and K. Majlesi, *J. Chem. Eng. Data*, **45**, 833, (2000).
31. F. Gharib, K. Zare and K. Majlesi, *J. Chem. Res.* **2000**, 186.
32. F. Gharib, M. Vadi, S. Momeni, and H. Jalali, *Inter. J. Chem.*, **12**, 55, (2002).
33. F. Gharib and A. Shamel, *Phys. Chem. Liq.*, **40**, 637, (2002).
34. F. Gharib and A. Nouri, Russ. *J. Inorg. Chem.*, **47**, 1101, (2002).
35. F. Gharib, K. Zare, A. Taghvamanesh, A. Shamel and G. Shafiee, *Main Group Met. Chem.*, **25**, 647, (2002).
36. F. Gharib, A. Shamel, A. Taghvamanesh and G. Shafiee, *Russ. J. Coord. Chem.*, **29**, 436, (2003).
37. F. Gharib and L. Afrazeh, *J. Chem. Eng. Data*, **48**, 999, (2003).
38. F. Gharib and M. Malekani, *Revs. Inorg. Chem.*, **23**, 97, (2003).