COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME : 31 ANNÉE : 1985

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculte des Sciences de l'Université d'Ankara

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(Received November 7, 1984 and Accepted April 26, 1985)

ABSTRACT

The composition and stability of the complex formed between diphenyltin dichloride, $Ph_2 SnCl_2$, and Na-3-alizarin sulphonate, alizarin red-S, have been studied spectrophotometrically in dilute ethanolic solutions. The effect of rise in the temperature, from 22–60° C, on the stability of the complex is recorded.

No direct change in colour was observed when dilute ethanolic solution of stannous chloride was added to alizarin red-S, but it was found that the complex requires 2–3 days to be formed.

Some physical properties of the red solid complex obtained from the reaction of $Ph_2 SnCl_2$ and alizarin red-S are reported.

INTRODUCTION

In a previous communication we reported[1] the preparations and properties of a number of diphenyltin dichloride complexes which are colourless air-stable solid adducts.

We wish to report now on the spectrophotometric investigation of the reaction of $Ph_2 SnCl_2$ and alizarin red-S in dilute ethanolic solutions, and in addition, the result of following up the stability of the formed complex on increasing the temperature and to illucidate the use of alizarin red-S in analytical determination of diphenyltin

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dichloride. The properties of the red-solid complex obtained from the reaction of the concentrated solutions in mixed ethanol-water as a solvent are also included.

The dyes 1, 2-dihydroxyanthraquinone, alizarin, and its Na- 3-alizarin-sulphonate, alizarin red-S, form coloured chelate complexes with many metallic ions, the latter being greatly soluble in water and organic solvents, is widely used in analytical chemistry of metal ions such as Th[2] and U[3].

We found that freshly prepared dilute ethanolic solution of alizarin red-S reacts immediately with a solution of diphenyltin dichloride in the same solvent forming coloured chelate complex. The complex formed does not change with time from the time of mixing up to 6 hours. No such immediate reaction, spectrophotometrically detectable, in the visible region, takes place under the same conditions with an ethanolic solution of stannous chloride and the chelating agent.

Materials and Methods. – All the spectral measurements in the region 600–300 nm were carried out using 1 cm quartz cells, on a Perkin-Elmer autosamplers for UV/VIS spectrophotometer model 555, equipped with liquid circulatory thermostat model U 3, operating at temperature range from –10° C to 65° C, with temperature stability of $\pm$ 0.02° C. Infrared spectrum was carried out, using KBr, in the region 4000–400 cm^{-1} on a Perkin-Elmer spectrophotometer model 398 equipped with a coesium iodide lens using KBr discs. Calibration of the instrument was carried out using polystyrene film.

Conductivities were measured using an electronic instrument model MC 1 MKV with balance indicator. Measurements were carried out using a conductivity cell of the diptype, having a cell constant of 0.1.

The freshly prepared ethanolic solutions were kept immersed in an electrically operating thermostat, maintaining a temperature at 25° C, before and during the experiments. Ph_2 $SnCl_2$, m.p. 42° C was obtained from BDH, $SnCl_2$, $2H_2O$ decomp. at 43° C was May and Baker grade. Alizarin red-S, Prolabo grade, was repeatedly crystallised from ethanol before use, m.p. $>$ 250° C. Solutions were prepared using analar analytical reagent ethanol 99.7 to 100 % v/v BDH grade. All the other solvents used were Analar grade.

Preparation of the Solid Complex. – When an orange red solution of alizarin red-S (0.36 g., 1.0 mmole) in ethanol-water mixture (100 ml) was mixed with a solution of Ph_2 $SnCl_2$ (0.34 g., 1.0 mole) in ethanol, direct change in colour to deep red was observed. After leaving the reaction mixture for few days, scarlet red powder was obtained, m.p. $>$ 250° C, Found: Cl, 10.3; Sn, 16.1 $C_{26}H_{19}$ Cl_2O_8 NaSSn requires: Cl, 10.1; Sn, 16.9 %. This complex is soluble in water to give a reddish solution,

The scarlet red solid is not extracted from chloroform, CCl_4, ethyl acetate, methyl cyanide, but can be extracted from tri-n-butyl phosphate and ethanol-water mixture.

RESULTS and DISCUSSION:

The reaction of ethanolic solutions of alizarin red-S with Ph_2 $SnCl_2$ gave a stable orange-red colour which can be successfully used for determing Ph_2 $SnCl_2$. A detailed study of the system was, threfore, undertaken.

The spectra of freshly prepared dilute ethanolic solutions of alizarin red-S and a mixture of equimolar solutions of alizarin red-S and Ph_2 $SnCl_2$ in the same solvent in the wavelength range 600–3000 nm at 22° C are given in Fig. 1. In this region of spectrum, ethanolic solution of Ph_2 $SnCl_2$ does not show any absorption band. From Fig. 1, it can be seen that λ_{max} for the chelating agent at 425 nm, as given by other authors[4,5], shifts on complex formation to 470 nm.

Effect of pH on the formation of the complex: – It is found that the formation of the complex is not affected by the change in the pH value between 3.6 and 5.2, below or above such pH range, the maximum absorption band shows a strong shift. A pH value of 4.6 has been chosen for all the measurements.

Composition of the complex in solution. – The composition of the complex was ascertained by the Job's method of continued variation[6], the molar ratio method[7] and by conductivity studies. These methods indicated the formation of a 1:1 complex. The complex obeys Beer's law in the concentration range from 0.5 to 6 x 10^{-4} M in ethanol. This indicates the possibility of analytically using alizarin red-S for quantitative determination of Ph_2 $SnCl_2$. The calibration curve may be extended to a wider concentration range, how-

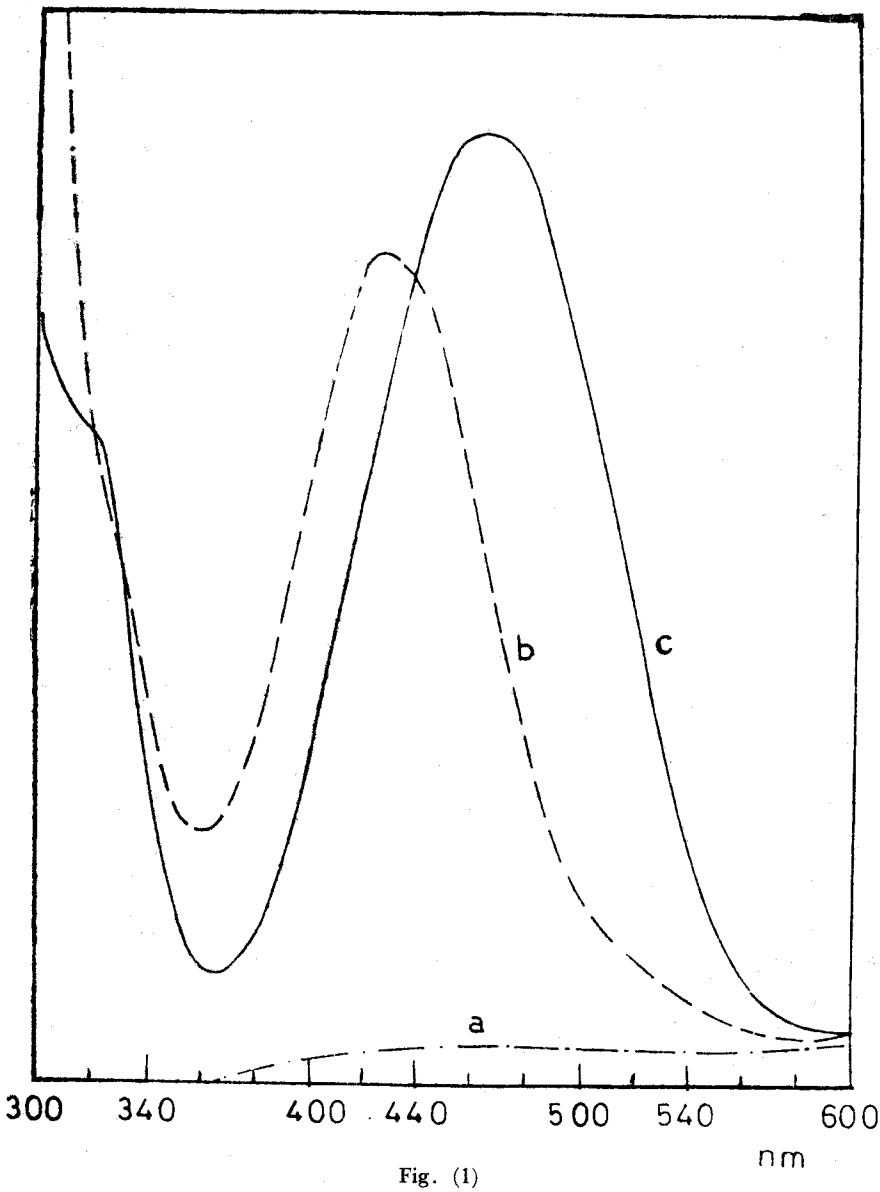

Fig. (1)

ever, the solid complex begins to precipitate above a limited concentration. It is reported that alizarin red-S forms red complex with tungsten, containing two molecules of the reagent for one metal atom.[8]

Molar absorptivity and reproducibility. – The molar absorption of the complex at λ_{max} 470 nm equal 11 x 10^3. Absorbance measurements with 10 identical samples containing 17.0 μg Ph_2 $SnCl_2$/ml. resulted in a mean absorbance of 0.56 with a standard deviation of 0.03. It was found that the ethanolic solution used of alizarin red-S should be freshly prepared, as the absorbence of such solution is only constant for few days, ~ 2, after which an increase in the absorbance was observed. This may be attributed to the interaction between the chelating ligand and the solvent. On mixing equimolar solutions of Ph_2 $SnCl_2$ and alizarin red-S in THF as a solvent λ_{max} was shifted from λ_{max} 430 nm in case of the free chelating agent to λ_{max} 450 nm after mixing. No such shift was observed on using acetone, ethyl acetate or cyclohexane as solvents.

When equimolar dilute ethanolic solutions of $SnCl_2$, $2H_20$ and alizarin red-S were mixed together, slight change in colour occurred, but the spectrum of the mixture indicated no change in the absorption maximum of the chelating agent (λ_{max} 430 nm). After 2–3 days a change in colour was obvious and detailed kinetic study of this reaction is under investigation.

Effect of temperature. – Fig. 2 shows the effect of the temperature increase on the stability of the formed complex, Ph_2 $SnCl_2$, alizarin red-S. It is clear that the complex is stable up to 30° C and on increasing the temperature a gradual decrease in absorbance, with slight shift in λ_{max}, occurs as given in the table, where curves are indicated by letters. At 60° C there is a complete dissociation with an increase in the absorbance characteristic for the chelating ligand at λ_{max} ~ 432 nm is obvious.

Table The Effect of increase of temperature on an equimolar ethanolic solutions of Ph_2 $SnCl_2$ and Alizarin red-S at total concentration of 0.5 x 10^{-4} M.

max (nm)	T °C	O.D.	A & B
470	25 & 30	0.56	A & B
470	32	0.54	C
464	36	0.52	D
460	42	0.49	E
460	48	0.47	F
454	56	0.43	G
444	58	0.49	H
432	60	0.51	I

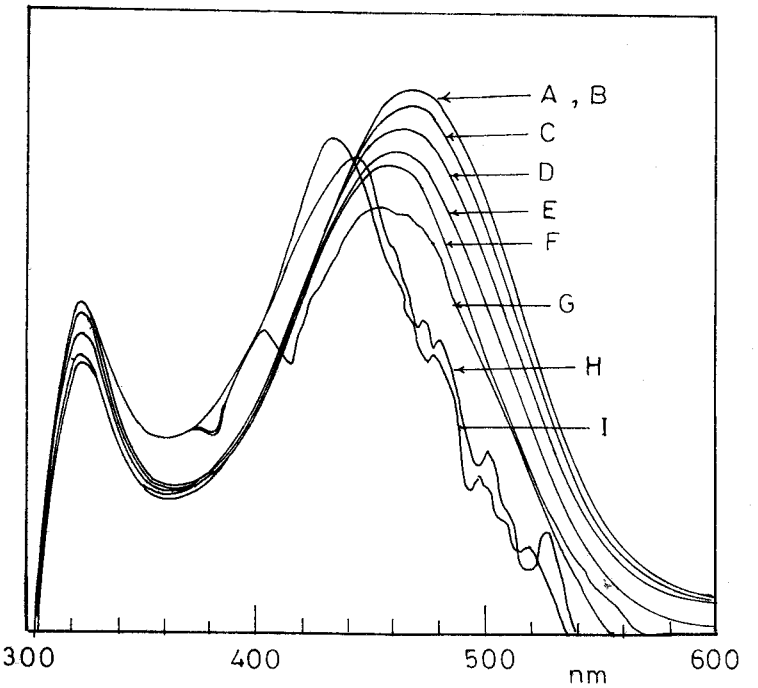

Fig.(2) The Effect of increase in temperature on the complex Ph_2SnCl_2, Alizarine red S.

Electrical conductance measurements were made with mixtures prepared according to Job's method of continuous variation. The results are represented graphically in Fig. 3, where the difference in specific conductivity (observed specific conductivity-the conductivity of the chelating agent, as that of Ph_2 $SnCl_2$ is nearly zero) are plotted against composition of the mixture, From the curve, it is evident that the components are in the mole ratio of 1:1 in the complex. This result substantiate those of the present finding.

A red-scarlet water soluble solid complex was obtained on mixing concentrated ethanolic solution of Ph_2 $SnCl_2$ with alizarin red-S, in water-ethanol mixture as a solvent, in the mole ratio of 1:1. Analytical results showed that the solid complex is Ph_2 $SnCl_2$, alizarin red-S. Infrared spectrum of the complex showed that the C=O stretching band which occurs in the free chelating agent at 1665 cm^{-1} [9], is shifted to lower frequency 1630 cm^{-1} on complexing,

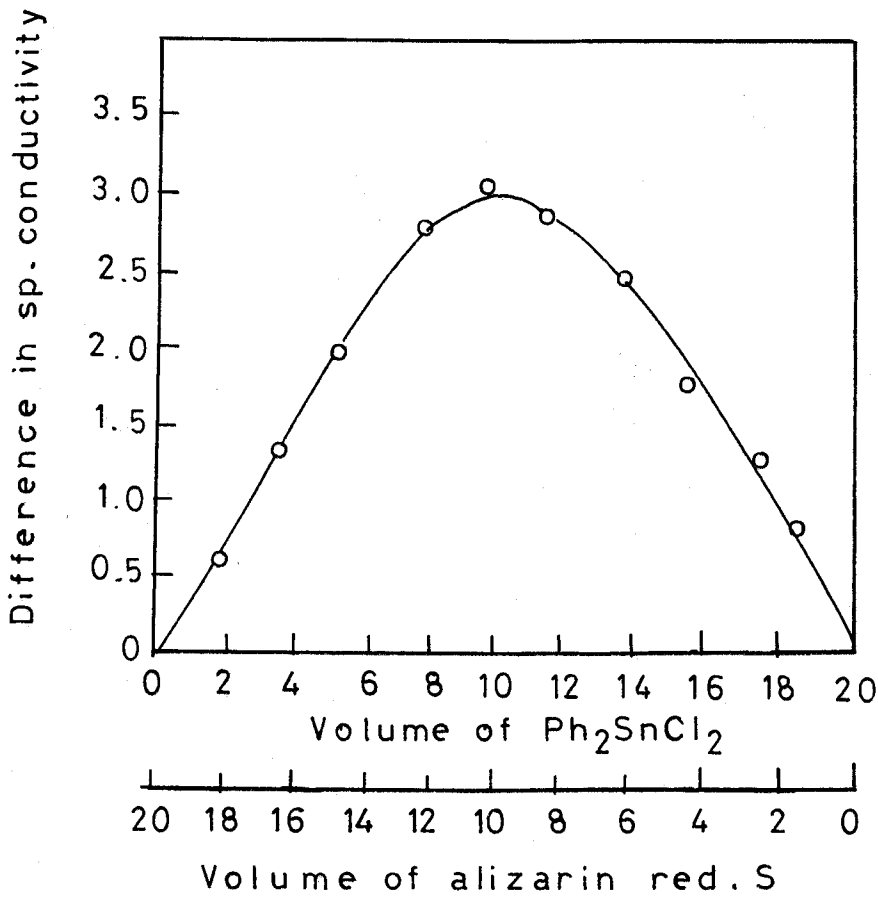

Fig. (3)

Fig. 4. This indicates that coordination occurred through the oxygen of the carbonyl groups.[10] No such band is present in the spectrum of Ph_2 $SnCl_2$.[1]

The band found at 430 cm^{-1} may be due to the coordinate bond Sn ← 0, similar results are reported.[11]

This complex is soluble in water to give a reddish solution, the spectrum of which λ_{max} at 520 nm, = 58.0.

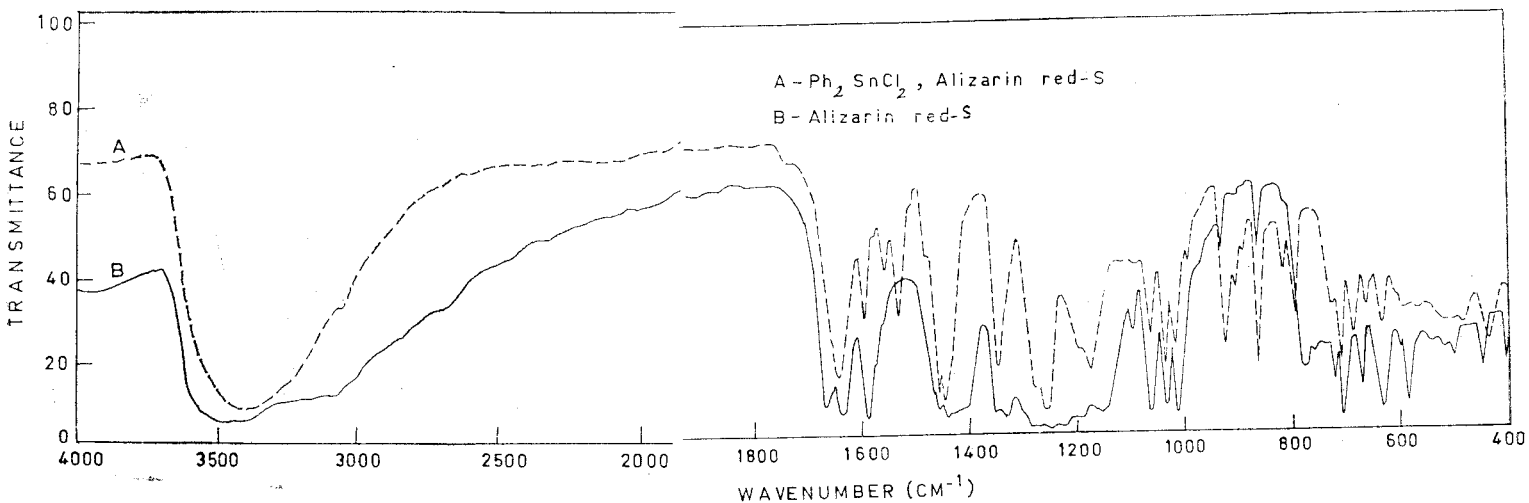
A - Ph_2SnCl_2 , Alizarin red-S
B - Alizarin red-S
TRANSMITTANCE
WAVENUMBER (CM^{-1})
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
A
B

Fig.(4)

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