J.Sci.Soc.Thailand, 14 (1988) 283-300

SPECTROSCOPIC AND CONDUCTOMETRIC STUDIES OF ION-PAIR FORMATION OF THALLIUM (I) ACETATE IN NON-AQUEOUS SOLVENTS*

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(Received 6 July 1988)

ABSTRACT

This paper presents evidence for the existence of two chemically distinct species of Thallium (I) in solutions of Thallium (I) acetate in acetonitrile, iso-*proply alcohol and* p-*dioxane. These species are the solvated free Thallium (I) ion and ion-pairs of Thallium (I) ion with acetate and formate ions. Ultra-violet absorption spectra of the Thallium (I) salts show that the position of an absorption maximum due to ion-pair formation occurs at longer wavelengths than that due to the free solvated ion. The ion-pair band is sensitive to changes in the nature of solvent and concentration of added tetramethyl ammonium acetate, while that of the solvated free ion is not strongly solvent dependent. Electrical conductivities of Thallium (I) acetate in water, and binary mixtures with acetonitrile,* iso-*propyl alcohol, and* p-*dioxane, were also determined at 25°C. The results show that Thallium (I) acetate behaves as a weak electrolyte existing largely as ion-pairs.*

INTRODUCTION

Thallium (I) ion, Tl^+, with 80 electrons and the ground state electronic configuration of [Xe] $4f^{14}\,5d^{10}\,5s^2$, is isoelectronic with atomic mercury. The electronic absorption of isolated Tl^+ ion which involves only the valence shell electron gives rise to 'Rydberg' spectra, typically the s-p transition. The ground state term of gaseous free Tl^+ is ${}^1S_0$ and the terms for the first low-lying excited state of configuration $6s^1\,6p^1$ are in order of increasing energy, ${}^3P_0$, ${}^3P_1$, ${}^3P_2$ and ${}^1P_1$. The allowed transitions from the ground states, ${}^1S_0$, are to the ${}^1P_1$ and ${}^3P_1$ levels with strong and medium relative intensities, respectively.

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* This paper was orally presented at the International Symposium on "Molecular and Dynamic Approaches to Electrolyte Solutions", Tokyo Institue of Technology at O-Okayama, January 12-14, 1988.

The absorption and emission spectra of Tl^+ ion have been studied extensively in different media.[1,2,3] The first theoretical interpretation of the absorption spectra was interpreted by Seitz.[4] He suggested a model based on the excited states of a free Tl^+ ion in a cubic field, *i.e.* a single Tl^+ ion occupying an alkali metal ion site in a sodium chloride type lattice.

The study of a Thallium-doped potassium chloride spectrum showed that Tl^+ ion replaces some K^+ ions in the crystal structure, giving rise to the growth of two principal absorption bands at 196 nm and 247 nm with a subsidiary one at 210 nm. The 196 nm band has been attributed to a ${}^1P_1 \leftarrow {}^1S_o$ transition and the 247 nm band to a ${}^3P_1 \leftarrow {}^1S_0$ transition in Tl^+ ion.[5,6] Ghosh[2] concluded that a second band at 253 nm of Tl^+ ion in fused silica and phosphate glass, is possibly due to a combination of dimers and higher aggregates of Tl^+ ions.

In water as solvent, an absorption band is observed at 213 nm for Tl(I) salts.[2] In aqueous alkali-halide solutions, the band at 213 nm has been observed to shift to about 243 nm in $TlCl$-$CaCl_2$, 247 nm in $TlCl$-KCl, and 265 nm in $TlBr$-KBr solutions.

Although Tl^+ ion has abnormally strong hydration, it is believed that it is one of the few univalent cations which associate appreciably with anions of low charge. The ultra-violet absorption spectra of solutions containing Tl^+ and OH^- ions have been measured by Bell and Panckhurst.[7] Freeman and Coworkers,[8] have reported that concentrated aqueous solutions of Tl^+ ion and univalent anions may contain ion-pairs in which Tl^+ and the anion are associated long enough to be treated in terms of an equilibrium. In non-aqueous solvents, TlCl, TlBr, TlI, TlOAc, TlOOCH, etc., are probably present, even in dilute solutions, largely as ion-pairs.

The various forms of ion-pairs may be shown by the following equilibria where S represents a solvent molecule :

$$\begin{tikzcd}
TIX_{(solid)} \arrow[r, leftrightarrows] & (Tl^+X^-)_{solv} \arrow[r, leftrightarrows] & Tl^+(S)X^- \arrow[r, leftrightarrows] & Tl^+{}_{solv} + X^-{}_{solv} \\
 & \text{Solvated} & \text{Solvent} & \text{Solvated} \\
 & \text{Contact ion-pair} & \text{Shared ion-pair} \arrow[dr, shift left] & \text{free ions} \arrow[d, shift left] \\
 & & & Tl^+(S)_nX^- \arrow[ul, shift left] \arrow[u, shift left] \\
 & & & \text{Solvent} \\
 & & & \text{Separated ion-pair}
\end{tikzcd}$$

The conductances of TlOAc and $TlClO_4$ in water at 25°C have been reported for the conductivity values at infinite dilution for TlOAc and $TlClO_4$, to be 115.63 and 142.65, respectively. The dissociation constants of TlOAc and $TlClO_4$ at 25°C in water have been reported to be 1.2 and 1.0, respectively. Tewari and Johari,[9] reported the limiting equivalent conductances of TlOAc and $TlNO_3$ in formamide at 25°C to be 31.20 and 20.00, respectively.

The chemical shifts observed in the nuclear resonance spectrum of Thallium (I) ion in various solutions have been reported. The shifts were interpreted in terms of the formation of ion pairs and there was evidence that in the ion-pair the Thallium (I) ion was predominantly ionic. A study of ion-pair behaviour of Thallium (I) salts has been reported.[10]

It is the purpose of this study to measure the ultra-violet absorption spectra and electrical conductivities of Thallium (I) acetate in water and binary aqueous solvent mixtures of acetonitrile, *p*-dioxane, and *iso*-propyl alcohol, in order to obtain information about ion solvation and ion-pair formation of the salts.

EXPERIMENTAL

Reagents and apparatus

The following spectro-grade solvents (Matheson Coleman & Bell) were used : acetonitrile, *p*-dioxane, and *iso*-propyl alcohol. Deionized water was prepared by passing distilled water through a 1 m column of mixed bed ion-exchange resin. Ultra-pure grade (99.999%) Thallium (I) acetate, TlOAc, (Alfa Inorganics, Inc.) was used without further purification, it was dried in a vacuum oven at 60°C for 2 hours and 110°C for 6 hours.

Electronic absorption spectra were recorded by means of a Cary Model 14 and a Unicam SP 8000 spectrophotometers. All measurements except those designed to study the temperature effect were run at room temperature. Measurements of absorption spectra at fixed temperatures were carried out on the Cary spectrophotometer using a thermostatted cell compartment; the temperatures were constant during measurements, within about ± 0.1°C. Quartz cells of 1.00 cm path length were used with a matched reference cell filled with solvent.

The conductance cell was constructed from a one-liter conical flask. The top 34/45 standard taper joint served as a salt cup dispenser, while the 24/40 side-arm connection was used for solvent addition. The electrodes, constructed from 0.2 mm thick platinum metal, were 14 mm in diameter and were backed with glass for extra rigidity. The electrode spacing was approximately 4 cm, giving a cell constant of about 0.7 cm^{-1}. The cell had copper wires silver-soldered directly to the platinum electrode leads. The cell was calibrated by the procedure of Lind, Zwolenik and Fuoss. The cell constant at several concentrations of potassium chloride was found to be 0.6970 cm^{-1}. Electrical conductance was measured with a Leeds and Norethrup Dike-Jones conductance Bridge in conjunction with a General Radio Model 1310-A signal generator and Model 1323-A tuned amplifier-null detector. The frequencies of the signals employed were 1,2 and 5 KHz. The change in measured resistance between 1 and 5 KHz was generally about 0.1%. A constant temperature of 25°C was maintained by using a thermostat bath which consisted of a seven-gallon glass vessel insulated with 2 inches of fiberglass and filled with light paraffin oil. The bath was stirred with a heavy duty stirring motor. Fisher Proportional Temperature Control with a thermistor probe and a 300 watt heating element provided temperature control. The bath temperature was adjusted to 25° ± 0.003°C with the use of a Beckmann differential thermometer.

RESULTS AND DISCUSSION

Absorption spectra of Thallium (I) salts

A survey of the UV absorption spectra of Thallium (I) salts was made in water. It was found that all of the salts used in this study showed a single absorption band at 213 nm. The absorption maxima of Thallium (I) salts in acetonitrile are summarized in Table 1. The absorption bands in the region between 209-220 nm shown in Table 1 are attributed to solvated free Tl^+ ion. On the other hand, the low energy bands at 242-256 nm region observed in acetonitrile are attributed to ion-pairs. It was found that $TlClO_4$ showed only a single absorption band at 212 nm whereas TlOAc and TlOOCH have two bands at 216-218 nm and 254-255 nm. The first of these bands (shorter wavelength) is due to solvated free Tl^+ ions and the second band (longer wavelength) to ion-pairs. The absorption spectra of Thallium (I) acetate in water, *p*-dioxane, methyl alcohol, *iso*-propyl alcohol, and acetonitrile are shown in Fig. 1.

It appears that solvent changes affect the absorption maximum of the band due to solvated free Tl^+ ion, i.e., the more polar the solvent, the higher the energy (shorter wavelength) of the absorption band. Polar solvents interact electrostatically with Tl^+ ion and tend to stabilize the ground state more than less polar solvents, giving rise to a decrease in s-p separation with decreasing polarity of the solvent. Addition of water to a solution of TlOAc in *iso*-propyl alcohol resulted in the increase in intensity of one band and the diminution of the other as illustrated by a super position of the spectra as shown in Fig. 2. These spectra indicate clearly the presence of two distinct absorbing species in the solvent system.

A strong dependence of the absorption spectra on water concentration was observed for TlOAc but not for $TlClO_4$ in *p*-dioxane/water mixtures suggesting that an equilibrium was occurring between free and associated species in TlOAc solutions.

$$\underset{\text{solvated contact ion-pair}}{[Tl^+OAc^-]_{(solv)}} \quad \rightleftharpoons \quad \underset{\text{solvated free ions}}{Tl^+_{(solv)} + OAc^-_{(solv)}}$$

The changes in absorption maxima with solvent composition for TlOAc and $TlClO_4$ in *p*-dioxane/water mixtures are given in Table 2. A dramatic change was observed for TlOAc in 95% *p*-dioxane mixture ; only 5% of water was required to shift the low energy band due to contact ion-pairs at 258 nm to 245 nm. When 50% water was added, all of the ion-pairs appeared to be converted to the solvated free Tl^+ ion since only a single absorption band was observed at 216 nm.

TABLE 1 Absorption maxima of Thallium(I) salts in acetonitrile

Compound	λ_{max} (nm)
TlF	210
TlCl	209 (sh), 245
TlBr	209 (sh), 246[a]
TlI	209 (sh), 247[b]
TlOH	209 (sh), 242
TlSCN	210 (sh), 260[c]
$TlNO_3$	210
$TlClO_4$	212
$TlBF_4$	212
TlOOCH (formate)	216 (sh), 254
$TlOOCCH_3$ (acetate)	218 (sh), 255
$TlOOCCH_2CH_3$ (propionate)	220 (sh), 256

sh = shoulder

[a, b, c] Anion absorption interferences

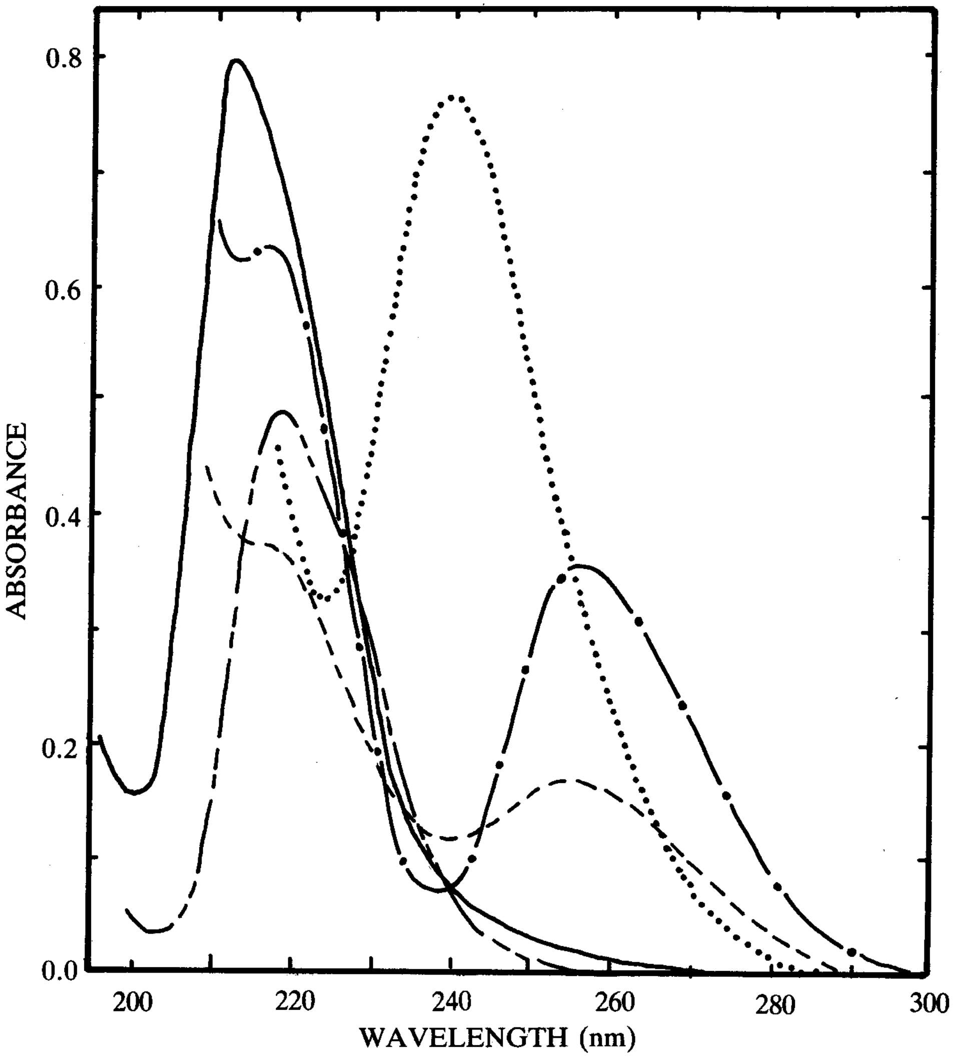

Fig. 1 Thallium (I) acetate spectrum in water (————), *p*-dioxane (—·—·—), methyl alcohol (— - — - —), *iso*-propyl alcohol (...........), and acetonitrile (----------) at 20°C : 1 cm cell.

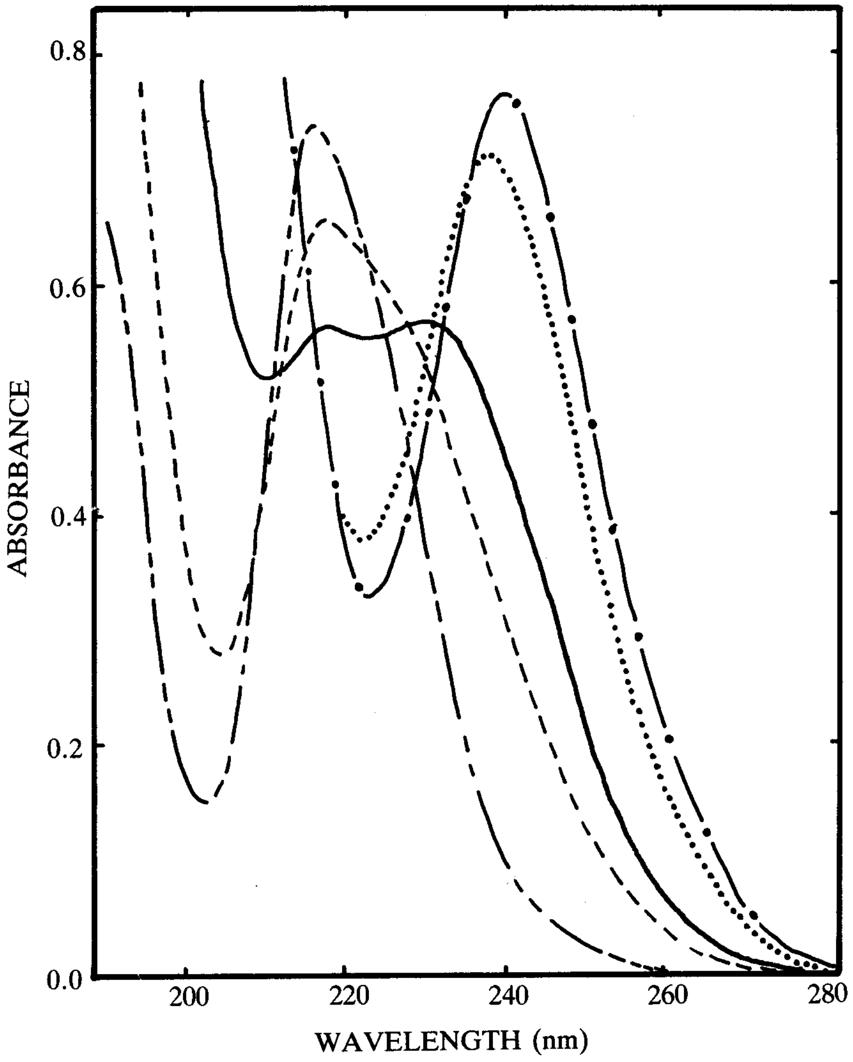

Fig. 2 Absorption spectra of Thallium (I) acetate in *iso*-propyl alcohol on addition of water at 20°C

$Tl^+ = 2.0 \times 10^{-3}$ M : 1 cm cell.

—·—·—	Pure *iso*-propyl alcohol
··········	2.5 % (v/v) water added
————	9.0 % (v/v) water added
-----------	13 % (v/v) water added
—-—-—	23 % (v/v) water added

TABLE 2. Absorption maxima of TlOAc and $TlClO_4$ in *p*-dioxane/water mixtures

% (w/w) *p*-Dioxane	Dielectric constant	λ_{max} (nm)	
		TlOAc	$TlClO_4$
100	2.2	220, 258	220
95	3.5	219, 245	219
80	11.5	216, 238	218
50	35.5	216	216
0	80.4	213	213

Addition of tetramethylammonium acetate to a solution of Thallium (I) perchlorate in acetonitrile resulted in a decrease of the intensity of the solvated free Tl^+ band at 212 nm and a simultaneous appearance of a new band identical with the low energy band of TlOAc in acetonitrile at 255 nm. The intensity of the 255 nm band increased with increasing quantities of added acetate ions. The high energy band appeared to shift from 212 to 218 nm upon the addition of acetate ion, presumably due to the strong absorption of the acetate ion at the tail of the band on the high energy side. It is obvious that the band observed at 255 nm is due to TlOAc ion-pairs. The similarity between the absorption spectrum of TlOAc in acetonitrile and that of $TlClO_4$ with added acetate ion in the same solvent can be seen from the spectra shown in Fig. 3.

Conductometric study of Thallium (I) acetate in Water and binary Water/Solvent mixtures.

The molar concentration and measured equivalent conductances of Thallium (I) acetate in water, acetonitrile/water, *p*-dioxane/water, and *iso*-propyl alcohol/water are summarized in Table 3. The equivalent conductances of Thallium (I) perchlorate in acetonitrile/water mixtures are shown in Table 4. Typical plots of equivalent conductance against $\sqrt{C}$ (phoreograms) for TlOAc and $TlClO_4$ are shown in Figures 4-7.

The plot for TlOAc in water was a straight line which was extrapolated to the limiting molar conductance of 115.54. Fig.4 illustrates the curves of equivalent conductances against $\sqrt{C}$ for TlOAc in water and in a series of acetonitrile/water mixtures. It can be seen that the first four curves show a linear relationship while the fifth one (86.8% acetonitrile solution) has an upward curvature which clearly indicates ion-pair formation. The phoreograms of TlOAc in a series of *p*-dioxane/water and acetonitrile/water mixtures are shown in Figures 5 and 6 respectively. It should be noted that curve III of Fig.5 in which the data was obtained from 69.7% *p*-dioxane/water solution also shows an upward curvature similar to curve V of Fig. 4. It is obvious that extensive association of TlOAc is occurring in 69.7% *p*-dioxane/water and 86.8% acetonitrile/water solutions. The limiting equivalent conductances in 86.8% acetonitrile/water and in 69.7% *p*-dioxane/water solutions could not be accurately determined because of the curvature of the phoreograms. The definite curvature on the phoreograms clearly indicates significant association in the two solvent systems. Figure 7 illustrates the phoreograms of TlOAc in a series of *iso*-PrOH/water mixtures. It is seen that all graphs show linear relationship between the equivalent conductance and concentration. It is obvious that TlOAc is existing largely as free solvated ions (Tl^+_{solv} and OAc^-_{solv}) in these solvent mixtures.

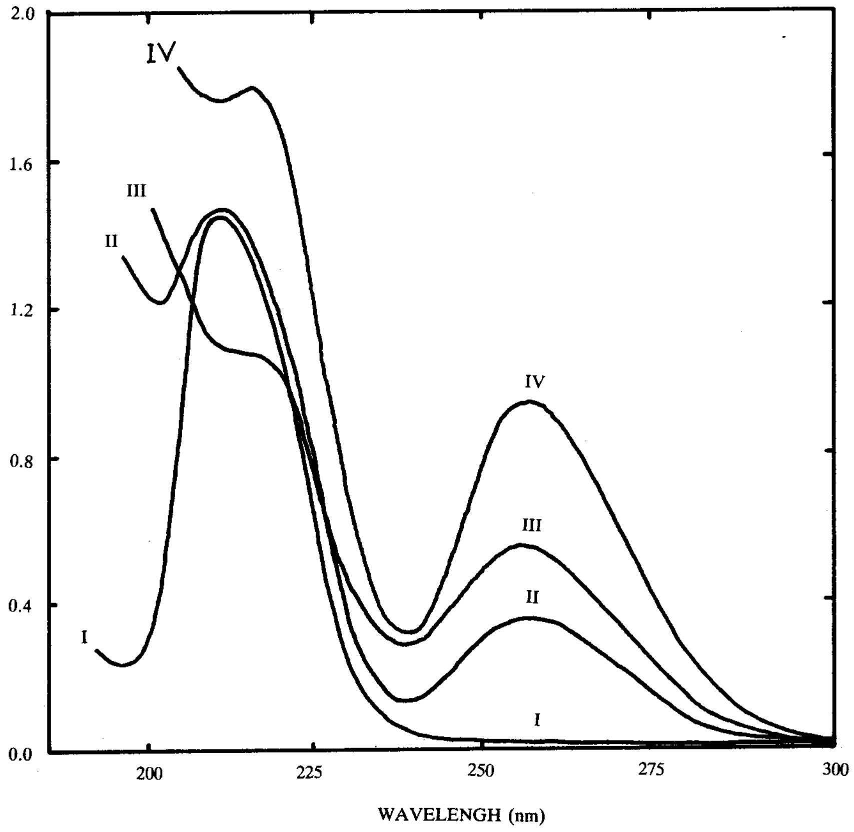

Fig. 3 Absorption spectra of $TlClO_4$, $TlClO_4$ with added acetate ion, and TlOAc in acetonitrile at 20°C : 1 cm cell.

Curve I - $TlClO_4$ (3.42×10^{-4} M)

Curve II- $TlClO_4$ (3.42×10^{-4} M) + Me_4NOAc (1.42×10^{-4} M)

Curve III-TlOAc (1.90×10^{-4} M)

Curve IV-$TlClO_4$ (3.42×10^{-4} M) + Me_4NOAc (3.35×10^{-4} M)

TABLE 3 Measured equivalent conductances of Thallium (I) acetate in water and binary water/solvent mixtures at 25°C

$C \times 10^4$	Λ	$C \times 10^4$	Λ
In water		**In 39.8% (w/w) *p*-dioxane**	
3.115	114.21	1.968	59.85
4.087	113.90	4.471	58.88
6.989	113.81	7.879	58.21
7.857	113.02	11.483	57.79
9.291	113.27	13.523	57.40
10.206	112.94	15.729	57.15
10.928	112.98	**In 52.7% (w/w) *p*-dioxane**	
15.368	112.53	2.309	49.35
In 20.6% (w/w) acetonitrile		5.368	48.00
1.517	99.92	8.287	47.03
3.319	99.86	11.587	46.09
5.461	99.78	15.031	45.05
7.762	99.49	17.684	44.45
9.757	99.44	**In 69.7% (w/w) *p*-dioxane**	
In 43.8% (w/w) acetonitrile		3.743	31.55
1.470	97.52	6.328	28.69
3.005	97.07	8.887	26.72
4.660	96.18	12.127	24.97
6.061	95.90	15.754	23.43
7.137	95.24	**In 38.5% (w/w) *iso*-PrOH**	
In 70.0% (w/w) acetonitrile		1.826	41.75
2.174	97.16	4.515	41.05
4.244	94.64	5.962	40.89
6.238	92.91	9.822	40.43
7.508	91.86	14.017	40.09
8.633	90.97	16.939	39.78
In 86.8% (w/w) acetonitrile		**In 49.8% (w/w) *iso*-PrOH**	
2.976	100.23	1.249	34.65
4.933	90.85	5.384	33.76
7.646	82.58	7.486	33.32
11.224	74.39	9.602	33.07
14.728	68.79	11.541	32.80
18.614	63.97		
In 73.3% (w/w) *iso*-PrOH			
1.407	24.64	9.434	21.16
3.749	23.38	12.564	20.29
5.695	22.50	15.716	19.57

TABLE 4 Measured equivalent conductances of Thallium (I) perchlorate at 25°C

$C \times 10^4$	Λ
In 86.8% (w/w) acetonitrile	
5.062	166.45
7.161	164.75
9.240	163.26
12.168	159.81
17.043	157.75

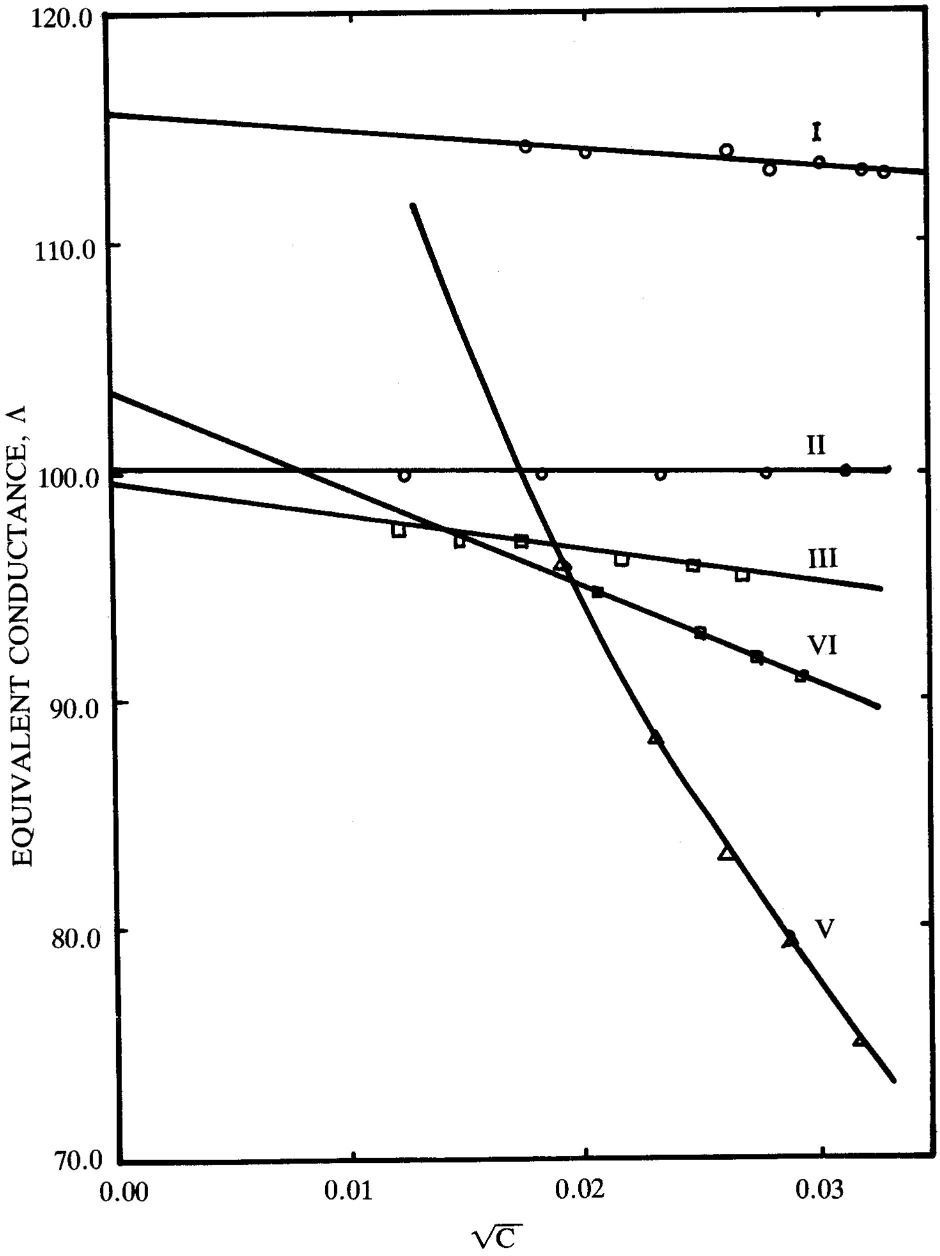

Fig. 4 Equivalent conductance as function of concentration for TlOAc in : water (curve I), 20.6% acetonitrile (curve II), 43.8% acetonitrile (curve III), 70.0% acetonitrile (curve IV), and 86.8% acetonitrile (curve V).

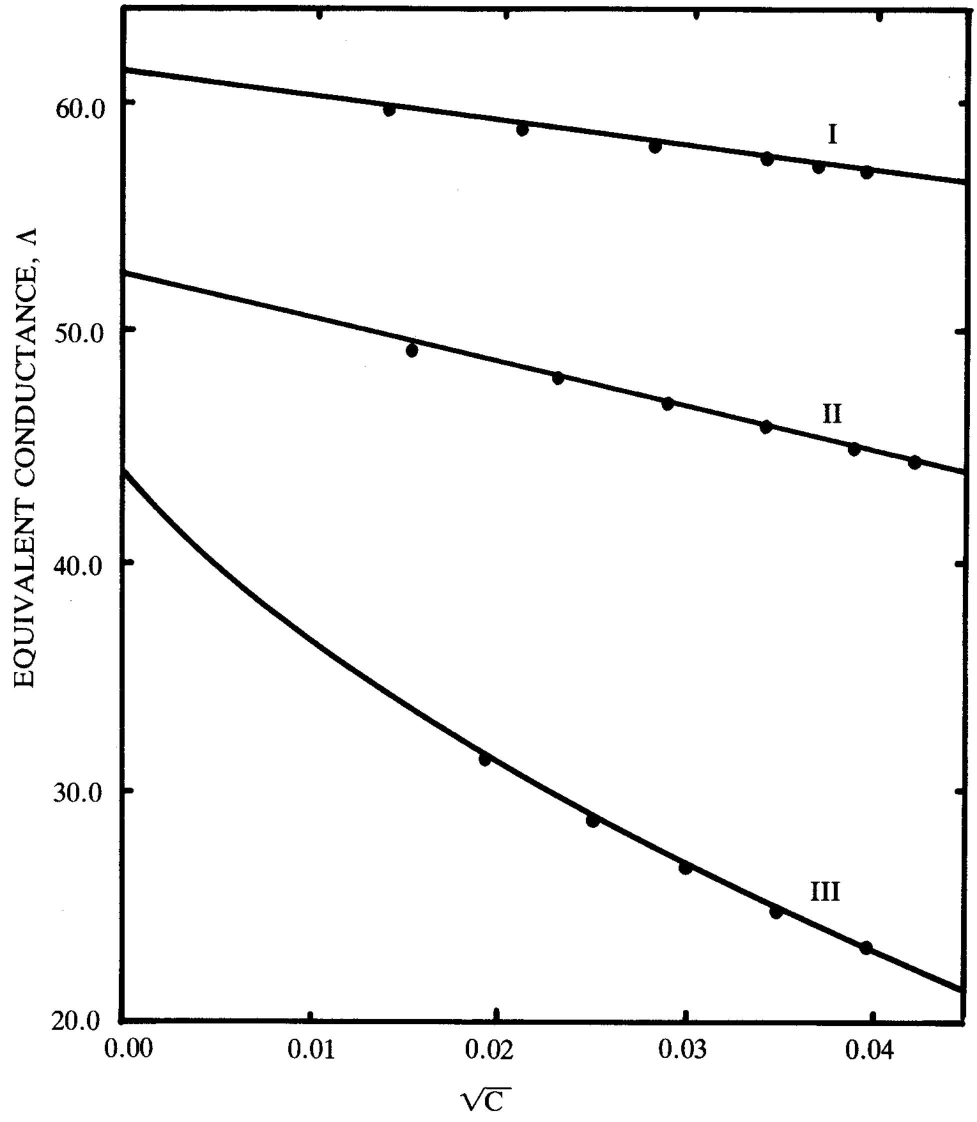

Fig. 5 Equivalent conductance as function of concentration for TlOAc in : 39.8% *p*-dioxane (curve I), 52.7% *p*-dioxane (curve II), and 69.7% *p*-dioxane (curve III).

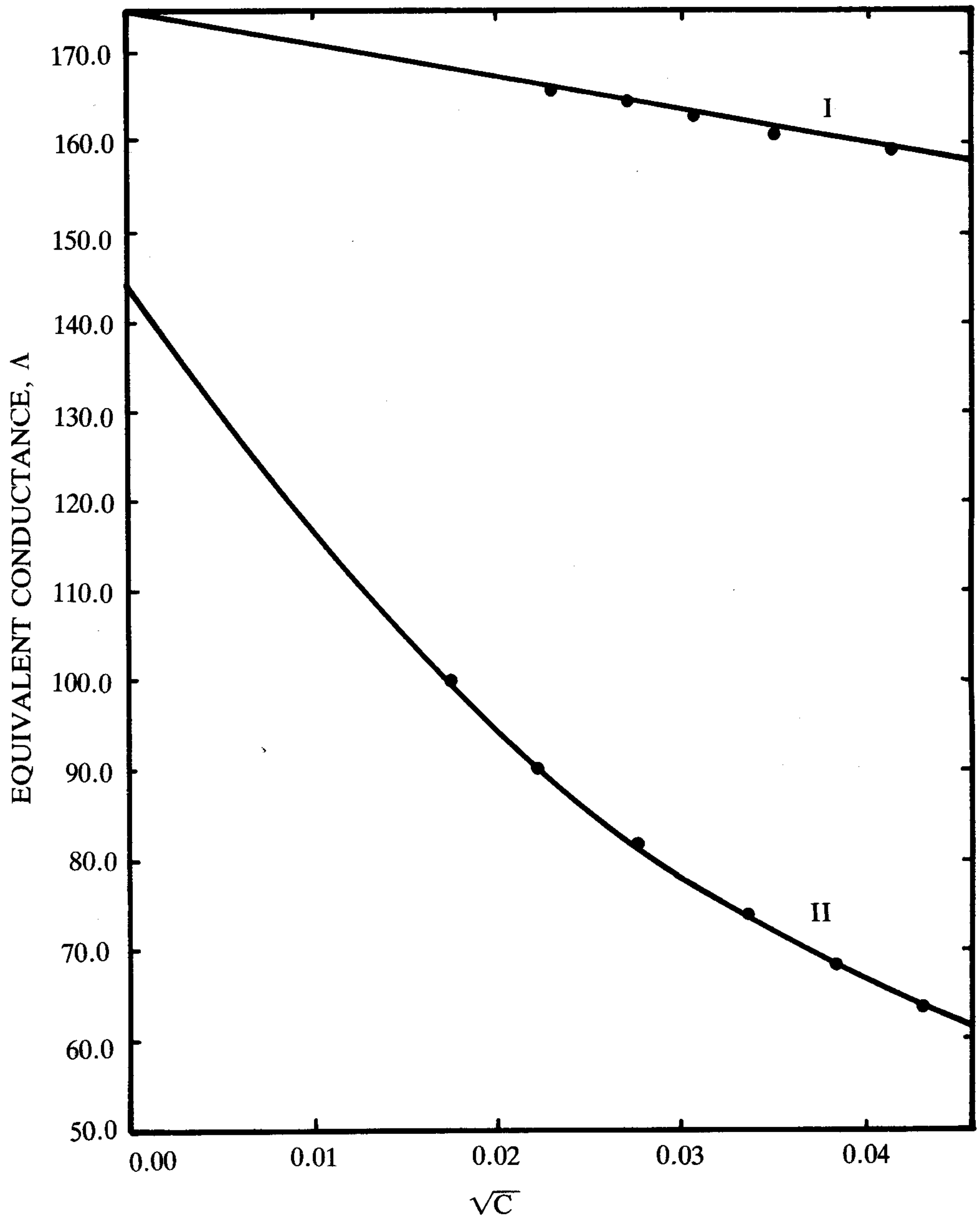

Fig. 6 Equivalent conductance as function of concentration for $TlClO_4$ (curve I) and TlOAc (curve II) in 86.8% acetonitrile/water mixture.

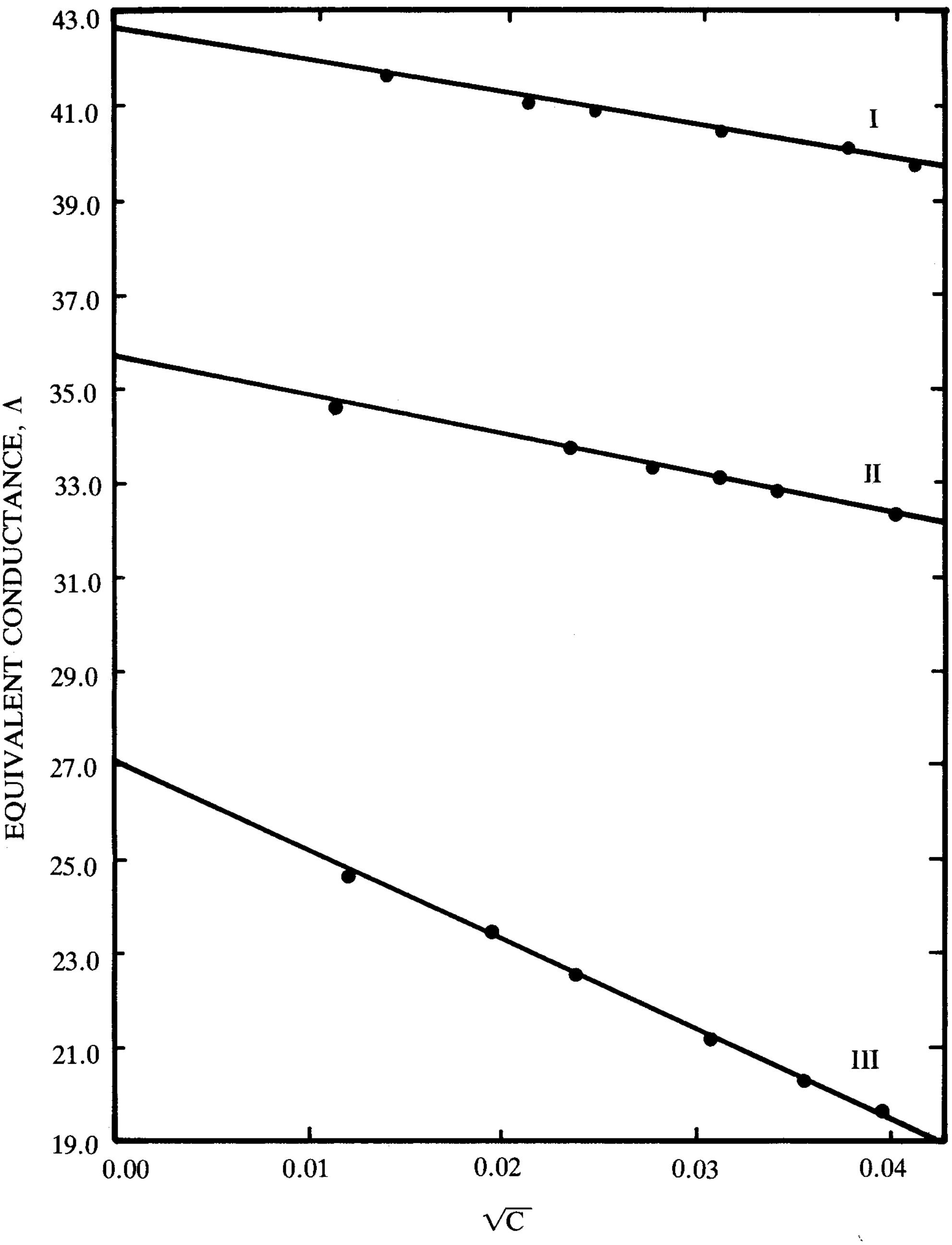

Fig. 7 Equivalent conductance as function of concentration for TlOAc in : 38.5% *iso*-PrOH (curve I), 49.8% *iso*-PrOH (curve II), and 73.3% *iso*-PrOH (curve III).

CONCLUSION

The experimental results of this study can be summarized as follows :

(i) The existence of TlOAc ion-pair in acetonitrile, *iso*-propyl alcohol, *p*-dioxane, and in some binary aqueous/nonaqueous solvent mixtures has been confirmed spectroscopically.

(ii) The absorption bands due to ion-pairs observed in the 238-264 nm region are distinguishable from that due to solvated free Tl^+ ions which is observed in the region of 212-220 nm.

(iii) The location of absorption bands of TlOAc ion-pairs has been found to be sensitive to changes in solvent and concentration of added tetramethyl ammonium acetate.

(iv) It has been found that TlOAc in 86.8% (w/w) acetonitrile/water mixture and in 69.7% (w/w) *p*-dioxane/water mixture, behaves as a weak electrolyte, whereas $TlClO_4$ shows strong electrolyte behaviour. The significant association observed in these solvent systems is attributed to ion-pair formation.

ACKNOWLEDGEMENT

The author would like to thank UNESCO in collaboration with ANAIC and the University of Chiang Mai for the financial support to present this paper at the Asian Chemical Congress 1988 in Seoul, Korea.

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บทคัดย่อ

รายงานวิจัยนี้ได้ยืนยันการดำรงอยู่ในสารละลายของอิออนอิสระแทลเลี่ยม และอิออนคู่ของแทลเลี่ยม ซึ่งเกิดจากการละลายเกลือแทลเลี่ยม (I) อะซิเตตในตัวทำละลายที่ไม่ใช่น้ำ เช่น อะซิโตนัยตริล ไอโซโพรพิลอัลกอฮอล์ และพาราไดออกเซน สารที่เป็นอิออนอิสระของแทลเลี่ยม (I) และอิออนคู่ของแทลเลี่ยม (I) ให้สเปกตรัมแบบดูดกลืนแสงในย่านอุลตราไวโอเลตที่มีความยาวคลื่น ณ จุดดูดกลืนแสงมากที่สุด แตกต่างกัน จากผลการทดลองพบว่าความยาวคลื่นที่ดูดกลืนแสงมากที่สุดซึ่งเกิดจากอิออนคู่ของเกลือแทลเลี่ยม (I) จะปรากฏที่ความยาวคลื่นยาวกว่าสเปกตรัมของแทลเลี่ยม (I) ที่เป็นอิออนอิสระ อิออนคู่ของแทลเลี่ยม (I) ให้สเปกตรัมที่มีความว่องไวต่อชนิดของตัวทำละลาย และต่อการเติมเกลืออัลคิลอัมโมเนียมอะซิเตต สำหรับความยาวคลื่นของการดูดกลืนแสงสูงสุดของแทลเลี่ยม (I) อิออนอิสระไม่ขึ้นอยู่กับชนิดของตัวทำละลายมากนัก ในการวิจัยนี้ยังได้รายงานผลของการศึกษาค่าการนำไฟฟ้าที่ 25° ซ ของเกลือแทลเลี่ยม (I) อะซิเตตที่ละลายในระบบตัวทำละลายผสมระหว่างตัวทำละลายที่ไม่ใช่น้ำกับน้ำ เช่น น้ำกับอะซิโตนัยตริลน้ำกับไอโซโพรพิลอัลกอฮอล์ และน้ำกับพาราไดออกเซน จากผลการทดลองพบว่าแทลเลี่ยม (I) อะซิเตตมีพฤติกรรมเป็นอิเลคโตรไลต์อย่างอ่อน โดยดำรงอยู่ในรูปของอิออนคู่ เมื่อระบบตัวทำละลายประกอบด้วยตัวทำละลายที่ไม่ใช่น้ำในเปอร์เซ็นต์สูงกว่าน้ำ