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ORIGINAL ARTICLE

Thermodynamic study of complex formation process of free base *meso*-tetraphenylporphyrins with dimethyl and dibutyltin(IV) dichloride: a new algorithm for a single thermometric titration

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Abstract A novel, fast and easy single sample measurement has been developed based upon temperature dependence of equilibrium constant in order to determine the enthalpy and entropy changes of a complexation reaction using spectrophotometric temperature titration. The method can be used in determination of the formation constant and thermodynamic parameters of the solutions that there are difficulties in their titration where volatile compounds are studying. Knowledge of component spectra is not required for the analysis. The formation constants of the interactions of ß-di and tri-brominated *meso*-tetraphenylporphyrins, and *meso*-tetrakis(4-methylphenyl) and (4-methoxyphenyl) porphyrins with Me_2SnCl_2 and Bu_2SnCl_2, have been determined in range of 0–25 °C utilizing van't Hoff relation, mass balance and equilibrium constant equations by an iterative least squares method with ΔH^0 as adjustable parameter. The outputs of analysis are the equilibrium constants, ligand and adduct spectral profiles, their concentrations as a function of temperature, the adjusted values of the standard enthalpy ΔH^0, and entropy ΔS^0 changes. The order of formation constants of the resulting 1:1 complexes decreased with increasing number of bromide substituents and increased with adding methyl and methoxy groups, and vary as $H_2T(4\text{-}CH_3O)PP > H_2T(4\text{-}CH_3)PP > H_2TPP > H_2TPPBr_2 > H_2TPPBr_3$ and $Me_2SnCl_2 > Bu_2SnCl_2$.

Keywords Complexation · Temperature titration · Enthalpy · Entropy · Porphyrin · Organotin(IV) · Iterative algorithm

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Introduction

Synthetic porphyrins have long been of great interest because of their application as photosynthetic mimics [1], photodynamic therapy agents [2–4], electrocatalysts [5], DNA binding agents [6–8], functional models of cytochrome P-450 [9], cancer treatment [10], electrochemical and optical sensors [11, 12], and also as light-energy conversion like solar cells [13–15]. On the other hand, interaction of various *meso*-tetraarylporphyrin macrocycles with different σ- and π-acceptors has been extensively investigated [16–23]. In these complexes, the porphyrin core was distorted and acted as an electron donor to the central atom of the acceptors by the pyrroleninenitrogens.

Besides, molecular interactions of organotin(IV) halides with a variety of uni- and bidentate nitrogen donor ligands have been studied [24–27]. Recently, more attention has concentrated on the antitumor properties of organotin(IV) halides, and a large number of studies have been made concerning the interactions of these compounds with biological systems [28–32]. Studies of compounds of the type R_2SnX_2L, where L is a bidentate N-donor ligand showed that increasing stability is thought to reduce activity by hindering the dissociation of the ligand which is necessary for binding between tin and DNA [33]. The molecular interactions of tetraarylporphyrins with π-acceptor molecules such as nitroaromatic systems [34, 35], tetracyanoethylene [17] and 2,3-dichloro-5,6-dicyanobenzoquinone have been studied [36].

Among the several physicochemical methods for studying the complexation equilibria in solution, spectrophotometry (i.e., UV–Vis) under broad experimental conditions and with subsequent computer treatment of experimental data is a very powerful method. Spectrophotometric methods are in general highly sensitive and as

such are suitable for studying chemical equilibria in solution. When the components involved in the chemical equilibrium have distinct spectral responses, their concentrations can be measured directly, and the determination of equilibrium constant is trivial. However, in many cases, the spectral responses of two and sometimes even more components overlap considerably and analysis is no longer straightforward. Several spectrophotometric methods have been developed to determine the equilibrium constants of chemical processes [37]. Occasionally, problems arise because of strong overlapping of chemical components involved in equilibrium and some uncertainties from using some complex mathematical algorithms, to solve such problems [38–40].

In view of these encouraging results, this led us to investigate the solution equilibria of organotin(IV) halide complexes with a number of *meso*-tetraphenylporphyrins. In the present work we investigated the thermodynamics of the adduct formation, such as standard enthalpy and entropy change on complexation, which are derived from the temperature dependence of the formation constant, for the interaction of dimethyl and dibutyltin(IV) dichloride with H_2TPP (*meso*-tetraphenylporphyrin), H_2TPPBr_3 (ß-tribrominated *meso*-tetraphenylporphyrin), H_2TPPBr_2 (ß-dibrominated *meso*-tetraphenylporphyrin), $H_2T(4\text{-}CH_3)PP$ (*meso*-tetrakis(4-methylphenyl)porphyrin), and $H_2T(4\text{-}CH_3O)PP$ (*meso*-tetrakis(4-methoxyphenyl) porphyrin) in chloroform as a solvent.

The conventional methods for the calculation of thermodynamic parameters of the complexation reactions, as we done in our previous work, are based on concentration titration in each temperature that there are some disadvantages as it is a time consuming procedure, grater amount of materials will be needed and some inaccuracy will be existed in titration of volatile compounds [22, 41].

For the first time we design and introduce an algorithm for the calculation of the thermodynamic constants and spectral profiles of component involved in the complexation reaction. This new algorithm, as shown in this work, is an efficient chemometric technique based on iterative least-squares minimization for spectrophotometric study of one-step complex formation with known stoichiometry, to determine thermodynamics in a single solution and without any knowledge of component spectra (any advance information).

Theory of proposed algorithm

The spectra recorded at different temperature can be expressed as a matrix, **D**. Each element of the matrix is indicated as d_{ij}, where the index, i, refers to the temperature for the rows and the wavelength of the measurement is the index, j, for the columns. The absorbance at any temperature and wavelength, d_{ij}, will be the sum of the contributions from the n components if the spectroscopic conditions are satisfied for the Beer–Lambert relationship to hold (narrow slit width, low stray light):

$$d_{ij} = \sum_{k=1}^{n} c_{ik} a_{kj} \tag{1}$$

where c_{ik}, in absorbance units, is the concentration of the kth component at the ith temperature and a_{kj}, is the spectrum normalized to unit concentration of the kth component at the jth wavelength. The relationship of Eq. 1 can be conveniently addressed as a matrix product:

$$\mathbf{D} = \mathbf{CA} \tag{2}$$

where **C** contains the temperature-dependent distribution curves for n components in its columns and **A** contains the absorption spectra of these components in its rows.

Considering a measurement of **D**, the task of data analysis is to decompose the matrix into its factors **C** and **A**, which can be utilized for subsequent identification and quantitation of the sample components. To obtain a unique and best fit solution, the columns of **C** must be linearity independent.

Consider the equilibrium expression of the one step complex formation:

$$\mathrm{M} + \mathrm{L} \rightleftarrows \mathrm{ML} \tag{3}$$

From the complex formation equilibriums it is clear that the total concentration of metal and ligand is constant. So, the mass balances of the system in different mole ratios of metal–ligand can be written as:

$$C_{\mathrm{L}} = [\mathrm{L}] + [\mathrm{ML}] \tag{4}$$

$$C_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{ML}] \tag{5}$$

The thermodynamic relation between the temperature and the equilibrium constant is the final constraint, which produces a unique solution. The equilibrium concentrations of the components in each temperature are related by the law of mass action [33, 42]:

$$K_F(T) = \frac{[\mathrm{ML}]_{(\mathrm{T})}}{[\mathrm{M}]_{(\mathrm{T})} \cdot [\mathrm{L}]_{(\mathrm{T})}} \tag{6}$$

Assuming the dependence of the formation constant $K_F(T)$ on temperature according to the van't Hoff equation:

$$\frac{\mathrm{d}\ln K_{\mathrm{F}}(T)}{\mathrm{d}(1/T)} = \frac{-\Delta H^0}{R} \tag{7}$$

where ΔH^0 is the molar enthalpy change, $R = 8.314$ J mol^{-1} K^{-1}, is the universal gas constant, and T is the temperature in Kelvin.

One of the distinguishing characteristic of the temperature-dependent data is the interdependence of the

distribution curve of the components involved, where the concentration of the free metal at a given temperature, as a combination of Eqs. 4–6, is given by:

$$[\mathrm{M}] = \frac{(\mathrm{KC_M} - \mathrm{KC_L} - 1) + \sqrt{(-\mathrm{KC_M} + \mathrm{KC_L} + 1)^2 + (4\mathrm{KC_M})}}{2K_\mathrm{F}(T)} \tag{8}$$

where $K_F(T)$ is the stability constant, and the concentration of free ligand is given by:

$$[\mathrm{L}] = \frac{\mathrm{C_L}}{(1 + K_\mathrm{F}(T)[\mathrm{M}])} \tag{9}$$

Finally, the concentration of 1:1 adduct is:

$$[\mathrm{ML}] = K_\mathrm{F}(T)[\mathrm{L}][\mathrm{M}] \tag{10}$$

The equilibrium concentration of ligand at different temperature can formed a column vector [L] and it is referred to the concentration profile of the ligand species. Assume that ligand and complex are the absorptive species in the measured wavelength range and in comparing with most real systems the metal ion species is not considered as an absorbing component. Thus, we have concentration matrix, **C**, with two columns, [L] and [ML]. In the cases that the under study metal ion species is absorbing (e.g., metalloporphyrins), a concentration matrix, **C**, with three columns, [L], [ML] and [M], would be expected.

Accorded with the linearly independent model of the distribution matrix, **C**, all which is needed to specify the elements in this matrix, is the ΔH^0 of the complex species formation in the system. According to Eq. 2, it can be written:

$$\hat{\mathbf{A}} = \mathbf{C}^{-1}\mathbf{D} \tag{11}$$

Given the stability constant, $K_F(T)$, or the concentration profile of two absorptive species, the pure absorption spectrum of each component can be obtained by means of least square regression:

$$\hat{\mathbf{A}} = \left(\mathbf{C}^T\mathbf{C}\right)^{-1}\mathbf{C}^T\mathbf{D} \tag{12}$$

which minimizes the squared error between the actual and calculated data matrices as shown in Eq. 13.

$$\mathbf{R} = \sum_i \sum_j \left(d_{ij} - \hat{d}_{ij}\right)^2 \tag{13}$$

where **R** is residual matrix and post multiplying of $\hat{\mathbf{A}}$ by **C** give:

$$\hat{\mathbf{D}} = \hat{\mathbf{A}}\mathbf{C} \tag{14}$$

An important advantage provides by means of the overdetermining the matrix C is that no advance thermodynamic information about the complexation processes of the under study system is required. The value of residual matrix obtained by the mentioned procedure depends on the correct definition of ΔH^0 used to build **C**. Choosing the closer amounts of ΔH^0 to the actual value, the smaller residual error, R, will be obtained. Consequently, the optimum value of ΔH^0 was found by minimizing **R** using simplex or a more sophisticated method like Levenberg–Marquardt algorithm. The Levenberg–Marquardt algorithm contains elements of both the steepest descent and Gauss–Newton methods [43, 44], but converges more rapidly than both of them. The Marquardt algorithm behaves like a steepest descent method under conditions for which the latter is efficient, that is, far from minimum. Close to the minimum, it behaves like the Gauss–Newton method, again under conditions where the latter efficient. The Marquardt programuses numerical differentiation so that analytical derivatives need not be provided by the user, as required in some Gauss–Newton programs [45, 46]. In practice, the solution is found by a simple search procedure. ΔH^0 is given as an arbitrary value, for which a trial formation constant in each temperature is calculated (Eq. 7). This is used to calculate trial concentration profiles (Eqs. 8–10), which are combined to a trial equilibrium constant. Each trial concentration distribution matrix also determines trial spectral responses (Eq. 11). Post multiplying of trial concentration distribution and trial spectral responses matrices determines $\hat{\mathbf{D}}$ (Eq. 14), and therefore **R** will be calculated from Eq. 13. The procedure is repeated for various initial values of ΔH^0 to obtain a more accurate minimized **R**.

Experimental

Reagents

Benzaldehyde, *N*-bromosuccinimide (NBS) and *para*-substituted benzaldehydes (Merck and Fluka) were used as received. Pyrrole (Fluka) was distilled before use. Propionic acid and chloroform (Merck) employed for the synthesis and the purification of porphyrins were used as received. Me_2SnCl_2 and Bu_2SnCl_2 (Merck) was used without further purification. Chloroform solvent for UV–Vis measurements was distilled over K_2CO_3 before use.

Apparatus

Absorption spectra were recorded on a Shimadzu (UV-1650PC) UV–Vis spectrophotometer using the Shimadzu UV–Vis ChemStation software for data acquisition. A quartz cuvette of 10 mm optical path was used for all

measurements. The temperature of the cell housing kept constants by a Shimadzu cell positioned (CPS-240A) thermostat.

Computer hardware and software

All absorbance spectra were digitized at one nanometer intervals in the wavelength range 320–720 and over a temperature range of 0–25 °C at 2.5 °C intervals. All calculations were run on a Toshiba computer with Pentium IV as central processing unit with windows Vista as operating system. The calculations were performed in the MATLAB (version 7.6, MathWorks, Inc.) environment.

Preparations

The free base *meso*-tetraphenylporphyrin (H_2TPP) was prepared and purified as reported previously [47]. $H_2T(4\text{-}X)PP$; $X = OCH_3$, CH_3 were prepared and purified by usual methods [48, 49].

H_2TPPBr_n; $n = 2$, 3 was prepared from H_2TPP and freshly recrystallized NBS according to the method reported by Bhyrappa and co-workers [50] with some modification.

Formation and purification of the free base porphyrins have been confirmed by 1H NMR spectroscopic data, as well as electronic spectral data (Tables 1, 2).

Spectroscopic measurements

In a typical measurement, excess folds of R_2SnCl_2 solution (0.02 M) in chloroform were added to 2.5 ml solution of each *meso*-tetraphenylporphyrin (10^{-5}–10^{-6} M) in chloroform. UV–Vis measurements were carried out by the thermal titration method at 0–25.0 ± 0.1 °C with 2.5 °C steps. UV–Vis spectra were recorded in the range of 320–720 nm approximately 10 min after raising each step in the temperature. The formation constants and other thermodynamic parameters of adduct formation were calculated by the algorithm described.

Table 1 UV–Vis data for the porphyrins in dichloromethane

	λ (nm)
H_2TPP	418, 515, 550, 590, 646
H_2TPPBr_2	423, 520, 595, 650
H_2TPPBr_3	427, 523, 599, 658
$H_2T(4\text{-}CH_3O)PP$	422, 516, 555, 648
$H_2T(4\text{-}CH_3)PP$	419, 515, 550, 649

Results and discussion

Spectral data analysis

Upon the addition of excess folds of R_2SnCl_2 (R = Me, Bu) to a solution of free base porphyrin in chloroform, the color changes to green. This changing in color is due to the interactions of R_2SnCl_2 with porphyrin. By addition of n-hexane to these green solutions, green powdered products were obtained slowly. Here, interactions of dimethyl- and dibutyltin(IV) dichloride with porphyrins were studied by means of UV–Vis spectrophotometry. Thus, we have conducted the thermal titration at constant concentration of porphyrins and R_2SnCl_2.

Since the interactions of R_2SnCl_2 with free base *meso*-tetraphenylporphyrins are very sensitive to temperature, the green color of the solution eventually changes to brown and returns to the primary color of free base porphyrin solution by increasing the temperature. So, these adduct formations are reversible and show a different order of stability with respect to temperature. For example, rising the temperature from 0 to 25 °C caused the large amount of $[(Me_2SnCl_2)H_2TPPBr_3]$ adducts to return to Me_2SnCl_2 and free bases H_2TPPBr_3, Fig. 1. Also the absorbance value increased at wavelength 426 nm that is corresponding to the λ_{max} of ligand in the absence of R_2SnCl_2. Dissociation of $[(R_2SnCl_2)H_2TPP]$ and $[(R_2SnCl_2)H_2T(4\text{-}CH_3)PP]$ at this temperature occurred to a lesser extent, while the $[(R_2SnCl_2)\ H_2T(4\text{-}CH_3O)PP]$ adduct showed a high degree of stability with respect to temperature. These observations supported by spectral variations in the course of temperature titration of the complexes.

Figure 2 shows typical titration spectra of ß-tri-brominated *meso*-tetraphenylporphyrin upon increasing addition of Me_2SnCl_2. Hypochromicity without any shift in Q-band were observed, which represents the existence of noncovalent interaction between R_2SnCl_2 and

Table 2 ^1H NMR data for the porphyrins and their assignments in $CDCl_3$

	β-pyrrole	*o*-phenyl	*m*- and *p*-phenyl	CH_3 and OCH_3	NH
H_2TPP	8.85 (s, 8H)	8.20–8.24 (m, 8H)	7.73–7.77 (m, 12H)	–	–2.77 (s, 2H)
H_2TPPBr_2	8.78 (m, 6H)	8.20–8.24 (m, 8H)	7.73–7.78 (m, 12H)	–	–2.83 (s, 2H)
H_2TPPBr_3	8.70–8.86 (m, 5H)	8.07–8.21 (m, 8H)	7.73–7.78 (m, 12H)	–	–2.85 (s, 2H)
$H_2T(4\text{-}CH_3O)PP$	8.86 (s, 8H)	8.10–8.14 (d, 8H)	7.30 (d, 8H)	4.09 (s, 12H)	–2.82 (s, 2H)
$H_2T(4\text{-}CH_3)PP$	8.85 (s, 8H)	8.08–8.11 (d, 8H)	7.50–7.57 (d, 8H)	2.65 (s, 12H)	–2.78 (s, 2H)

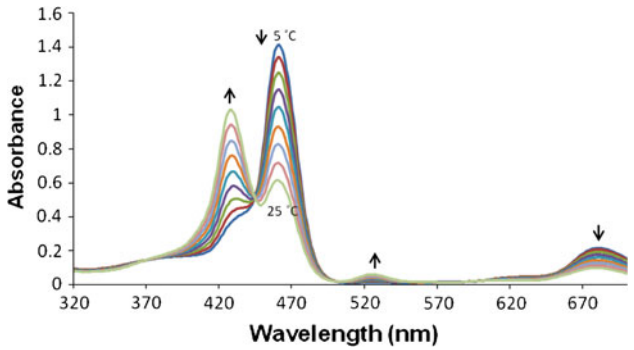

Fig. 1 Thermal dissociation spectra of Me_2SnCl_2–H_2PPBr_3 adduct: 30 µl of Me_2SnCl_2 (0.0196 M) + 2.5 ml of H_2TPPBr_3 (7×10^{-6} M) in chloroform. The temperature varied from 0 to 25 °C

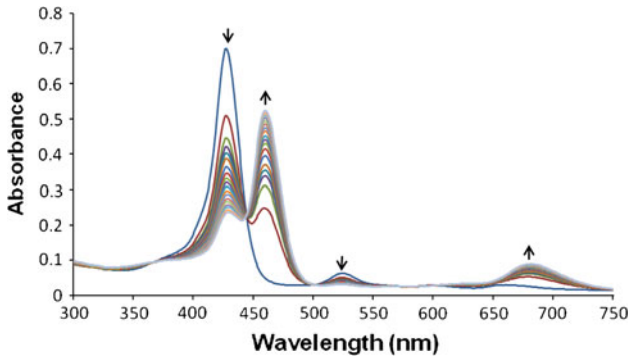

Fig. 2 Spectral titration of H_2TPPBr_3 (2×10^{-6} M, 2.5 ml) with Me_2SnCl_2 (0.02 M) in chloroform

meso-tetraphenylporphyrins. The appearance of four simultaneous isosbestic points in porphyrins spectra clearly indicates the existence of a simple equilibrium between free porphyrins and 1:1 porphyrin-R_2SnCl_2 complex.

Thermodynamic studies

The thermodynamic parameters are useful tools for investigating these interactions and understanding the relative stability of adducts. The equilibrium constants were determined at several temperatures by analyzing a single sample using temperature-dependent UV–Vis absorption spectra and the above algorithm. In a separate strategy the absorption spectra-mole ratio data were fitted to the different chemical models according to the stoichiometry of the resulting adduct between Lewis acids and porphyrins. The assumed models are: (1) formation of the 1:1 adduct; (2) formation of the 2:1 adduct; (3) simultaneous formation of the 1:1 and 2:1 adducts. The resulting data are processed by SQUAD [51, 52] and multivariate curve resolution methods. To fit the models to the experimental data, 20 points, is measured by the sum of squares of the deviations of the point calculated by the model from the related experimental points. For the proposed models, the formation of 1:1 adducts of acid to base showed the best fitting and the produced error sum of squares was between 10^{-2} and 10^{-3} which indicates the formation of 1:1 adducts is predominate.

The data of Tables 3 and 4 show that the equilibrium constants of the formed adducts from thermal titration, have an increasing trend from H_2TPPBr_3, H_2TPPBr_2, H_2TPP, $H_2T(4\text{-}CH_3)PP$, to $H_2T(4\text{-}CH_3O)PP$. For example, at 5 °C there is the following order of formation constants: Me_2SnCl_2–H_2TPPBr_3 < Me_2SnCl_2–H_2TPPBr_2 < Me_2SnCl_2–H_2TPP < Me_2SnCl_2–$H_2T(4\text{-}CH_3)PP$ < Me_2SnCl_2–$H_2T(4\text{-}CH_3O)PP$. The corresponding formation constants are varied as 4.33, 4.64, 5.28, 5.86 and 6.26 respectively.

On the other hand, the type of alkyl substituent, R on R_2SnCl_2 influences the interactions of the corresponding organotin(IV) dichloride with free base *meso*-tetraphenylporphyrins, and consequently their adduct formation constants. Thus, the greater stability constant for Me_2SnCl_2 reactions with respect to Bu_2SnCl_2's was observed. This is probably due to (1) steric hindrance arising in R_2SnCl_2 from R = Me to R = Bu make adduct formation unfavorable. (2) Better electron-withdrawing nature of the butyl group in comparing with the methyl reduces the acidic strength of the lewis acid and therefore decreases its interaction with the free base *meso*-tetraphenylporphyrins.

Van't Hoff plots of these formation constants, led to the other thermodynamic parameters ΔH^0 and ΔS^0. Tables 5 and 6 show the thermodynamic parameters obtained for the interactions of Me_2SnCl_2 and Bu_2SnCl_2 with ß-di and tri-brominated *meso*-tetraphenylporphyrins, and *meso*-tetrakis(4-methylphenyl) and (4-methoxyphenyl) porphyrins in chloroform.

The results in these tables show that the type and the number of substituents on the porphyrins skeleton and also the kind of organic substituents on acceptor significantly influence their affinities to interaction. Both the changes of free energies and the enthalpies of adduct formation become more negative through the series from H_2TPPBr_3, H_2TPPBr_2, H_2TPP, $H_2T(4\text{-}CH_3)PP$, to $H_2T(4\text{-}CH_3O)PP$, considerably, which indicates the stronger interaction in the sequence.

The ligand, H_2TPPBr_3, and its corresponding complex, [(Me_2SnCl_2) H_2TPPBr_3], calculated spectral profiles and their concentrations as a function of temperature are shown in Fig. 3. As it was expected, the concentration of the adduct decreases by increasing the temperature.

In Spite of the variations mentioned above which have decisive effects on the thermodynamics parameters of complex formation of *meso*-tetraphenylporphyrins and Me_2SnCl_2 and Bu_2SnCl_2, the $T\Delta S$ versus ΔH^0 plot shows an acceptably good linear correlation (Fig. 4) suggesting the existence of enthalpy–entropy compensation in the complexation reactions. The observed linear correlation between $T\Delta S$ and ΔH^0

Table 3 The formation constants log$K$ for Me_2SnCl_2 adducts with *meso*-tetraphenylporphyrins in $CHCl_3$ solvent

Adduct	Temperature (°C)								
	5	7.5	10	12.5	15	17.5	20	22.5	25
Me_2SnCl_2–H_2TPPBr_3	4.33 ± 0.01	4.21 ± 0.02	4.10 ± 0.01	3.98 ± 0.09	3.87 ± 0.02	3.76 ± 0.02	3.66 ± 0.07	3.55 ± 0.01	3.45 ± 0.06
Me_2SnCl_2–H_2TPPBr_2	4.64 ± 0.02	4.46 ± 0.01	4.29 ± 0.06	4.12 ± 0.05	3.95 ± 0.02	3.78 ± 0.03	3.62 ± 0.07	3.46 ± 0.05	3.30 ± 0.01
Me_2SnCl_2–H_2TPP	5.28 ± 0.04	5.06 ± 0.06	4.84 ± 0.08	4.64 ± 0.04	4.43 ± 0.01	4.23 ± 0.02	4.04 ± 0.03	3.84 ± 0.02	3.65 ± 0.03
Me_2SnCl_2–$H_2T(4\text{-}CH_3)PP$	5.86 ± 0.02	5.58 ± 0.09	5.31 ± 0.03	5.04 ± 0.01	4.77 ± 0.05	4.51 ± 0.01	4.25 ± 0.02	3.99 ± 0.06	3.75 ± 0.02
Me_2SnCl_2–$H_2T(4\text{-}CH_3O)PP$	6.26 ± 0.01	5.95 ± 0.03	5.64 ± 0.08	5.34 ± 0.03	5.04 ± 0.01	4.75 ± 0.002	4.46 ± 0.06	4.18 ± 0.03	3.90 ± 0.01

Table 4 The formation constants log$K$ for Bu_2SnCl_2 adducts with *meso*-tetraphenylporphyrins in $CHCl_3$ solvent

Adduct	Temperature (°C)								
	5	7.5	10	12.5	15	17.5	20	22.5	25
Bu_2SnCl_2–H_2TPPBr_3	3.61 ± 0.04	3.50 ± 0.07	3.40 ± 0.06	3.30 ± 0.05	3.20 ± 0.01	3.10 ± 0.07	2.99 ± 0.02	2.90 ± 0.01	2.81 ± 0.03
Bu_2SnCl_2–H_2TPPBr_2	3.99 ± 0.08	3.84 ± 0.01	3.70 ± 0.03	3.56 ± 0.08	3.43 ± 0.05	3.30 ± 0.01	3.16 ± 0.02	3.03 ± 0.01	2.90 ± 0.02
Bu_2SnCl_2–H_2TPP	4.68 ± 0.02	4.47 ± 0.01	4.25 ± 0.03	4.05 ± 0.04	3.84 ± 0.09	3.64 ± 0.01	3.45 ± 0.06	3.25 ± 0.02	3.06 ± 0.01
Bu_2SnCl_2–$H_2T(4\text{-}CH_3)PP$	5.21 ± 0.02	4.94 ± 0.03	4.66 ± 0.01	4.40 ± 0.05	4.13 ± 0.01	3.87 ± 0.02	3.62 ± 0.02	3.37 ± 0.01	3.12 ± 0.07
Bu_2SnCl_2–$H_2T(4\text{-}CH_3O)PP$	5.56 ± 0.03	5.26 ± 0.02	4.98 ± 0.01	4.69 ± 0.07	4.41 ± 0.08	4.14 ± 0.02	3.87 ± 0.05	3.61 ± 0.03	3.35 ± 0.04

Table 5 The overall thermodynamic parameters a Me_2SnCl_2 adducts with *meso*-tetraphenylporphyrins in $CHCl_3$ solvent

Adduct	ΔH^0	ΔS^0
Me_2SnCl_2–H_2TPPBr_3	−70 ± 3	−169 ± 6
Me_2SnCl_2–H_2TPPBr_2	−106 ± 6	−293 ± 13
Me_2SnCl_2–H_2TPP	−130 ± 5	−363 ± 8
Me_2SnCl_2–$H_2T(4\text{-}CH_3)PP$	−167 ± 3	−491 ± 12
Me_2SnCl_2–$H_2T(4\text{-}CH_3O)PP$	−187 ± 6	−554 ± 10

ΔH^0 (kJ mol^{-1}) and ΔS^0 (J K^{-1} mol^{-1})

Table 6 The overall thermodynamic parameters a Bu_2SnCl_2 adducts with *meso*-tetraphenylporphyrins in $CHCl_3$ solvent

Adduct	ΔH^0	ΔS^0
Bu_2SnCl_2–H_2TPPBr_3	−63 ± 3	−158 ± 10
Bu_2SnCl_2–H_2TPPBr_2	−86 ± 6	−233 ± 11
Bu_2SnCl_2–H_2TPP	−128 ± 2	−361 ± 9
Bu_2SnCl_2–$H_2T(4\text{-}CH_3)PP$	−165 ± 4	−490 ± 12
Bu_2SnCl_2–$H_2T(4\text{-}CH_3O)PP$	−175 ± 3	−522 ± 8

ΔH^0 (kJ mol^{-1}) and ΔS^0 (J K^{-1}mol^{-1})

values can be expressed as $T\Delta S = T\Delta S^0 + \alpha\Delta H^0$ with $T\Delta S^0 = 17.8$ kJ mol^{-1}, $\alpha = 0.966$ ($R^2 = 0.992$) for thermodynamics data of complex formation process of *meso*-tetraphenylporphyrins and R_2SnCl_2 (R = Me and Bu). The similar trends were reported from the thermodynamics study of the reactions with largely accompanying with changing in electrostatic interactions during the association reactions or host–guest phenomena [53–55]. The results indicate that the entropic effect comprise two components. The first component $T\Delta S^0$ is disproportion of enthalpy changes and the second is proportional to it. The proportionality constant α might be regarded as a quantitative measure of the enthalpy–entropy compensation. For thermodynamics data of complex formation process of *meso*-tetraphenylporphyrins and diaryltindichlorids, $\alpha = 0.966$, only about 3 % of the increase in ΔH^0 contributed to formation stability. The intercept with value close to zero $T\Delta S^0 = 17.8$ kJ mol^{-1} detects that the under study complex formation process, can be classified as enthalpy driven.

Conclusion

In this paper a new algorithm is reported to characterize the thermodynamics of a single sample of *meso*-tetraphenylporphyrins complex formation process by means of temperature titration spectrophotometry**.** The formation constant, equilibrium concentration profiles for the ligand, and adduct were determined. The thermodynamic parameters of the complex formation reactions were calculated from the dependence of formation constant on the temperature (van't Hoff equation). The iterative least-squares method appears to be well suited to the spectral resolution in a mixture of absorptive ligand, and complex. The thermodynamics data showed the complexation reaction is enthalpy driven and the type and the number of substituents in the both involved molecules, Lewis acid and porphyrin, has pronounced effect on the stability of the resulting complexes. For further studies, developing such algorithm to estimate the thermodynamic parameters of the formation

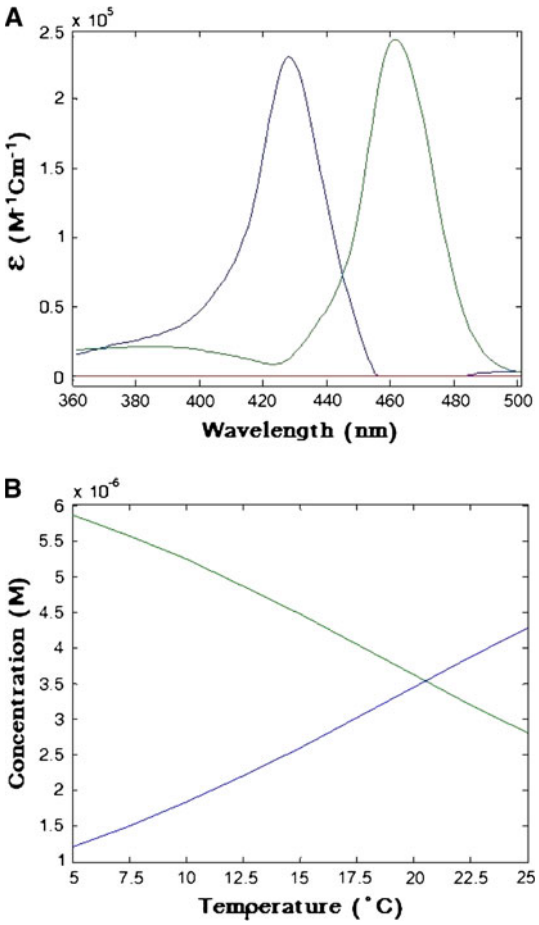

Fig. 3 Calculated **A** spectral profile and **B** concentration of H_2TPPBr_3 (*blue lines*), and [(Me_2SnCl_2) H_2TPPBr_3] (*green lines*)

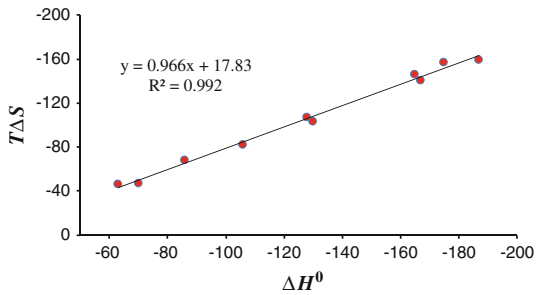

Fig. 4 $T\Delta S$ versus ΔH^0 for complex formation of *meso*-tetraphenylporphyrins and Me_2SnCl_2 and Bu_2SnCl_2

of the 2:1 adduct or simultaneous formation of the 1:1 and 2:1 adducts with temperature titration of a single sample would be desirable.

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