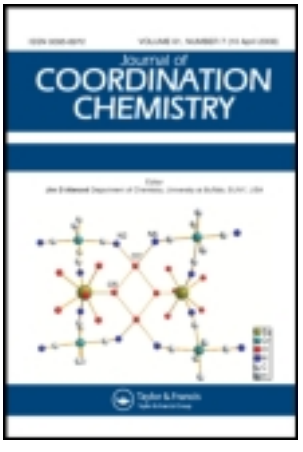

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Coordination properties of bidentate (N,O) and tridentate (N,O,O) heterocyclic alcohols with dimethyltin(IV)

Ahmed A. El-Sherif [a]
[a] Department of Chemistry , Faculty of Science, Cairo University , Cairo, Egypt
Published online: 08 Apr 2011.

To cite this article: Ahmed A. El-Sherif (2011) Coordination properties of bidentate (N,O) and tridentate (N,O,O) heterocyclic alcohols with dimethyltin(IV), Journal of Coordination Chemistry, 64:7, 1240-1253

To link to this article: http://dx.doi.org/10.1080/00958972.2011.565755

Journal of Coordination Chemistry
Vol. 64, No. 7, 10 April 2011, 1240–1253

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Coordination properties of bidentate (N,O) and tridentate (N,O,O) heterocyclic alcohols with dimethyltin(IV)

AHMED A. EL-SHERIF*

Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt

(*Received 23 November 2010; in final form 19 January 2011*)

The complex-formation equilibria of dimethyltin(IV) (DMT) with 4-hydroxymethyl imidazole (HMI) and 2,6-dihydroxymethyl pyridine (PDC) have been investigated. Stoichiometry and stability constants for the complexes formed were determined at different temperatures and 0.1 mol L^{-1} $NaNO_3$ ionic strength. The concentration distribution of the complexes in solution was evaluated as a function of pH. The effect of dioxane as a solvent on both protonation constants and formation constants of DMT complexes with HMI and PDC are discussed. The thermodynamic parameters ΔH° and ΔS° calculated from the temperature dependence of the equilibrium constants were investigated.

Keywords: Complex formation equilibria; Dimethyltin(IV); 4-Hydroxymethyl imidazole; 2,6-Dihydroxymethyl pyridine; Potentiometric titration

1. Introduction

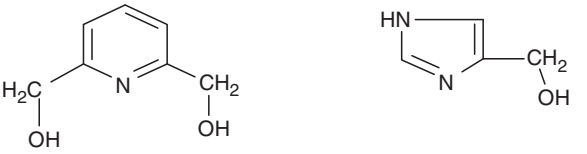
Heterocyclic compounds play a significant role in many biological systems [1] and many authors have used these compounds as ligands in coordination compounds [2–15]. Several authors have focused on the increasing amount of both organic and inorganic tin that has recently been evaluated as the third most important pollutant element in the ecosystem; raising concern that tin may enter the human food chain [16]. Some organometallic tin(IV) compounds are toxic [17].

From a bioinorganic point of view, heterocyclic alcohols are of importance as ligands containing (N,O) donors can model coordination environments that mimic both the structure and function of active sites of metal enzymes [18–23]. The studies of such ligands are relevant to medicine as potential chelators for the removal of toxic metals from the body, such as organometallic tin compounds, since dimethyltin(IV) (DMT) in aqueous solution has a strong affinity toward oxygen-donors [24]. The solution equilibrium studies of organotin and biologically important ligands have gained importance due to the pharmaceutical application of organotin compounds.

As a part of our studies on coordination chemistry of bio-relevant ligands and organotin(IV) compounds [25–29], formation equilibria of dimethyltin with bidentate (N,O) 4-Hydroxymethyl imidazole (HMI) and tridentate (N,O,O) 2,6-dihydroxymethyl

*Email: aelsherif72@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.565755



PDC HMI

Scheme 1. Structural formula of heterocyclic alcohol ligands (HMI and PDC).

pyridine (PDC) ligands are of interest. In this article we report a quantitative study of the formation equilibria of dimethyl(IV) with HMI and PDC ligands. The thermodynamic parameters calculated from the temperature dependence of the equilibrium constants were investigated. The effect of dioxane as a solvent on both the protonation constants and the formation constants of DMT complexes with HMI and PDC are discussed.

2. Experimental

2.1. *Materials and reagents*

HMI and PDC were obtained from Aldrich Chem.DMT dichloride was supplied by Merck Chem. Co. Dioxane was provided by Aldrich Chem. Co. Carbonate-free NaOH (titrant) was prepared by diluting the content of BDH-concentrated volumetric solution vials and standardized against potassium hydrogen phthalate solution. All solutions were prepared in deionized H_2O. The structural formulae of the heterocyclic alcohols are given in scheme 1.

2.2. *Instruments*

Potentiometric measurements were made using a Metrohm 686 titroprocessor equipped with a 665 Dosimat (Switzerland-Herisau). A thermostatted glass-cell was used equipped with a magnetic stirring system, a Metrohm glass electrode, a thermometric probe, a microburet delivery tube, and a salt bridge connected with the reference cell filled with a KCl solution in which a saturated calomel electrode was dipped. The titroprocessor and electrode were calibrated with standard buffer solutions, potassium hydrogen phthalate (pH 4.008), and a mixture of KH_2PO_4 and Na_2HPO_4 (pH 6.865) at 25.0°C. The number of experimental points for each titration was 100 for HMI and 150 for PDC.

2.3. *Procedure and measurements*

Proton association constants of the ligands were determined potentiometrically by titrating the ligand ($40\,cm^3$) solution ($1.25 \times 10^{-3}\,mol\,L^{-1}$) of constant ionic strength

($0.1\,mol\,L^{-1}$, adjusted with $NaNO_3$). The hydrolysis constants of the DMT were determined by titrating 40 mL of ligand ($1.25 \times 10^{-3}\,mol\,L^{-1}$) solution. The stability constants of the DMT complexes were determined by titrating 40 mL of ligands ($1.25 \times 10^{-3}\,mol\,L^{-1}$) and DMT ($1.25 \times 10^{-3}\,mol\,L^{-1}$). The temperature was maintained constant by a Colora ultrathermostat. All titrations were performed in a purified N_2 atmosphere using aqueous $0.05\,mol\,L^{-1}$ NaOH as titrant. The titration solution mixtures had a volume of 40 mL. Temperature was maintained constant inside the cell by circulating thermostated water through the double-wall titration vessel under a slow and constant stream of N_2. The pH meter readings were converted into hydrogen ion concentration by titrating a standard acid solution ($0.05\,mol\,L^{-1}$), the ionic strength of which was adjusted to $0.1\,mol\,L^{-1}$, with standard base solution ($0.05\,mol\,L^{-1}$). The pH is plotted against p[H]. The relationship $pH - p[H] = 0.05$ was observed. [OH^-] values were calculated using a pK_w value of 13.921 at 25°C. For the variable temperature studies the values of pK_w were employed at 20°C ($pK_w = 14.126$), 30°C ($pK_w = 13.753$), and 35°C ($pK_w = 13.660$).

The pH-meter readings (B) recorded in dioxane–water solutions were converted to hydrogen ion concentration [H^+] by using the widely used relation given by the Van Uitert and Hass equation, equation 1 as shown below [30]

$$-\log_{10}[H^+] = B + \log_{10} U_H, \tag{1}$$

where $\log_{10} U_H$ is the correction factor for solvent composition and ionic strength for which B is read. Values of pK_w in dioxane–water mixtures were determined as described previously [31, 32]; various amounts of standard NaOH solution were added to a solution containing 0.1 mol L $NaNO_3$. The [OH^-] was calculated from the amount of base added. The [H^+] was calculated from the pH value. The product of [OH^-] and [H^+] was taken. The mean values obtained in this way at 25°C for $-\log_{10}[H^+][OH^-]$ are $pK_w = 14.17$, 14.37, 14.50, 15.44, and 15.68 for 12.5%, 25%, 37.5%, 50%, and 62.5% dioxane–water solutions, respectively.

Equilibrium constants evaluated from the titration data (table 1) are defined by equations (1) and (2), where M, L, and H stand for the DMT ion, ligand (HMI or PDC), and proton, respectively.

$$p(SnMe_2) + q(L) + r(H) \rightleftharpoons (SnMe_2)_p(L)_q(H)_r \tag{2}$$

$$\beta_{pqr} = \frac{[(SnMe_2)_p(L)_q(H)_r]}{[SnMe_2]^p[L]^q[H]^r} \tag{3}$$

2.4. *Data processing*

The calculations were obtained from 100 to 150 data points in each titration using the computer program MINIQUAD-75 [33]. The stoichiometry and stability constants of the complexes formed were determined by trying various possible composition models. The model selected gave the best statistical fit and was chemically consistent with the titration data without giving any systematic drifts in the magnitudes of various residuals, as described elsewhere [33]. The fitted model was tested by comparing the

Table 1. Formation constants of DMT complexes with HMI and PDC in aqueous solutions at different temperatures.

System	Temp. (°C)	p	q	r[a]	log β[b]	S[c]
Dimethyltin	15	1	0	−1	−3.56(0.01)	5.4E−8
		1	0	−2	−9.05(0.01)	
		1	0	−3	−19.79(0.04)	
		1	0	−4	−30.41(0.04)	
		2	0	−2	−4.23(0.01)	
		2	0	−3	−9.52(0.01)	
		2	0	−4	−15.23(0.01)	
PDC		0	1	1	4.57(0.004)	3.2 E−8
HMI		0	1	1	6.53(0.006)	1.2E−8
Dimethyltin–PDC		1	1	0	4.34(0.02)	4.6E−8
		1	1	−1	0.53(0.008)	
		1	1	−2	−4.78(0.02)	
Dimethyltin–HMI		1	1	0	6.38(0.09)	4.6E−8
		1	1	−1	0.85(0.08)	
Dimethyltin	20	1	0	−1	−3.31(0.01)	6.1E−8
		1	0	−2	−8.64(0.01)	
		1	0	−3	−19.27(0.05)	
		1	0	−4	−30.71(0.02)	
		2	0	−2	−3.77(0.01)	
		2	0	−3	−8.91(0.02)	
		2	0	−4	−14.44(0.01)	
PDC		0	1	1	4.43(0.007)	3.0E−8
HMI		0	1	1	6.27(0.004)	2.4E−7
Dimethyltin–PDC		1	1	0	4.53(0.02)	1.4E−8
		1	1	−1	0.78(0.008)	
		1	1	−2	−4.51(0.02)	
Dimethyltin–HMI		1	1	0	6.58(0.02)	2.6E−7
		1	1	−1	1.12(0.06)	
Dimethyltin	25	1	0	−1	−3.03(0.01)	4.3E−8
		1	0	−2	−8.21(0.01)	
		1	0	−3	−18.73(0.03)	
		1	0	−4	−29.54(0.02)	
		2	0	−2	−3.12(0.01)	
		2	0	−3	−8.13(0.02)	
		2	0	−4	−13.59(0.02)	
PDC		0	1	1	4.34(0.004)	9.9E−9
HMI		0	1	1	6.03(0.007)	3.0E−8
Dimethyltin–PDC		1	1	0	4.64(0.01)	9.2E−9
		1	1	−1	0.96(0.009)	
		1	1	−2	−4.29(0.02)	
Dimethyltin–HMI		1	1	0	6.78(0.08)	9.4E−7
		1	1	−1	1.39(0.08)	
Dimethyltin	30	1	0	−1	−2.81(0.01)	6.6E−8
		1	0	−2	−7.91(0.02)	
		1	0	−3	−18.38(0.05)	
		1	0	−4	−28.71(0.02)	
		2	0	−2	−2.87(0.02)	
		2	0	−3	−7.84(0.04)	
		2	0	−4	−13.06(0.04)	
PDC		0	1	1	4.24(0.005)	1.7E−10
HMI		0	1	1	5.77(0.01)	2.1E−8
Dimethyltin–PDC		1	1	0	4.86(0.02)	1.1E−8
		1	1	−1	1.21(0.01)	
		1	1	−2	−4.02(0.02)	
Dimethyltin–HMI		1	1	0	6.98(0.05)	5.1E−7
		1	1	−1	1.66(0.05)	

(*Continued*)

Table 1. Continued.

System	Temp. (°C)	p	q	r[a]	log β[b]	S[c]
Dimethyltin	35	1	0	−1	−2.49(0.02)	6.9E−8
		1	0	−2	−7.54(0.02)	
		1	0	−3	−17.95(0.06)	
		1	0	−4	−28.20(0.03)	
		2	0	−2	−2.27(0.03)	
		2	0	−3	−7.11(0.04)	
		2	0	−4	−12.34(0.04)	
PDC		0	1	1	4.13(0.004)	1.9E−9
HMI		0	1	1	5.51(0.02)	5.9E−9
Dimethyltin–PDC		1	1	0	5.01(0.02)	2.4E−8
		1	1	−1	1.41(0.007)	
		1	1	−2	−3.81(0.01)	
Dimethyltin–HMI		1	1	0	7.18(0.02)	7.2E−7
		1	1	−1	1.93(0.05)	

[a]p, q, and r are the stoichiometric coefficients corresponding to DMT, HMI or PDC and H^+, respectively.
[b]Standard deviations are given in parentheses.
[c]Sum of square of residuals.

Table 2. Thermodynamic parameters for equilibria of DMT complexes.

Equilibrium	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	ΔG° (kJ mol^{-1})
PDC			
(1) $L + H^+ \rightleftharpoons LH^+$	−35.7	−36.7	−24.8
HMI			
(2) $L + H^+ \rightleftharpoons LH^+$	−89.2	−184.0	−34.0
$Sn(Me)_2$-PDC			
(3) $Sn(Me)_2(H_2O)_3^{2+} + L \rightleftharpoons Sn(Me)_2L^{2+} + H_2O$	56.7	280	−26.7
(4) $Sn(Me)_2(H_2O)_2L^{2+} \rightleftharpoons Sn(Me)_2LH^+_{-1} + H^+$	−18.1	10.3	−21.1
(5) $Sn(Me)_2(H_2O)_2LH^+_{-1} \rightleftharpoons Sn(Me)_2LH_{-2} + H^+$	−7.40	74.3	−30.0
$Sn(Me)_2$-HMI			
(6) $Sn(Me)_2(H_2O)_3^{2+} + L \rightleftharpoons Sn(Me)_2L^{2+} + H_2O$	67.9	358	−38.7
(7) $Sn(Me)_2(H_2O)_2L^{2+} \rightleftharpoons Sn(Me)_2LH^+_{-1} + H^+$	−23.8	23.4	−30.7

L denotes 4-hydroxymethyl imidazole (HMI) or 2,6-dihydroxymethyl pyridine (PDC).

experimental titration data points and the theoretical curve calculated from the values of the acid dissociation constant of the ligand and the formation constants of the corresponding complexes. The results are summarized in tables 1–3. The species distribution diagrams were obtained using the program SPECIES [34] under the experimental condition employed. All the measurements were carried out in our laboratory in Cairo University.

3. Results and discussion

The proton association constants of the ligands and the formation constants of the binary complexes were determined under the same experimental conditions of ionic strength and temperature.

Table 3. Formation constants of DMT complexes with HMI and PDC in dioxane-water solutions at different compositions.

System	% Dioxane	*p*	*q*	*r*[a]	log β[b]	*S*[c]
Dimethyltin	12.5	1	0	−1	−3.27(0.01)	1.3E−7
		1	0	−2	−8.70(0.02)	
		1	0	−3	−19.53(0.06)	
		1	0	−4	−30.09(0.03)	
		2	0	−2	−3.68(0.02)	
		2	0	−3	−8.94(0.05)	
		2	0	−4	−14.52(0.04)	
PDC		0	1	1	4.41(0.02)	4.2E−7
HMI		0	1	1	6.13(0.07)	1.2E−7
Dimethyltin–PDC		1	1	0	3.90(0.01)	1.03E−8
		1	1	−1	0.52(0.004)	
		1	1	−2	−4.73(0.006)	
Dimethyltin–HMI		1	1	0	5.09(0.1)	4.5E−7
		1	1	−1	0.21(0.07)	
Dimethyltin	25	1	0	−1	−3.39(0.00)	1.0E−8
		1	0	−2	−8.99(0.01)	
		1	0	−3	−19.83(0.01)	
		1	0	−4	−31.30(0.01)	
		2	0	−2	−3.92(0.01)	
		2	0	−3	−9.27(0.04)	
		2	0	−4	−15.11(0.03)	
PDC		0	1	1	6.25(0.01)	6.1E−7
HMI		0	1	1	5.51(0.02)	5.9E−9
Dimethyltin–PDC		1	1	0	3.66(0.02)	1.7E−8
		1	1	−1	0.43(0.004)	
		1	1	−2	−4.99(0.007)	
Dimethyltin–HMI		1	1	0	4.85(0.04)	2.1E−7
		1	1	−1	0.05(0.02)	
Dimethyltin	37.5	1	0	−1	−3.53(0.01)	1.4E−8
		1	0	−2	−9.23(0.01)	
		1	0	−3	−20.18(0.02)	
		1	0	−4	−31.83(0.01)	
		2	0	−2	−4.17(0.01)	
		2	0	−3	−9.61(0.03)	
		2	0	−4	−15.59(0.03)	
PDC		0	1	1	4.61(0.01)	2.3E−7
HMI		0	1	1	6.35(0.04)	4.3E−7
Dimethyltin–PDC		1	1	0	3.47(0.02)	1.5E−8
		1	1	−1	0.33(0.004)	
		1	1	−2	−5.33(0.008)	
Dimethyltin–HMI		1	1	0	4.65(0.04)	3.5E−7
		1	1	−1	−0.12(0.06)	
Dimethyltin	50	1	0	−1	−3.60(0.01)	2.8E−8
		1	0	−2	−9.43(0.01)	
		1	0	−3	−20.58(0.02)	
		1	0	−4	−32.52(0.02)	
		2	0	−2	−4.30(0.01)	
		2	0	−3	−9.78(0.04)	
		2	0	−4	−16.03(0.04)	
PDC		0	1	1	4.71(0.02)	2.3E−8
HMI		0	1	1	6.44(0.02)	2.9E−7
Dimethyltin–PDC		1	1	0	3.08(0.01)	1.7E−8
		1	1	−1	0.26(0.003)	
		1	1	−2	−5.57(0.008)	
Dimethyltin–HMI		1	1	0	4.46(0.07)	3.7E−7
		1	1	−1	−0.28(0.06)	

(*Continued*)

Table 3. Continued.

System	% Dioxane	p	q	r[a]	log β[b]	S[c]
Dimethyltin	62.5	1	0	−1	−3.68(0.01)	8.7E−8
		1	0	−2	−9.62(0.02)	
		1	0	−3	−20.89(0.04)	
		1	0	−4	−33.26(0.05)	
		2	0	−2	−4.47(0.01)	
		2	0	−3	−9.90(0.03)	
		2	0	−4	−16.51(0.04)	
PDC		0	1	1	4.82(0.01)	1.2E−8
HMI		0	1	1	6.55(0.03)	4.3E−7
Dimethyltin–PDC		1	1	0	2.80(0.02)	5.03E−8
		1	1	−1	0.16(0.005)	
		1	1	−2	−5.81(0.008)	
Dimethyltin–HMI		1	1	0	4.25(0.05)	2.2 E−7
		1	1	−1	−0.48(0.06)	

[a]p, q, and r are the stoichiometric coefficients corresponding to DMT, PDC or HMI and H^+, respectively.
[b]Standard deviations are given in parentheses.
[c]Sum of square of residuals.

3.1. *Formation equilibria of DMT with PDC and HMI*

The potentiometric titration curves of PDC and HMI in the presence and absence of DMT are compared. The titration curve of the complex is significantly lower than the PDC or HMI titration curves, corresponding to the formation of a complex through the release of a hydrogen ion. The potentiometric titration curve of DMT–PDC is given in figure 1. The titration data as calculated, taking into consideration all feasible theoretical models, were compared with those experimentally obtained. The equilibrium patterns were chosen to lie between the observed and calculated data applying accurate statistical analysis involving the sum of squares of residuals. At this point, all protonation constants were kept constant, and the computer program MINIQUAD was applied for a second stage of refinement. The results show the formation of $[Sn(Me)_2(PDC)]^{2+}$. After complete formation, the titration curve drift is associated with the ionization of the two hydroxyl groups of PDC after complex formation. Therefore, the whole titration data obtained fit a model involving the formation of $[Sn(Me)_2(HMI)]^{2+}$ and $[Sn(Me)_2(HMI,H_{-1})]^{+}$ for HMI ligand and three species $[Sn(Me)_2(PDC)]^{2+}$, $[Sn(Me)_2(PDC,H_{-1})]^{+}$, and $[Sn(Me)_2(PDC,H_{-2})]$ for PDC [35–41] as shown in scheme 2. Diorganotin(IV) compounds form complexes with various structures. It was concluded that diorganotin(IV) complexes are five coordinate (R_2SnL (L, tridentate ligand)) [42]. In our case PDC is tridentate ligand, so a trigonal bipyramidal structure is assumed as shown in scheme 2. The same finding was reported for diorganotin(IV)–mercaptocarboxylato complexes [43].

The estimation of the concentration distribution of various species in solution provides a useful picture of DMT binding in the biological system. The concentration distribution diagrams for dimethyltin complexes with PDC and HMI are shown in figure 2. The main species under physiological conditions are 11-1 for DMT–HMI and 11-2 for DMT–PDC at pH = 6 and pH = 8, respectively.

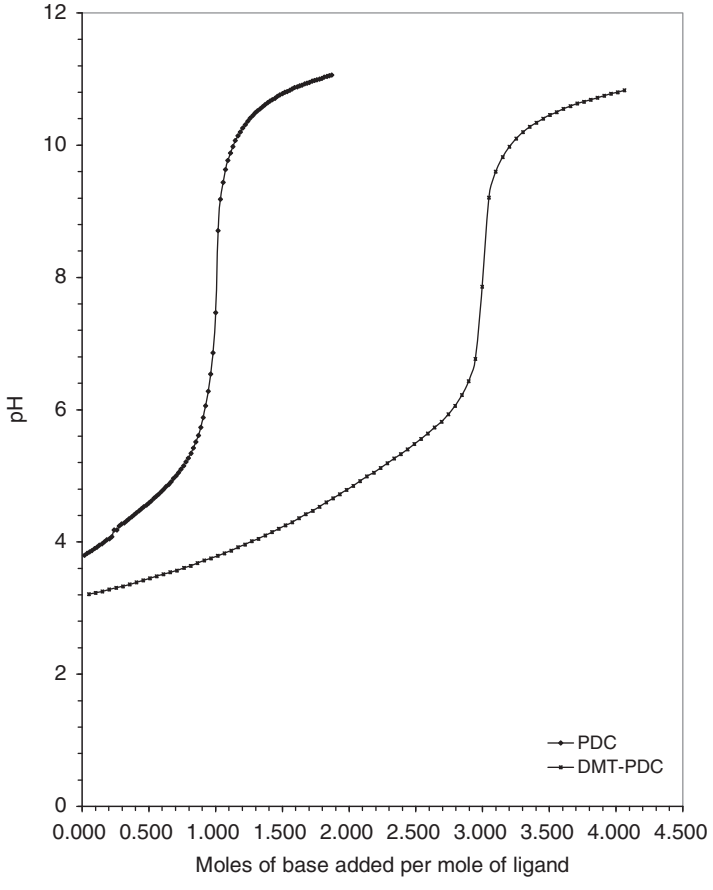
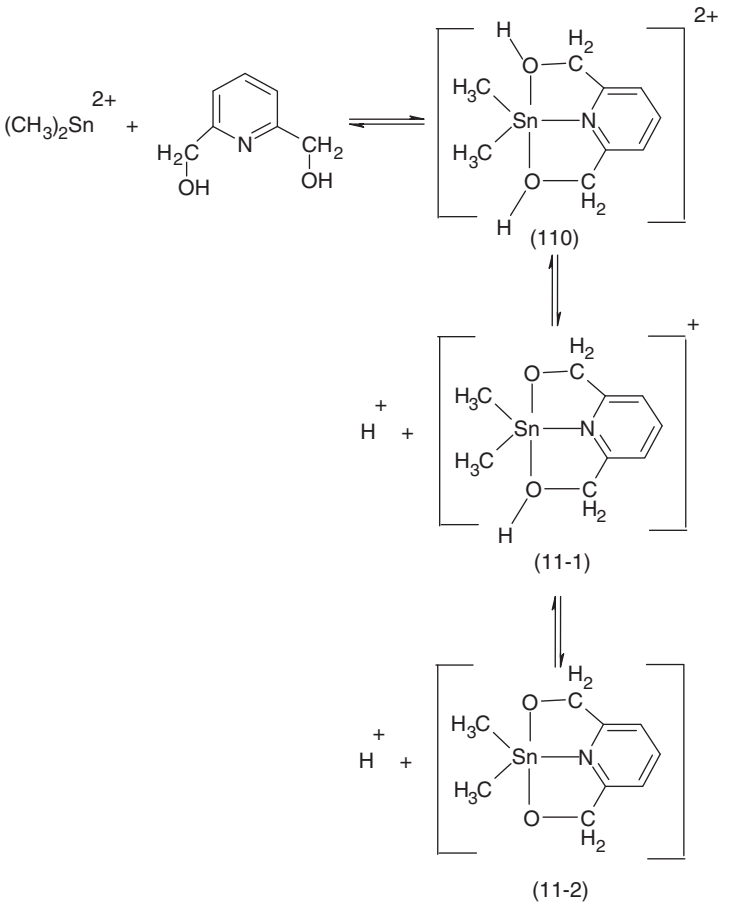


Figure 1. Potentiometric titration curves of dimethyltin with PDC.

3.2. *Effect of temperature*

Values obtained for the thermodynamic parameters ΔH°, ΔS°, and ΔG°, associated with protonation of PDC/HMI and its complex formation with DMT were calculated from the temperature dependence of the data in table 1. ΔH° and ΔS° were obtained by linear least-squares fit of $\ln K$ *versus* $1/T$ ($\ln K = -\Delta H^\circ/\mathrm{RT} + \Delta S^\circ/R$) leading to an intercept $\Delta S^\circ/R$ and a slope $-\Delta H^\circ/R$, where K is the equilibrium constant (figure 3). The main conclusions from the data can be summarized as follows.

1. All values of ΔG° for complexation are negative, indicating that the complexation reaction is spontaneous.
2. Negative values of ΔH° in reactions 4 and 5 show that the chelation process is exothermic, indicating that the complexation reactions are favored at low temperatures.
3. The large positive entropy values for both dimethyltin–PDC and dimethyltin–HMI complexes in reactions 3 and 6 indicate a release of water and breaking of hydrogen bonds.



Scheme 2. Proposed formation equilibria for complexes of PDC with DMT.

4. By comparing the change in entropy and free energy for reactions 4 and 5 (table 2), $-\Delta G_5^\circ > -\Delta G_4^\circ$ and $\Delta S_5^\circ > \Delta S_4^\circ$, attributed to complete neutralization of the positive charge of $(Me)_2Sn^{2+}$ by ionization of a second hydroxyl group.
5. The ΔS^0 values for reactions 3–7 are positive, indicating that increase in entropy by the release of bound solvent on chelation is greater than the decrease resulting from the chelation process itself. This may happen because solvent molecules arranged in an orderly fashion around the ligand and the metal ion have acquired a more random configuration on chelation. This is referred to as a gain in configurational entropy.
6. Complexation reactions 3 and 6 between DMT and PDC and HMI are surprisingly endothermic with ΔH values of 56.7 and 67.9 kJ mol^{-1}, respectively, similar to those found by Kramer [44] and El-Sherif *et al.* [28]. This can be interpreted by assuming that the enthalpy change is a net summation of two opposing effects, the exothermic complexation, and the endothermic liberation of ordered water of hydration, confirmed by large ΔS° (280 and 358 J K^{-1} mol^{-1}) for reactions 3 and 6, respectively.

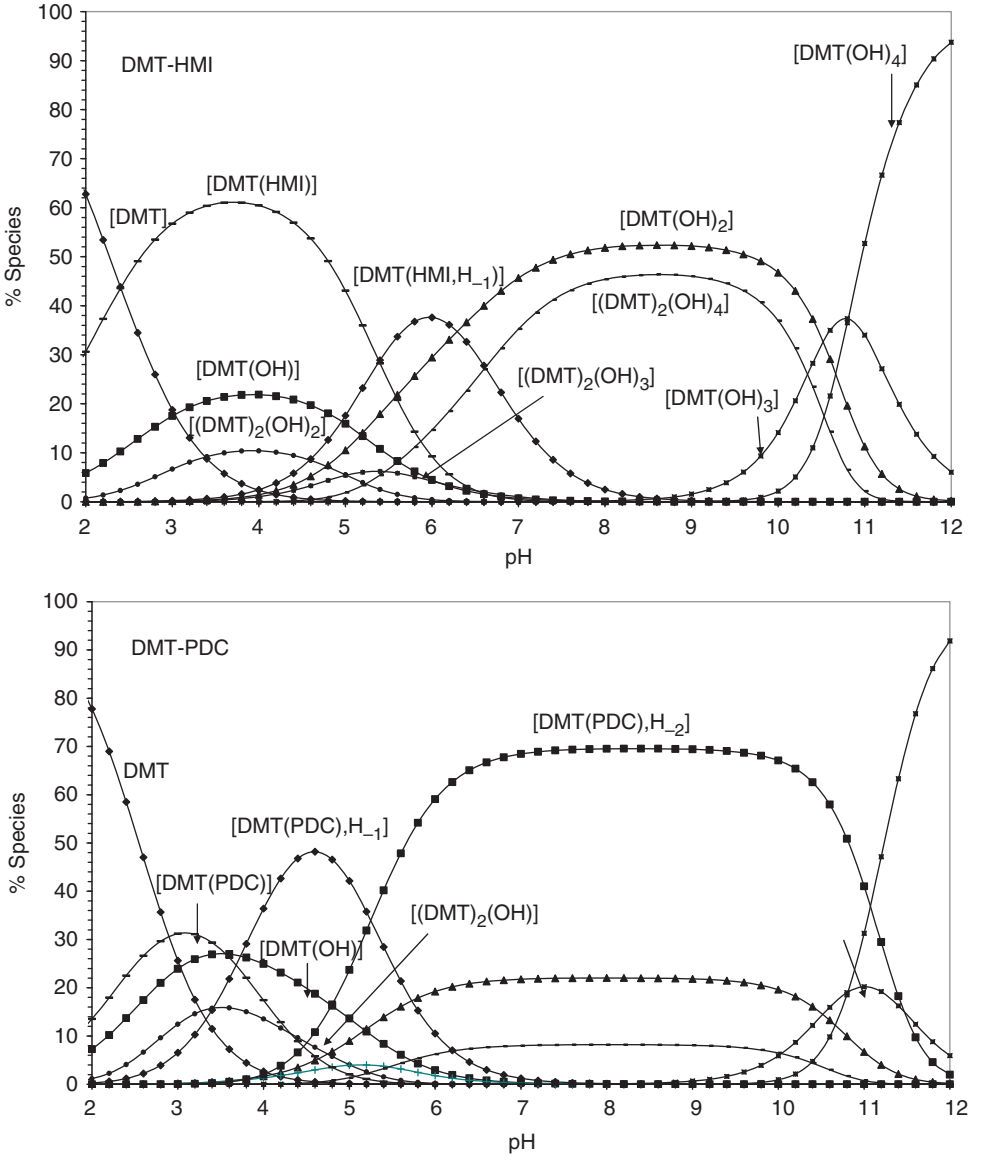


Figure 2. Concentration distribution of various species as a function of pH in the dimethyltin–HMI and dimethyltin–PDC system.

3.3. *Effect of solvent*

"Effective" or "equivalent solution" dielectric constants in proteins [45, 46] or active site cavities of enzymes [47] are small compared to that in bulk water. The estimates for the dielectric constants in such locations range from 30 to 70 [44–48]. Hence by using aqueous solutions containing 10–50% dioxane, one may simulate to some degree the situation in active site cavities [48] and extrapolate the data to physiological conditions. The solvent effect on the acid dissociation constants of a ligand [49] can be summarized

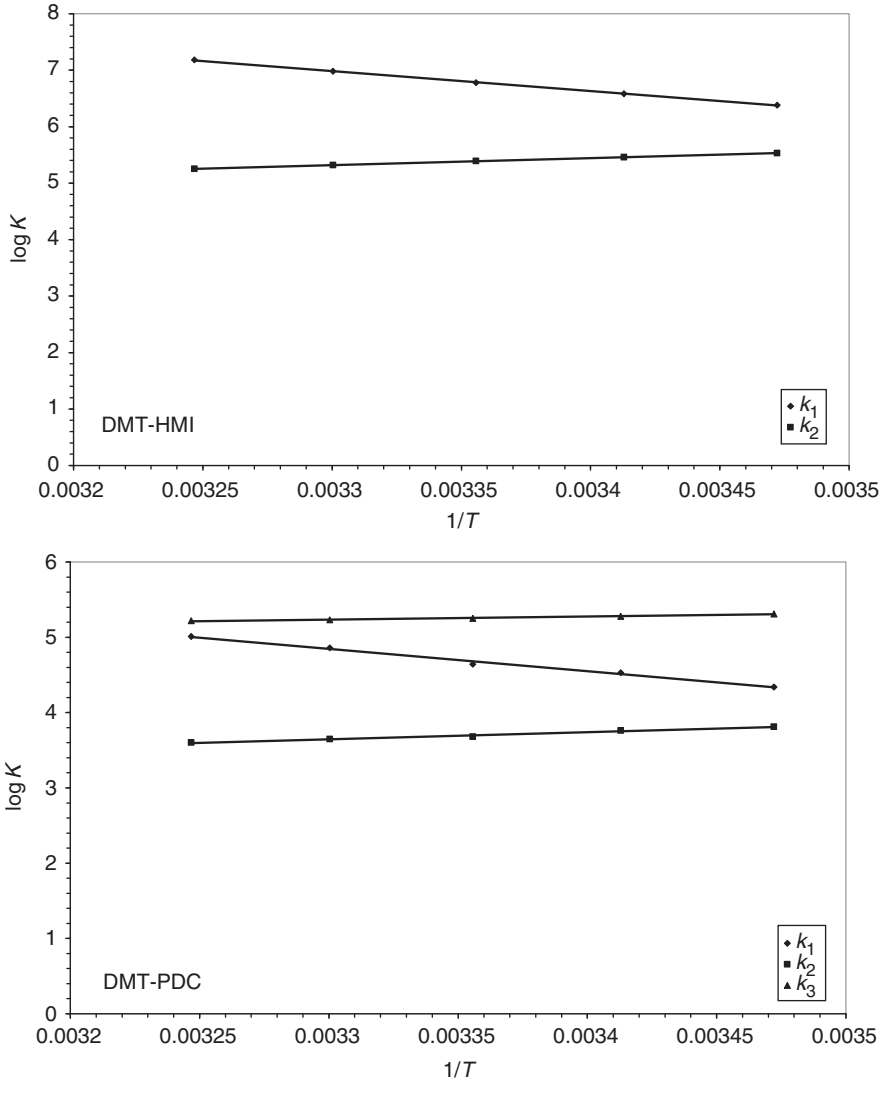


Figure 3. Effect of temperature on the formation constants of dimethyltin–HMI and dimethyltin–PDC systems.

as follows: (i) As the solvent dielectric constant decreases, the pK_a of the ligand increases and *vice versa*. (ii) On decreasing the extent of hydrogen bonding in water by an organic solvent, the proton-accepting properties of water increases, and consequently the pK_a of the ligand decreases. (iii) Increasing proton solvation by an organic solvent is accompanied by a decrease in the pK_a of ligand.

A careful examination of media effects on the equilibrium constants (table 3) reveals the following features: (1) pK_a (nitrogen) of PDC and HMI increases linearly with increasing percentage of organic solvent in the medium. This may be correlated with the ability of a solvent of relatively low dielectric constant to increase the electrostatic

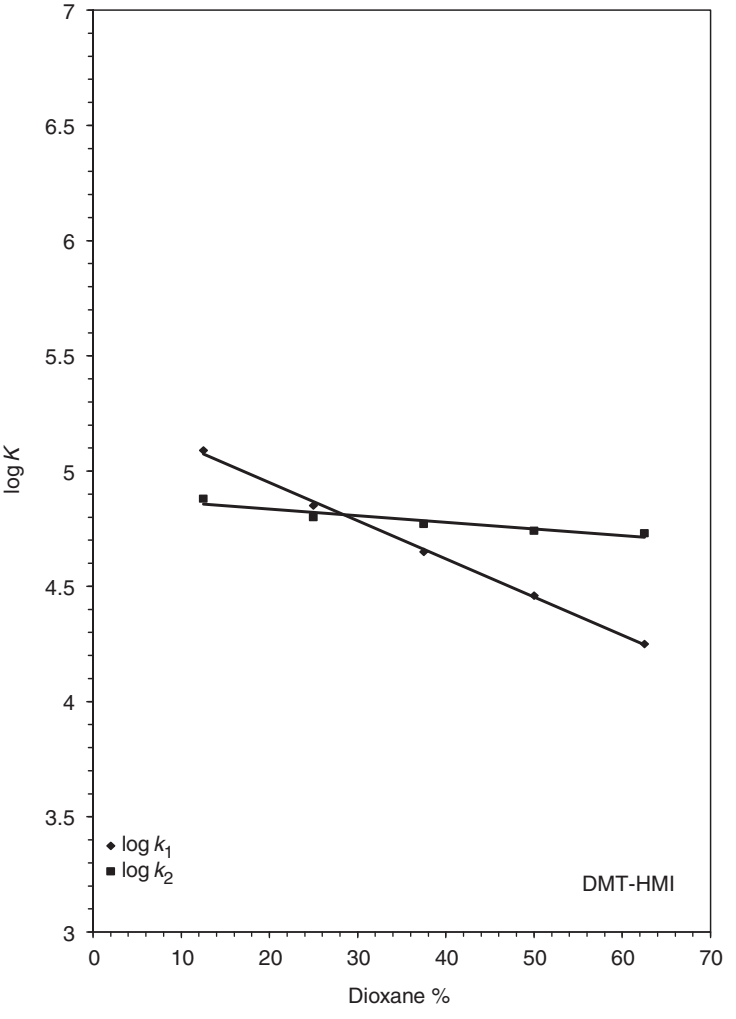


Figure 4. Effect of dioxane on the formation constants of dimethyltin–HMI systems. Curves: $\log K_1$ corresponds to 110 species and $\log K_2$ corresponds to 11-1 species.

forces between the proton and the ligand anion, and consequently the pK_a value increases. (2) Deprotonation constants of DMT complexes with PDC and HMI, calculated using equations 4 and 5, figures 4 and 5, decrease upon the addition of dioxane to an aqueous solution (table 3).

$$pK_1^H = \log \beta_{110} - \log \beta_{11-1} \tag{4}$$

$$pK_2^H = \log \beta_{11-1} - \log \beta_{11-2} \tag{5}$$

This can be explained by better solvation of hydrophobic species $(CH_3)_2Sn^{2+}$/ and $(CH_3)_2SnCl_2$ by dioxane resulting in lower complex stability. This behavior is in agreement with that proposed for alkyltin(IV) complexes with d-glucosamine [50], inosine, and inosine-5′-monophosphate [51].

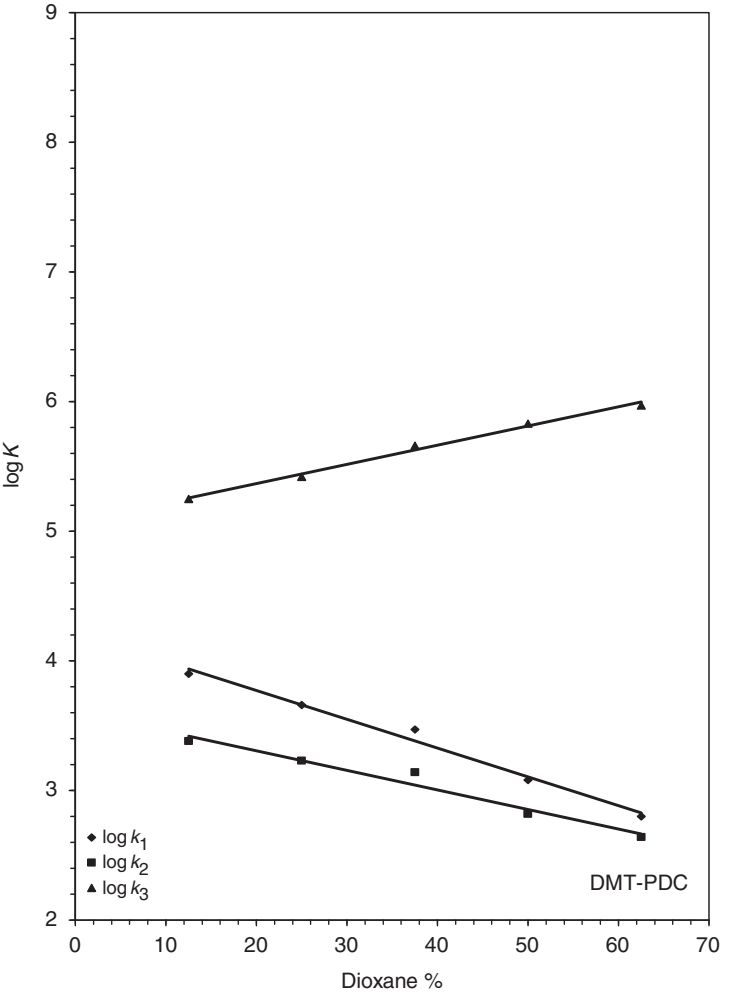


Figure 5. Effect of dioxane on the formation constants of dimethyltin–PDC systems. Curves: $\log K_1$ corresponds to 110 species, $\log K_2$ corresponds to 11-1 species, and $\log K_3$ corresponds to 11-2 species.

4. Conclusions

We describe the formation equilibria of dimethyltin complexes with PDC and HMI heterocyclic alcohols. Traditionally, water has been considered as the solvent to represent biological conditions. Although this is generally true, a lower polarity has been detected in some biochemical micro-environments, such as active sites of enzymes and side chains in proteins, simulated better by water/dioxane mixtures. Consequently, a study of dimethyltin with PDC and HMI complex formation equilibria in dioxane–water solutions of different compositions could be of biological significance. The formation of dimethyltin complexes with PDC and HMI is more favored in biological environments of lower dielectric constant.

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