The Complexing of the Thallium(I) Ion with Other Solvents in Acetonitrile. Investigation Using a Cation-sensitive Glass Electrode

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The complexing of the thallium(I) ion with other common solvents has been studied in acetonitrile by using a univalent cation-sensitive glass electrode. A method similar to that developed to study the complexing of sodium[1] and lithium ions[2] was employed. Mono-, di-, and tri-solvated species were formed with DMF, SDMF, DMA, pyridine, formamide, and DMSO. Tetra-solvated species were also formed with *N*-methylformamide and HMPA. The complex formation constants for the mono-solvated thallium(I) ion were 4.1 with DMF, 5.6 with SDMF, 6.9 with DMA, 11 with pyridine and formamide, 12 with *N*-methylformamide, 15 with DMSO, and 1.0×10^2 with HMPA. Prior to these experiments, the cation-sensitive glass electrode was confirmed to respond to the thallium(I)-ion activity in different solvents by comparing its behavior with that of a thallium-amalgam electrode. When water was the complexing solvent the potential of the glass electrode was not stable, and therefore, a thallium-amalgam electrode was used instead of a glass electrode to obtain the hydration constants of the thallium(I) ion in acetonitrile. Mono- and di-solvated species were formed with water and the hydration constant for the mono-solvated species was 1.1. The amalgam electrode and the glass electrode were used to obtain the constants with DMSO.

In previous papers,[1,2] the author and collaborators have reported a potentiometric method to obtain the formation constants of complexing for the sodium and lithium ions with other common solvent molecules in acetonitrile (AN). A univalent cation-sensitive glass electrode was used as an indicator. In the present experiment, a similar method was used to determine the formation constants of the complexing of the thallium(I) ion with other solvents in AN. Emf measurements of Cell I were carried out.

$$\underset{(A)}{\mathrm{Ag}|0.005\mathrm{M\ AgNO_3(AN)}}\|\underset{(B)}{0.1\mathrm{M\ Et_4NClO_4(AN)}}\|$$

$$\underset{(C)}{5\times 10^{-4}\mathrm{M\ TlClO_4} + 0.01\mathrm{M\ Et_4NClO_4(AN+D)}}|$$

glass electrode

Cell I

A solution of 0.1 M of tetraethylammonium perchlorate (Et_4NClO_4) in AN was in compartment B in place of the 0.1 M of tetraethylammonium picrate(Et_4NPi) used in previous work,[1,2] in order to avoid the interaction between thallium(I) and picrate ions. The dissociation constant pK^d of thallium(I) picrate in AN at 25 °C has been determined using a conductometric method to be 2.6.[3] The validity of this substitution of the bridge electrolyte in compartment B has been discussed.[4,5] To obtain the complex formation constants the following relations were used:

$$\beta_x = \frac{(\mathrm{M}^+_{\mathrm{xD}})}{(\mathrm{M_s}^+)[\mathrm{D}]^{\mathrm{x}}} \tag{1}$$

$$R_1 = \left\{\frac{(\mathrm{M_s}^+)_{\mathrm{AN}}}{(\mathrm{M_s}^+)_{\mathrm{AN-D}}} - 1\right\}/[\mathrm{D}] = \sum_{i=1}\beta_i[\mathrm{D}]^{i-1} \tag{2}$$

$$R_j = (R_{j-1} - \beta_{j-1})/[\mathrm{D}] = \sum_{j=2}\beta_j[\mathrm{D}]^{j-2} \tag{3}$$

$$\frac{(\mathrm{M_s}^+)_{\mathrm{AN}}}{(\mathrm{M_s}^+)_{\mathrm{AN-D}}} = 10^{(E_{\mathrm{AN}}-E_{\mathrm{AN-D}})/59} \tag{4}$$

All symbols have the same meaning as those in a previous report.[2] Assumptions similar to those in previous papers[1,2] were made: (i) solvent D in the AN–D mixtures is monomeric, (ii) the activity of AN does not change upon the addition of D and is equal to unity, (iii) the salt-effect activity coefficient of the thallium(I) ion, as calculated using the Debye-Hückel equation, is equal for both pure AN and AN–D mixtures, (iv) the amount of D consumed by the solvation of the ions of an indifferent electrolyte is negligible, and (v) the liquid-junction potential between the solutions in the salt bridge B and compartment C in Cell I does not change upon the addition of D. All of these assumptions appear to be satisfied approximately under the experimental conditions of these experiments when $[\mathrm{AN}] \gg [\mathrm{D}]$.

Using this method, formation constants β_x for such D as methanol, *N,N*-dimethylformamide (DMF), *N,N*-dimethylthioformamide (SDMF), *N,N*-dimethylacetamide (DMA), pyridine, formamide, *N*-methylformamide, dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA) were obtained, and the constants β_x for water were obtained with the thallium-amalgam electrode instead of the glass electrode, as will be described later.

Prior to the determination of the formation constants, the glass electrode was confirmed to respond well to the activity of the thallium(I) ions with a Nernstian slope in such diverse solvents as AN, methanol, DMF, and DMSO. This is shown in Fig. 1, where the relation between the potentials of the glass electrode and the thallium-amalgam electrode is plotted. When water was the solvent, the plot deviated from a straight line, as shown in Fig. 1, and more time was needed to attain a steady potential than in the cases of the other solvents.

Apparatus and Reagents

Apparatus. Most of the apparatus and experimental techniques for the determination of the formation constants β_x are the same as those in previous reports.[1,2] The arrangement of Cell I is that shown in Fig. 1 of Ref. 1, except that

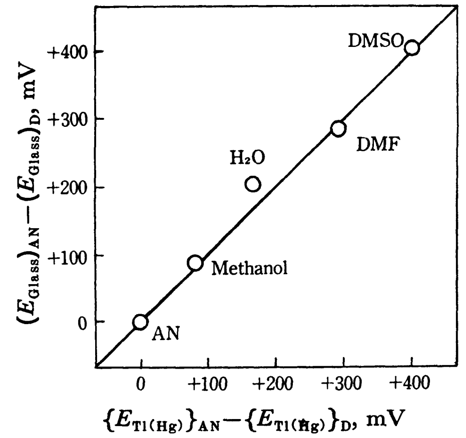

Fig. 1. Relation between potentials of monovalent cation-sensitive glass electrode and those of the thallium-amalgam electrode in various solvents both referred to the values in AN.

5×10^{-4} M of $TlClO_4$ was used in place of 10^{-3} M of $NaClO_4$ or 10^{-3} M of $LiClO_4$ in compartment C and 0.1 M of Et_4NClO_4 was used in place of 0.1 M of Et_4NPi in the compartment B. The thallium-amalgam electrode was used to obtain the hydration constants for thallium(I) ions in AN (*cf.* Cell II).

Reagents. Thallium(I) perchlorate was prepared by neutralizing perchloric acid with an aqueous thallium(I) hydroxide solution prepared by passing a thallium(I) formate solution through a column of Amberlite IRA 411 ion-exchange resin in OH-form[3] and was dried at 70 °C in a high vacuum. The SDMF was prepared from DMF and phosphorus pentasulfide, according to the method of Willstatter and Wirth.[6] The other solvents and reagents used in this experiment were prepared by the same methods as those described in previous reports.[1,2]

Results

Response of the Glass Electrode to the Activity of Thallium(I) Ions in Different Solvents. The glass electrode used in this study had a slope of 58 mV on a logarithm scale of the thallium(I)-ion concentration between 2×10^{-3} and 1.6×10^{-5} M in AN–0.01 M Et_4NClO_4. If corrected for a change in the salt-effect activity coefficient, the response to pa_{Tl^+} is very near the Nernstian slope of 59 mV. The glass electrode also responds well to differences in the activity of thallium(I) ions in several different solvents except water as indicated above and Ref. 4.

Complexing of Thallium(I) Ions with Other Solvents in AN. From the emf measurements using Cell I, the values of

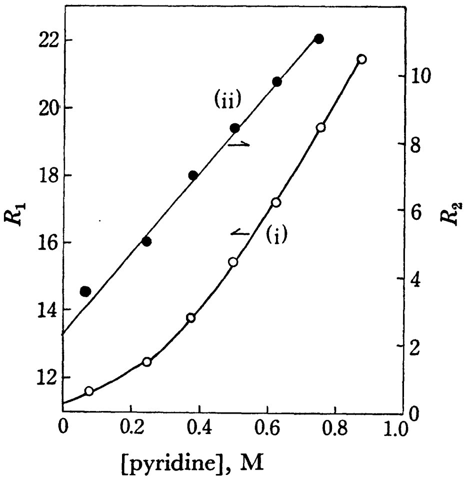

Fig. 2. R_1–[pyridine] (Curve i) and R_2–[pyridine] (Curve ii) relations.

Table 1. Complex formation constants of thallium(I) ions with other solvents in AN

Solvent	Upper mol added (M)	β_1	β_2	β_3	β_4
PC	0.4	(<0.3)			
Methanol	1.0	$0._9$			
		(4.5) [1.1]	$(6._7)$ [0.4]		
H_2O	0.8	1.1*	$0._2$*		
		[1.8]	[1.8]		
DMF	0.9	4.1	$3._1$	$3._4$	
		(16) [2.5]	(1.1×10^2) $[2._1]$	$(6._7\times10)$ $[1._2]$	
SDMF	0.5	5.6	12	$3._8\times10$	
DMA	0.5	6.9	$4._6$	$1._5\times10$	
		(62) [5.3]	(8.7×10^2) [11]	$(1._9\times10^3)$ $[6._4]$	
Pyridine	0.9	11	$2._0$	$1._2\times10$	
		(5.2) [0.7]	$(2._7)$ [0.5]		
Formamide	0.8	11	$8._1$	$2._0\times10$	
		(20)	(90)		
N-Methylformamide	0.5	12	15	$1._9\times10$	$2._0\times10^2$
		(25)	(2.5×10^2)		
DMSO	0.5	15	54	$1._2\times10^2$	
		15*	45*	$1._2\times10^2$*	
		(49) [6.0]	(9.7×10^2) [11]	$(3._2\times10^3)$ $[1._4\times10]$	
HMPA	0.06	1.0×10^2	$2._1\times10^3$	$2._2\times10^4$	$7._3\times10^5$
		(2.1×10^3) [29]	(3.1×10^5) $[3._2\times10^2]$	$[1._3\times10^3]$	

Each value of β is the average of two measurements. Values in parentheses ( ) and brackets [ ] are those for lithium[2] and sodium ions,[1] respectively. Asterisks indicate the values obtained with the thallium-amalgam electrode. (at 25±0.1 °C)

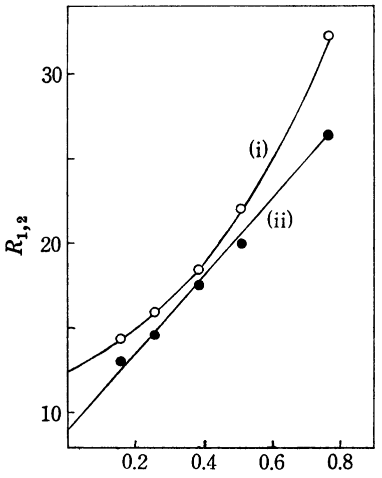

Fig. 3. R_1–[HOCNH$_2$] (Curve i) and R$_2$–[HOCNH$_2$] (Curve ii) relations.

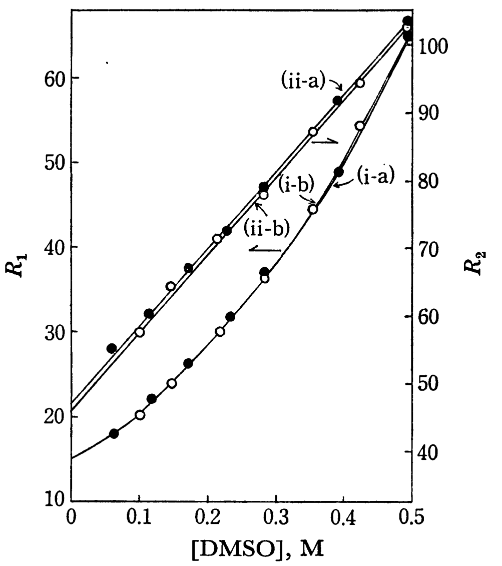

Fig. 4. R_1–[DMSO] (Curve i-a, i*-b) and R_2–[DMSO) (Curve ii-a, ii*-b) relations. * results obtained with the amalgam electrode.

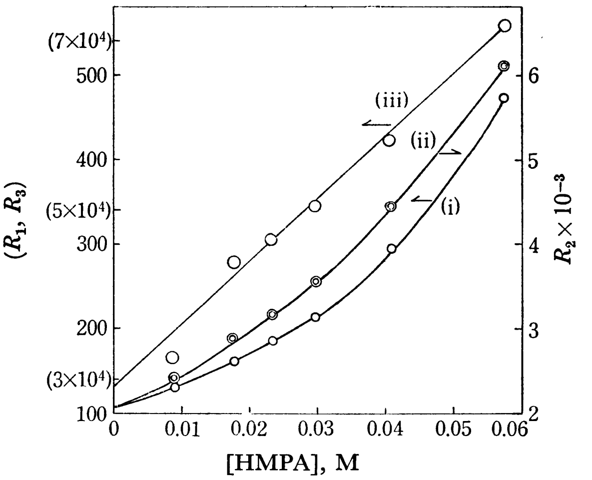

Fig. 5. R_1–[HMPA] (Curve i), R_2–[HMPA] (Curve ii), and R_3–[HMPA] (Curve iii) relations.

the formation constant β_X were calculated using Eqs. 2—4. The results are summerized in Table 1. The maximum concentrations of D added to the AN solution are also shown in Table 1. Figures 2—5 show several examples of the R_1–[D], R_2–[D], and R_3–[D] relations for the determination of the formation constants. When water was added as the complexing solvent D to the compartment C of the Cell I, the rate of potential change was very slow and the steady potential attained was not reproducible. Hydration constants were thus obtained using the thallium-amalgam electrode (Cell II) instead of the glass electrode (Cell I).

Ag|0.005M AgNO$_3$(AN)‖0.1M Et$_3$NClO$_4$(AN)‖
(A) (B)
5×10^{-4}M TlClO$_4$ + 0.01M Et$_4$NClO$_4$(AN + D)|
(C)
thallium-amalgam electrode
Cell II

The thallium content in the amalgam (5.4×10^{-2} M) was determined by the same titration method as that of Ref. 4. The amalgam electrode was sufficiently stable during the period of the emf measurements, so long as the solution in compartment C in Cell II was deaerated. Prior to the determination of the hydration constants of thallium(I) ions with DMSO in AN was also studied with the thallium-amalgam electrode and the formation constants obtained with the two different electrodes agreed fairly well (*cf.* Table 1). Figures 4 and 6 show some examples of the R_1–[DMSO], R_2–[DMSO], and R_1–[H$_2$O] relations obtained with the amalgam electrode.

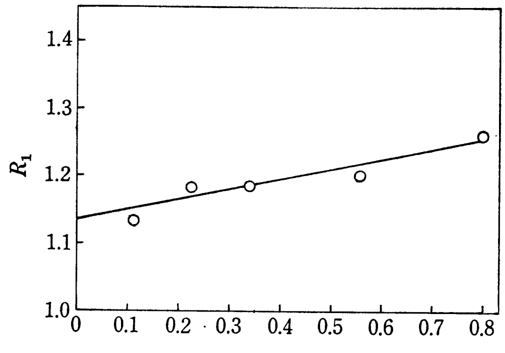

Fig. 6. R_1–[H$_2$O] relation.

Discussion

From Fig. 1, it appears reasonable to consider that the glass electrode can respond to the activity of thallium(I) ions in solvents of different species or compositions.

It was indicated in previous reports[1,2] that pyridine, which has a strong basic character but a low dielectric constant, solvates to sodium and lithium ions only to a small extent. The β_1 increased in the case of sodium ions in order: pyridine<methanol<H$_2$O<DMF<DMA<DMSO, and in the case of lithium ions: methanol<pyridine<DMF<DMSO<DMA. On the other hand, in the case of thallium(I) ions, β_1 increased in order: methanol<H$_2$O<DMF<DMA<pyridine<

DMSO. The strong complexing of pyridine with thallium(I) ions seems to be acceptable considering the strong basic character of pyridine. In the complexing of thallium(I) ions in AN with other solvents formation constants up to β_4 were obtained in the cases of *N*-methylformamide and HMPA. On the other hand, in the cases of lithium ions in AN with these solvents only β_1 and β_2 were obtained. The results may be explained by the fact that the radius (r_c) of the thallium(I) ion is considerably greater than that of the lithium ion. SDMF must solvate to thallium(I) ions more strongly than DMF on the basis of considerations of hard and soft acids and bases. This trend appears in the values in Table 1. In general, the degree of complexing β_x of thallium(I) ions with these solvents in AN was intermediate between those of lithium and sodium ions.

TABLE 2. EFFECT OF THE CONCENTRATION OF AN INDIFFERENT ELECTROLYTE ON THE COMPLEX FORMATION CONSTANTS OF THALLIUM(I) IONS WITH DMSO IN AN

Concn of Et_4ClO_4(M)	β_1	β_2	β_3
0	1.5×10	4.4×10	$1._3\times10^2$
	1.5×10	4.8×10	$1._1\times10^2$
0.01	1.5×10	4.8×10	$1._1\times10^2$
	1.5×10	6.0×10	$1._4\times10$
0.1	1.2×10	3.9×10	$6._4\times10$
	1.3×10	3.7×10	$6._2\times10$

From the results of Table 2, the effect of the concentration of the indifferent electrolyte on complex formation constants of thallium(I) ions with DMSO in AN may be recognized, that is, the values of β_3 for 0.1 M of Et_4NClO_4 are about one-half of those in 0 and 0.01 M of Et_4NClO_4. In the presence of 0.1 M Et_4NClO_4, ion association between thallium(I) and perchlorate ions may occur. The association constant of thallium(I) perchlorate in AN is 32,[7] compared with the constants for sodium and lithium perchlorates of *ca.* 11[8] and *ca.* 4[9] respectively. The addition of DMSO to the AN solution may cause the dissociation of the ion-associated thallium(I) perchlorate and decrease the potential change, and then the apparent value of β_x may become small. Dissociation, of course, may occur as the DMSO content in AN increases. But a complete discussion cannot be made concerning the results in Table 2, because the reliability of these constants (β_x) obtained using the present method appears to be within $\pm10\%$ for β_1 for the dipolar aprotic solvents and might be somewhat less for β_1 for the other solvents and for β_2–β_4.

Many studies have been made concerning solvation phenomena of the sodium ion as noted previously.[1] Recently, Kuntz and Cheng have published the results of experiments on the solvation of some protic solvents with ions in non-aqueous systems using IR measurements,[10] in which the solvation constants (β_1) of lithium ions with methanol and sodium ions with water in AN were described to be 3.4 and 1.3, respectively. These values agree fairly well with those shown in Table 1.

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