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Physico-Chemical Studies of σ-bonded-dialkyltin(IV) Cations with N-(cyclohexyl)-2-Mercaptoacetamides

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In the present work, the physico-chemical characteristics of some σ-bonded dialkyltin(IV) cations with N-(cyclohexyl)-2-mercapto-acetamides were described.

INTRODUCTION

Incorporation of pH correction, in data obtained from the potentiometric titration of N-(cyclohexyl)-2-mercaptoacetamides with NaOH solution in dioxane-water (3 : 1, v/v) at 30 ± 0.1°C in a medium of constant ionic strength μ = 0.1 M (NaCl) gave the value of thermodynamic dissociation constant pk_D as 11.33 ± 0.03. Under similar conditions of solvent composition, temperature and ionic strength the thermodynamic stepwise formation constant of the complexes formed between dialkyltin(IV) cations {$(CH_3)_2SnCl_2$, $(C_2H_5)_2SnCl_2$, $(n\text{-}C_4H_9)_2SnCl_2$} and the above ligand. Using method of least squares gave log B_2 as 15.19 respectively. 14.79 and 14.49 respectively. This order is in accordance with Irving-Williams series. Derivatives of the above metals have also been synthesised and characterised.

EXPERIMENTAL

Several methods are available for the preparation of N-(cyclohexyl)-2-mercaptoacetamides[1–5]. As regards efficiency of the yield Sircar method[6] is the best and this was used for preparation of N-(cyclohexyl)-2-mercaptoacetamides. Dioxane was purified by a standard procedure[3]. Dioxane-water mixture (3 : 1, v/v) was used in preparing metal salt, ligand and NaCl solution.

Procedure

The solutions containing ligand (0.01 M) or ligand and metal ions (0.01 M and 0.0025 M) were titrated potentiometrically at μ = 0.1 M (NaCl) and 30 ± 0.1°C with 0.5 M and 0.1 M carbonate-free NaOH solutions. The changes in pH were recorded as a function of (OH^-) and suitable pH corrections were incorporated.

Calibration of Glass Electrode

According to Van Uitert and Haas[7], the pH meter reading (B) in an aqueous dioxane medium is related to the hydrogen ion concentration

$$-\log (H^+) = B + \log U_{H^\circ} \quad (1)$$

where the value of the correction factor, $\log U_H$, at a fixed temperature and composition of the medium is related to the activity coefficient by the relation

$$-\log U_H = \log U_{H^\circ} - \log (1/\nu\pm) \quad (2)$$

The value of $\log U_{H^\circ}$ was calculated by using an expression given by Rao and Mathur[8]. For the temperature dependence in dioxane-water mixture (3 : 1, v/v):

$$\log U_{H^\circ} = (0.007HO6)t + 0.828 \quad (3)$$

where 't' is the temp. in °C.

The value of $\log (1/\nu\pm)$ was determined either by interpolation of the plot of $\log (1/\nu\pm)$ vs. mean molality (M ±) in dioxane- water mixture (3:1, v/v) at 30° from the data given by Harned and Owen[9] for HCl or by employing the following polynomial given by Irving and Mahnot[10].

$$\log (1/\nu\pm)\ 30°C = 0.0933 + 1.0351n_2 + 0.3142n_2^2 + 6.6350n_2^3 \quad (4)$$

Where n_2 is the mol fraction of dioxane-recalculated with the atomic weight C = 12.01, H = 1.008.

The value of $\log (1/\nu\pm)$ turned out to be 0.920 and 0.9212 respectively by using the above two methods. In the present work the value 0.920 was employed for the evaluation of $\log U_H$ by using Eq. (2) {1.050 – 0.920 = 0.130}.

Calculation of Thermodynamic Dissociation Constant and Stepwise Formation Constant

The stoichiometric dissociation constant (P_{qD}) of N-(cyclohexyl)-2-mercaptoacetamides was calculated by the following expression:

$$-\log qD = -\log (H^+) + \log \frac{(HL)}{(NaOH) + (H^+) - (OH^-)} - 1 \quad (5)$$

where the correct pH was obtained by adding 0.130 to the pH meter reading (B).

The thermodynamic dissociation constant Pk_D was calculated from the relationship[9] given by Rao and Mathur.

$$Pk_D = Pq_D + 2 \log (1/\nu\pm) \quad (6)$$

Substituting the value of av. Pq_D (9.49 ± 0.03) and $2 \log (1/\nu\pm)$(1.84) the value of Pk_D turned out to be (11.33 ± 0.03).

The following equations were used to express the formation of 1 : 2 metal-ligand complexes in dioxane-water (3 : 1, v/v):

$$M^{2+} + L^- = ML^+; \quad q_1 = \frac{[ML^+]}{[M^{2+}][L^-]} \quad (7)$$

$$ML^+ + L^- = ML_2; \quad q_2 = \frac{[ML_2]}{[ML^+][L^-]} \quad (8)$$

The values of log q_1 and q_2 for the complexes of dialkytin(IV) cations with N-(cylohexyl)-2-mercoptoacetamides system were computed from the data for $\bar{n}$ and $\bar{L}$, using the Irving-Rossotti[11] equation and the following expressions:

$$\log (L^-) = \log (L_0) - (NaOH) - (H^+) + (OH^-) - \log \frac{(H^+)}{q_D} \qquad (9)$$

$$\bar{n} = (L_0) - (L^-)\frac{(H^+)}{q_D} + 1 \qquad 1/(M_0) \qquad (10)$$

$$\frac{\bar{n}}{(n-1)(L^-)} = \frac{(2-\bar{n})(L^-)}{(n-1)} \qquad q_1q_2 - q_1 \qquad (11)$$

where (L_0), (M_0) are total ligand and metal concentrations and $\bar{n}$ is the formation number calculated from the pH data obtained prior to the precipitation of metal complex during the titration of the metal-ligand mixture with NaOH.

Calculation of Stepwise Formation Constants by Interpolation at Half $\bar{n}$ Values and Correction Terms Method

Interpolation at half $\bar{n}$ values: In a system, where N = 2, the formation curve, between $\bar{n}$ and PL remains symmetrical about the mid-point. Interpolation of $\bar{n}$ at 0.5 and 1.5, respectively, On the PL-axis will directly give the value of q_1 and q_2. The method, however, is not accurate because of the two reasons:

(i) Only two points, viz., at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ are taken into consideration and the rest of the points are omitted, and

(ii) Smoothening of the curve $(\bar{n}, PL)$ is essential.

Correction term method: The method was suggested by Irving and Rossotti[11] for the calculation of stoichiometric stepwise formation constants, q_1 and q_2. According to this method,

$$\log q_1 = P^{L_1-d} + y \qquad 12(d)$$

$$\log q_2 = P^{L_1+d} - y \qquad (13)$$

where the value of y, the 'correction term', is given by the expression

$$y = \log \frac{2(1-d)}{d + \sqrt{d^2 + 4(1-d^2)q_2/q_1}}$$

The magnitude of y depends upon the value of d and the ratio q_2/q_1.

If P^{L_1-d} and P^{L_1+d} are two scattered points on the smoothened formation curve, disposed symmetrically about the mid-point, then the following expression is applicable to the curve.

$$\Delta P^{L_d} = P^{L_1-d} - P^{L_1+d} = \log \frac{[q_1]}{[q_2]} + 2y \qquad (15)$$

By using eqs. corresponding values of y and ΔPL have been calculated for nine values of d for each of series of values of q_1/q_2 ranging from 10^5 to 10^{-2}. The relationship between y and ΔPL was shown graphically for which the necessary data were given by Irving and Rossotti[11].

The correction term method was applied to pairs of values ($\bar{n}$, PL) symmetrically disposed about the mid-point. The process was repeated for several values of d and the mean value of the calculated stepwise formation constants was taken. The formation curves for metal chelates of N-(cyclohexyl)-2-mercaptoacetamides was shown in Figs. 1–3.

The thermodynamic stepwise formation constants were then computed from the relationship[7]

$$\log k_1 = \log q_1 + 4 \log (1/\nu \pm)$$

$$\log k_2 = \log q_2 + 2 \log (1/\nu \pm)$$

The values of $\log k_1$, $\log k_2$ and $\log B_2$ have been listed in the Table below.

THERMODYNAMIC STABILITY CONSTANTS OF $(CH_3)_2SnCl_2$, $(C_2H_5)_2SnCl_2$ AND $(n\text{-}C_4H_9)_2SnCl_2$ WITH N-(CYCLOHEXYL) 2-MERCAPTOACETAMIDE SYSTEMS

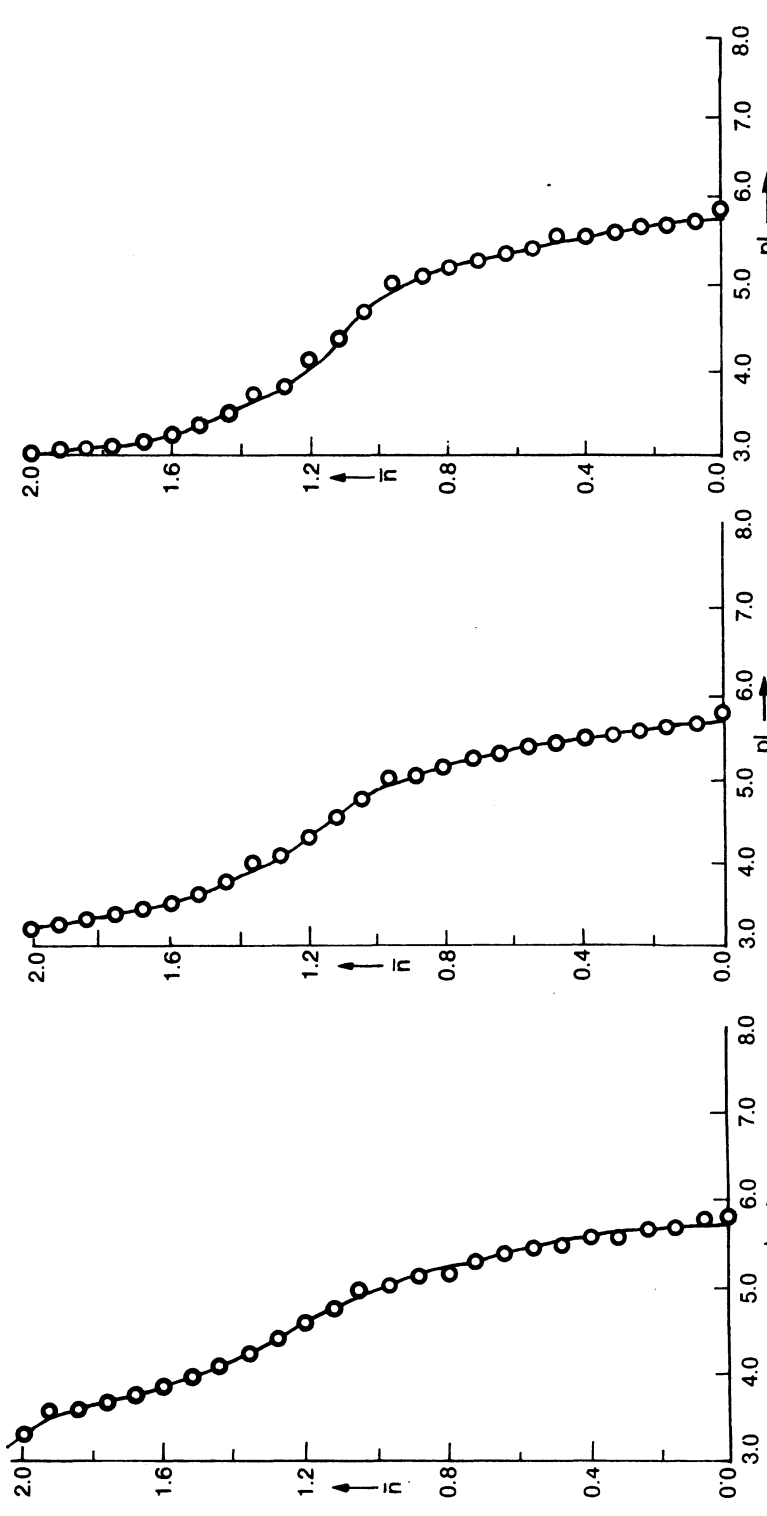
Solvent: Dioxane-Water Mixture (75 per cent v/v);
μ = 0.1 M NaCl; Temp. = 30 ± 0.1°C.

	$(CH_3)_2SnCl_2$	$(C_2H_5)_2SnCl_2$	$(n\text{-}C_4H_9)_2SnCl_2$
	Interpolation at Half $\bar{n}$ Values		
$\log k_1$	9.18	9.11	9.15
$\log k_2$	5.83	5.51	5.21
$\log \beta_2$	15.01	14.62	14.36
	Correction Term Method		
$\log k_1$	9.16	9.18	9.17
$\log k_2$	5.97	5.59	5.32
$\log \beta_2$	15.13	14.77	14.49
	Least-Squares Method		
$\log k_1$	9.14	9.09	9.16
$\log k_2$	6.05	5.70	5.33
$\log \beta_2$	15.19	14.79	14.49

RESULTS AND DISCUSSION

Dissociation constant of N-(cyclohexyl)-2-mercaptoacetamide (Pq_D = 9.49 ± 0.03) is lower than expected. This is because of the fact that in the saturated non-planar, chair planar conformation of the ligand, the mercaptoacetamido group is at the axial position of the ring. So the C–OH group is linked to one of the sulphur lone pairs of electrons through hydrogen bonding; as a consequence of this SH proton ionises more readily than could be anticipated.

It forms much weaker complexes with σ-bonded dialkyltin dichloride, as shown by the following values of $\log q_1$ and $\log q_2$.



Formation curve of $(CH_3)_2SnCl_2$–(C_6H_{11})–NHCOCH$_2$SH System in dioxane- water mixture (75%) at 30 ± 0.1°C (μ = 0.1) NaCl.

Fig. 1

Formation curve of $(C_2H_5)_2SnCl_2$–(C_6H_{11})–NHCOCH$_2$SH system in dioxane- water mixture (75%) at 30 ± 0.1°C (μ = 0.1) NaCl.

Fig. 2

Formation curve of $(n\text{–}C_4H_9)_2SnCl_2$–$(C_6H_{11})$NHCOCH$_2$SH system in dioxane-water mixture (75%) at 30 ± 0.1°C (μ = 0.1) NaCl.

Fig. 3

$(CH_3)_2SnCl_2$, $\log q_1 = 5.46$, $\log q_2 = 4.21$,

$(C_2H_5)_2SnCl_2$, $\log q_1 = 5.41$, $\log q_2 = 3.86$,

$(n\text{-}C_4H_9)_2SnCl_2$, $\log q_1 = 5.48$, $\log q_2 = 3.49$.

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ERRATA

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