

## Solvent Effect on the Synergic Extraction of Thulium(III) with Acetylacetonone and 1,10-Phenanthroline

SHIGETO NAKAMURA, HISANORI IMURA and NOBUO SUZUKI\*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

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### Summary

The synergic extraction equilibrium of Tm(III) with acetylacetonone (Hacac) and 1,10-phenanthroline (phen) in various organic solvents has been studied. The adduct formation constants,  $\beta_s$ , for Tm(acac)<sub>3</sub>-phen, were determined in heptane, cyclohexane, carbon tetrachloride, benzene and chloroform. The solvent effect on  $\beta_s$  is explained in connection with the activity coefficients of the neutral ligand, the chelate, and the adduct in the organic solvent. The activity coefficients can be calculated from the corresponding solubility parameters on the basis of the regular solution theory, and the solubility parameters of the solutes were estimated from their two-phase partition coefficients. It is demonstrated that  $\beta_s$  in different organic solvents except those having a specific interaction with the solute, such as chloroform, can be calculated by the present approach.

### Introduction

The synergic extraction of metal chelates has been investigated in various combinations of chelating extractants and neutral ligands, and generally interpreted in the formation of mixed ligand complexes between metal chelates and additional neutral ligands in the organic phase [1]. In the synergic extraction, the organic solvent plays an important role, and the solvent effect has been quantitatively discussed on the basis of the regular solution theory [2–4]. However, most of the studies on synergic extraction have been carried out using unidentate neutral ligands such as tributyl phosphate and trioctylphosphine oxide; few have used bidentate ligands. Recently the adduct formation constants of some rare earth(III) 2-thenoyltrifluoroacetate chelates with a bidentate neutral ligand, such as 1,10-phenanthroline and 2,2'-bipyridine, have been reported [5, 6]. However, the order of magnitude of their values in corresponding

organic solvents was different. Thus a more detailed investigation of synergic extraction involving the bidentate ligand is desirable.

In the present paper, the synergic extraction of Tm(III) with acetylacetonone (Hacac) and 1,10-phenanthroline (phen) in various organic solvents is investigated and the adduct formation constants are determined. The partition coefficients of Tm(III) tris-acetylacetonate chelate as well as of phenanthroline for various organic solvents are also determined. These values and the solvent effect on adduct formation are discussed quantitatively using the regular solution theory.

### Experimental

#### Materials

A radioisotope, <sup>168</sup>Tm as a tracer, was produced by 30–60 MeV bremsstrahlung irradiation of thulium oxide (99.99% purity) with a linear electron accelerator at Tohoku University. A radioactive Tm(III) solution was prepared by dissolving a known amount of the irradiated sample in hydrochloric acid, evaporating to dryness, and re-dissolving in 10<sup>-3</sup> M perchloric acid solution.

Acetylacetonone was washed with diluted ammonia solution and redistilled after drying. Reagent grade 1,10-phenanthroline was used as obtained.

Chloroform was washed with redistilled water several times before use. The other organic solvents were purified by ordinary methods [7].

Unless otherwise stated, reagents used were of guaranteed reagent grade.

#### Apparatus

The  $\gamma$ -activity of <sup>168</sup>Tm was measured with an NaI (TI) well-type scintillation detector connected with a single-channel analyzer.

The extraction vial was shaken with a mechanical shaker at 330 strokes per minute.

The pH value of the equilibrated aqueous phase was measured with a glass electrode.

\*Author to whom correspondence should be addressed.

### Determination of the Partition Coefficient ( $P_S$ ) and the Acid Dissociation Constant ( $K_{HS}$ ) of Phen

Ten ml of an organic solution containing a known amount ( $10^{-5}$ – $10^{-3}$  M) of phen were shaken for 1 hour with 10 ml of an aqueous solution of pH 8–10 containing 0.1 M sodium perchlorate. Concentration of the ligand in the aqueous or organic phase was determined spectrophotometrically [8] and the partition coefficient ( $P_S$ ) was calculated. The acid dissociation constant of protonated phen ( $K_{HS}$ ) can be calculated from the following equation:

$$K_{HS} = \frac{[H^+]}{P_S/D_S - 1} \quad (1)$$

where  $D_S$  denotes the distribution ratio of phen at different pH. The dissociation constant ( $pK_{HS}$ ) was determined to be 5.04 at pH 3–10 in the cyclohexane distribution system.

### Extraction of Tm(III)

An aqueous solution (10 ml) containing  $10^{-5}$  M Tm(III) labelled with  $^{168}\text{Tm}$  was placed in a 50 ml centrifuge tube with a ground glass stopper. An organic solution (10 ml) containing  $10^{-1}$  M acetylacetone and  $10^{-5}$ – $10^{-3}$  M phen was added and shaken for 1–3 hours at 25 °C and centrifuged. An aliquot was taken from each phase and the  $\gamma$ -activity was measured. The distribution ratio ( $D$ ) of Tm(III) was calculated. The extraction equilibration was confirmed by the agreement between the distribution ratios of Tm(III) in forward and backward extraction.

The pH value of the aqueous phase was adjusted with  $5 \times 10^{-3}$ – $10^{-2}$  M piperazine-*N,N'*-bis(2-ethanesulfonic acid) and sodium hydroxide solution, and the equilibrium pH value was measured immediately after shaking. The buffer component of less than  $10^{-2}$  M has no influence on the extraction of Tm(III). Ionic strength was adjusted to 0.1 with sodium perchlorate.

### Theoretical

The distribution ratio ( $D_o$ ) of a trivalent cation,  $M^{3+}$ , with a chelating extractant, HA, can be expressed as follows:

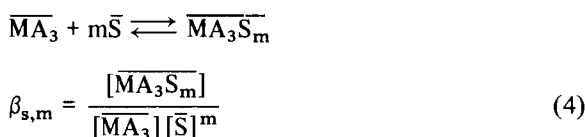
$$D_o = \frac{[\overline{MA_3}]}{[M^{3+}] + \sum [MA_n^{3-n}]} = \frac{P_M \beta_3 [A^-]^3}{1 + \sum \beta_n [A^-]^n} \quad (2)$$

where the bar denotes the organic phase,  $\beta_n$  the formation constant of  $MA_n^{3-n}$  in the aqueous phase,  $P_M$  the partition coefficient of  $MA_3$  and  $A^-$  the chelating anion in the aqueous phase.

In the synergic extraction of  $M^{3+}$  with HA and neutral ligand, S, the distribution ratio ( $D$ ) can be expressed as follows:

$$D = \frac{[\overline{MA_3}] + \sum [\overline{MA_3 S_m}]}{[M^{3+}] + \sum [MA_n^{3-n}]} = \frac{P_M \beta_3 [A^-]^3 (1 + \sum \beta_{s,m} [\overline{S}]^m)}{1 + \sum \beta_n [A^-]^n} \quad (3)$$

where  $\beta_{s,m}$  is the adduct formation constant in the organic phase corresponding to the following equilibrium:



From eqns. (2) and (3), the following relation is obtained:

$$D/D_o = 1 + \sum \beta_{s,m} [\overline{S}]^m \quad (5)$$

This equation can be rewritten if only  $MA_3 S_m$  is the dominant species in the organic phase:

$$\log(D/D_o) = \log \beta_{s,m} + m \log [\overline{S}] \quad (6)$$

The plot of  $\log(D/D_o)$  against  $\log [\overline{S}]$  will be a straight line with a slope of  $m$ .

## Results and Discussion

### Extraction of Tm(III) with Acetylacetone

The extraction of Tm(III) with Hacac was carried out and the plots of  $\log D_o$  against  $\log [acac^-]$  are given in Fig. 1 the equilibrium concentration of  $acac^-$  in the aqueous phase was calculated as follows:

$$[A^-] = \frac{C_{HA}}{(P_{HA} + 1)[H^+]/K_{HA} + 1} \quad (7)$$

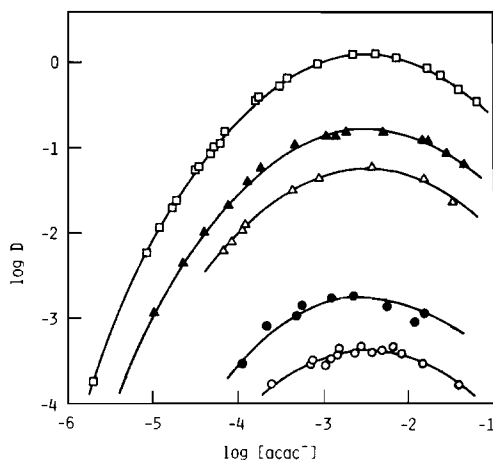


Fig. 1. The extraction of Tm(III) with 0.1 M Hacac in various organic solvents.  $\square$ : chloroform,  $\blacktriangle$ : benzene,  $\triangle$ : carbon tetrachloride,  $\bullet$ : cyclohexane,  $\circ$ : heptane.

where  $P_{\text{HA}}$  and  $K_{\text{HA}}$  denote the partition coefficient and the acid dissociation constant of Hacac respectively, and  $C_{\text{HA}}$  the initial concentration. The literature values of  $K_{\text{HA}}$  and  $P_{\text{HA}}$  were adopted, i.e.  $\log K_{\text{HA}} = -8.88$  [9], and  $\log P_{\text{HA}} = -0.05$  for heptane [10], 0.01 for cyclohexane [11], 0.50 for carbon tetrachloride [12], 0.74 for benzene [12] and 1.37 for chloroform [12].

The plots for each organic solvent system give a curve with a maximum. This indicates the presence of the lower and higher complexes of Tm(III) with  $\text{acac}^-$  in the aqueous phase, for example,  $\text{Tm}(\text{acac})_2^{2+}$ ,  $\text{Tm}(\text{acac})_3$  and  $\text{Tm}(\text{acac})_4^-$ , which may be formed successively with increasing concentration of  $\text{acac}^-$ . A decrease of  $\log D_o$  in the higher concentration region may not be due to hydrolysis of Tm(III) but to the formation of  $\text{Tm}(\text{acac})_4^-$ . The presence of such an anionic chelate was confirmed by ion-pair extraction with tetraphenylarsonium (tpa) cation as follows.

If an ion pair complex,  $(\text{tpa})_y^{y+} \cdot \text{Tm}(\text{acac})_{3+y}^{y-}$ , is formed and extracted into chloroform, the distribution ratio ( $D_i$ ) of M(III) in the presence of organic cation  $\text{B}^+$  is generally written by the following equation:

$$D_i = \frac{[\text{MA}_3] + \sum [\text{B}_y^{y+} \cdot \text{MA}_{3+y}^{y-}]}{[\text{M}^{3+}] + \sum [\text{MA}_n^{3-n}]} = \frac{P_M \beta_3 [\text{A}^-]^3 + \sum K_{i,y} \beta_{3+y} [\text{B}^+]^y [\text{A}^-]^{3+y}}{1 + \sum \beta_n [\text{A}^-]^n} \quad (8)$$

$$K_{i,y} = \frac{[\text{B}_y^{y+} \cdot \text{MA}_{3+y}^{y-}]}{[\text{MA}_{3+y}^{y-}] [\text{B}^+]^y} \quad (9)$$

where  $K_{i,y}$  is the ion-pair extraction constant. From eqns. (2) and (8),  $D_i/D_o$  is written as:

$$D_i/D_o = 1 + \sum \frac{K_{i,y} \beta_{3+y} [\text{B}^+]^y}{P_M \beta_3} [\text{A}^-]^y \quad (10)$$

Figure 2 shows the plots of  $\log(D_i/D_o)$  against  $\log[\text{acac}^-]$  at a constant concentration of  $\text{tpa}^+$ . A

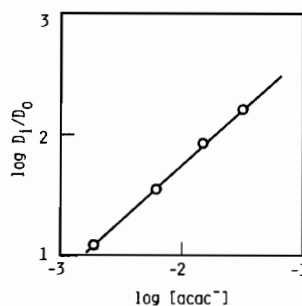


Fig. 2. The ion-pair extraction of Tm(III) with Hacac and tpa into chloroform.  $[\text{Hacac}]_{\text{init.}} = 1.0 \times 10^{-1}$  M,  $[\text{tpa}^+]_{\text{init.}} = 1.0 \times 10^{-2}$  M, pH = 8.5–10.0, shaking time 4 h.

straight line with a slope of 0.92 suggests the presence of predominant extracted species of a 1 to 1 ion-pair complex, like  $\text{tpa}^+ \cdot \text{Tm}(\text{acac})_4^-$ . The tetrakis  $\beta$ -diketonato chelate of rare earth(III) has been isolated and its structure analyzed [13], hence it is natural to consider the anionic chelate,  $\text{Tm}(\text{acac})_4^-$ , under these conditions.

Equation (2) is rewritten as follows:

$$D_o = \frac{P_M}{1/k_1 k_2 k_3 [\text{A}^-]^3 + 1/k_2 k_3 [\text{A}^-]^2 + 1/k_3 [\text{A}^-] + 1 + k_4 [\text{A}^-]} \quad (11)$$

where  $k_n$  ( $n = 1-4$ ) is the successive formation constant of  $\text{Tm}(\text{acac})_n^{3-n}$  in the aqueous phase. The values of  $P_M$  and  $k_n$  in the chloroform system were computed by the least squares fitting method, using the computer program SALS (University of Tokyo). The logarithmic values of  $P_M$  and  $k_n$  ( $n = 1-4$ ) are obtained as 0.24 for  $P_M$ , 5.30 for  $k_1$ , 4.74 for  $k_2$ , 3.22 for  $k_3$  and 1.79 for  $k_4$ . These values, except for  $k_4$ , are close to those in the literature, 6.05 for  $k_1$ , 4.76 for  $k_2$  and 3.48 for  $k_3$ , respectively [14]. A noticeable deviation of the present  $k_1$  value from the literature is partially due to the lack of reproducible data in the lower concentration region of  $\text{acac}^-$ . However, as is clearly understood from eqn. (11), such a small deviation of  $k_1$  has no influence on the following calculation of  $P_M$  by curve analysis.

TABLE I. Equilibrium Constants in the Synergic Extraction Systems of Tm(III).

Solvent	$\delta_o$	$\log P_S$	$\log P_M$	$\log \beta_s$	$\ln \beta_s^x$ (experimental)	$\ln \beta_s^x$ (calculated) <sup>a</sup>
Heptane	7.43	-1.09	-3.23	6.97	17.96	18.02
Cyclohexane	8.20	-0.97	-2.61	6.53	17.25	17.09
Carbon tetrachloride	8.58	0.15	-1.10	6.18	16.56	16.62
Benzene	9.16	0.78	-0.63	5.84	15.86	15.92
Chloroform	9.3	2.98	0.24	4.59	13.08	15.75

<sup>a</sup>Calculated from eqn. (21).

The values of  $P_M$  in other organic solvent systems were calculated using  $k_n$  obtained in the present work (Table I). The solid lines in Fig. 1 represent the extraction curves calculated from the determined values of  $P_M$  and  $k_n$  using eqn. (11). The good agreement with the experimental data in each system is clearly observed. The values of  $P_M$  are about two or three orders of magnitude smaller than those of tris(acetylacetonato)chromium(III) or cobalt(III) in the same solvent systems [15, 16]. It is well known that these first transition metal(III) chelates with acetylacetonone have coordinatively saturated octahedral structures and a coordination number of the central metals of six. On the other hand, tris acetylacetonate chelates of Yb(III) [17] and La(III) [18] have been isolated as the monohydrate and dihydrate forms respectively, and the coordination numbers of the central metals have been reported to be seven or eight from X-ray diffraction. Therefore the lower  $P_M$  of the tris acetylacetonate chelate of Tm(III) may be ascribed to the hydrated state of the chelate.

#### Synergic Extraction of Tm(III) with Hacac and Phen

The plots of the logarithm of  $D/D_0$  against the logarithm of the equilibrium concentration of phen in the various organic phases, according to eqn. (5), are shown in Fig. 3. The concentration of phen in the organic phase was calculated as follows:

$$[\bar{S}] = \frac{C_S}{1 + (1 + [H^+]/K_{HS})/P_S} \quad (12)$$

where  $C_S$  denotes the initial concentration of phen in the organic phase. The acid dissociation constant of protonated phen,  $K_{HS}$ , is  $10^{-5.04}$  and the partition coefficient of phen,  $P_S$ , is determined experimentally as listed in Table I. These plots in Fig. 3 give straight lines with a slope of unity. A deviation

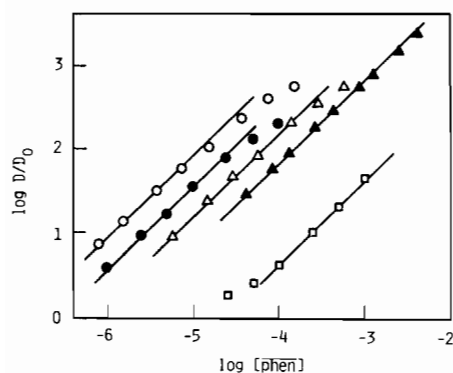


Fig. 3. Effect of the concentration of phen in the organic phase on the synergic extraction of Tm(III). ○: heptane (pH 7.5), ●: cyclohexane (pH 6.9), △: carbon tetrachloride (pH 6.5), ▲: benzene (pH 6.1), □: chloroform (pH 6.3).

from the straight line in the higher concentration range of phen may account for an interaction between Hacac and phen in the organic phase. This result means that the mol ratio of Tm(acac)<sub>3</sub> to phen in the adduct complex is 1:1. The coordination number of Tm(III) in this adduct complex seems to be eight and this may be supported by the X-ray crystallographic study on a similar mixed ligand complex, Eu(acac)<sub>3</sub>phen [19].

Adduct formation constants,  $\beta_s$ , are also summarized in Table I. These values are remarkably influenced by the solvents, and they decrease in the following order; heptane > cyclohexane > carbon tetrachloride > benzene > chloroform. This order is the same as that in many other synergic extraction systems, for instance, the Mn(II)–Htta–phen [8] and Sc(III)–Htta–tributyl phosphate [3] systems.

#### Quantitative Treatment of the Solvent Effect

The solvent effect on the synergic extraction can be quantitatively discussed by considering the activity coefficients,  $\gamma$ , of the solutes in different solvents. A thermodynamic adduct formation constant,  $\beta_s^\circ$ , is defined as follows:

$$\beta_s^\circ = \frac{X_{MS}}{X_M X_S} \cdot \frac{\gamma_{MS}}{\gamma_M \gamma_S} = \beta_s^x \cdot \frac{\gamma_{MS}}{\gamma_M \gamma_S} \quad (13)$$

where  $X$  is the mol fraction of the solute in the organic phase, and the subscripts MS, M and S denote the adduct, chelate and neutral ligand, respectively, and  $\beta_s^x$  the adduct formation constant in mol fraction units.

The activity of a nonelectrolyte solute,  $a_c$ , can be expressed based on the regular solution theory [20] as:

$$\ln a_{c,o} = \ln X_{c,o} + \frac{V_c}{RT} \phi_o^2 (\delta_c - \delta_o)^2 \quad (14)$$

where  $V$ ,  $\delta$  and  $\phi$  are the molar volume, the solubility parameter and the volume fraction, respectively, and the subscripts c and o denote the solute and the organic solvent, respectively. Since the concentration of the solute is very low in the present experiments,  $\phi_o$  is approximately unity. Accordingly, the activity coefficient can be estimated from the solubility parameters of the components as:

$$\ln \gamma_{c,o} = \frac{V_c}{RT} (\delta_c - \delta_o)^2 \quad (15)$$

The solubility parameter of the solvents,  $\delta_o$ , is given in the literature, but that of the solutes concerned is not. The partition coefficient of a solute expressed in mol fraction,  $P_c^x$ , is related to the activity coefficient as:

$$P_c^x = \frac{X_{c,o}}{X_{c,a}} = \frac{\gamma_{c,a}}{\gamma_{c,o}} \quad (16)$$

where the subscript a denotes the aqueous phase.

From eqns. (15) and (16) the next equation can be derived:

$$\ln P_c^x = - \frac{V_c}{RT} (\delta_c - \delta_o)^2 + \ln \gamma_{c,a} \quad (17)$$

hence:

$$\frac{RT}{V_c} \ln P_c^x + \delta_o^2 = 2\delta_c\delta_o + \left( \frac{RT}{V_c} \ln \gamma_{c,a} - \delta_c^2 \right) \quad (18)$$

Since the second term of the right hand side of eqn. (18) is independent of the organic solvent, the solubility parameter of the solute,  $\delta_c$ , can be calculated from the slope in the plots of the left hand against  $\delta_o$  for various organic solvents. The partition coefficients of the Tm(III)-acetylacetonate chelate and phen are experimentally obtained.

The molar volume of phen has been quoted as 142 cm<sup>3</sup>/mol in the literature [21]. The molar volume of the chelate was assumed to be equal to that of Dy(acac)<sub>3</sub> and Yb(acac)<sub>3</sub>, 269 cm<sup>3</sup>/mol [22], and that of the adduct to be the sum of the molar volumes of the chelate and phen, 411 cm<sup>3</sup>/mol. These plots for phen and Tm(acac)<sub>3</sub> are shown in Figs. 4 and 5 respectively. Similar plots cannot be simply drawn for the adduct, because the partition coefficient of the adduct in the left hand side of eqn. (18) cannot be measured directly. The hypothetical partition coefficient of the adduct,  $P_{MS}^x = \frac{[MA_3S]}{[MA_3S]}$ , can be shown as eqn. (19) by the combination of adduct formation constants in both phases,  $\beta_s^x$  in the organic phase and  $\beta_{s,a}^x$  in the aqueous phase, with the partition coefficients of metal chelate ( $P_M^x$ ) and phen ( $P_S^x$ ):

$$P_{MS}^x = \frac{\beta_s^x P_M^x P_S^x}{\beta_{s,a}^x} \quad (19)$$

From eqns. (18) and (19), the following equation is derived:

$$\begin{aligned} \frac{RT}{V_{MS}} \ln P_{MS}^x + \delta_o^2 \\ = 2\delta_{MS}\delta_o + \left( \frac{RT}{V_{MS}} \ln \gamma_{MS,a} \beta_{s,a}^x - \delta_{MS}^2 \right) \end{aligned} \quad (20)$$

where  $P_{MS}^x$  denotes  $P_{MS}^x \cdot \beta_{s,a}^x$  and equals the product of the constants obtained experimentally,  $\beta_s^x P_M^x P_S^x$ . Now the solubility parameter of the adduct can be calculated by similar plots as shown in Fig. 6. Figures 4, 5 and 6, for phen, Tm(acac)<sub>3</sub> and

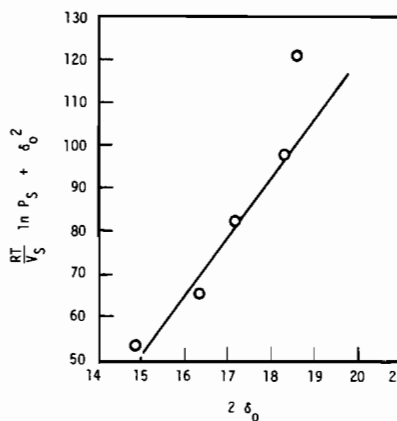


Fig. 4. Plots of eqn. (18) for phen in different solvent systems.

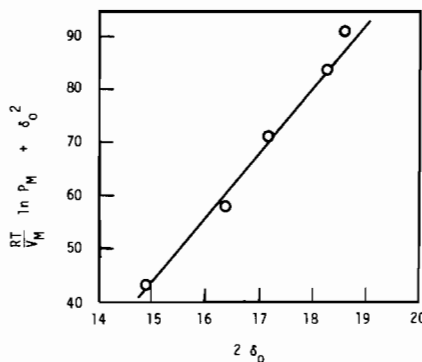


Fig. 5. Plots of eqn. (18) for the chelate in different solvent systems.

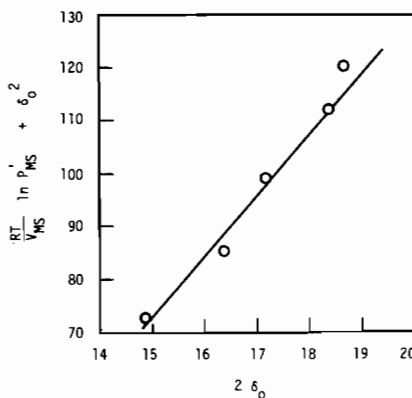


Fig. 6. Plots of eqn. (20) for the adduct in different solvent systems.

Tm(acac)<sub>3</sub>phen show a good linear relationship for heptane, cyclohexane, carbon tetrachloride and benzene but not for chloroform, and the solubility parameter of each solute can be calculated by the least squares method of the plots for four solvents. The solubility parameters of phen, Tm(acac)<sub>3</sub> and Tm(acac)<sub>3</sub>phen are 13.15, 12.03 and 11.54, respectively. A deviation observed in the plot for chloro-

form, especially in the phen system, is ascribed to a specific interaction between solute and solvent such as hydrogen bonding. Such an interaction has been ascertained by infrared spectroscopy in the pyridine–chloroform system [23]. The observed solubility parameter of phen seems to be rather large compared with that of similar nitrogen containing aromatic compounds such as pyridine (10.62) or quinoline (10.8) which are calculated from the vaporization energy and the molar volume of the pure liquid. It is well known that phen has a strong tendency to form a monohydrate in the solid state. This may imply that phen is extracted as a hydrated form with a larger solubility parameter. The observed solubility parameter of the adduct  $\text{Tm}(\text{acac})_3\text{phen}$  is lower than those of both phen and  $\text{Tm}(\text{acac})_3$ . Since the central metal of the adduct molecule is surrounded by the nonpolar parts of  $\text{acac}^-$  and phen, the adduct may become more lipophilic than free phen or  $\text{Tm}(\text{acac})_3$  itself.

The activity coefficient of each solute in different organic solvents can be calculated by eqn. (15) from the solubility parameters obtained above. As shown in Fig. 7 the plots of  $\ln \beta_s^x$  against  $\ln \gamma_{\text{MS}}/\gamma_{\text{M}}\gamma_{\text{S}}$  are close to a straight line with a slope of  $-1$  for most

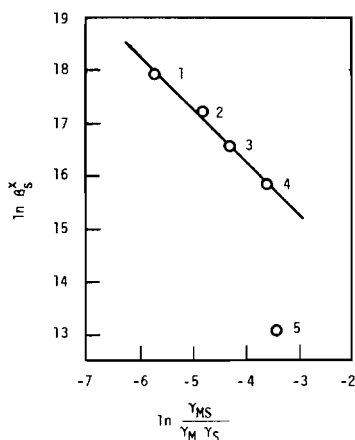


Fig. 7. Relation between the adduct formation constant and the activity coefficients in the organic phase. 1: heptane, 2: cyclohexane, 3: carbon tetrachloride, 4: benzene, 5: chloroform.

solvents except chloroform, as was to be expected from eqn. (13). This demonstrates that the present approach to the solvent effect on adduct formation is quite reasonable. The thermodynamic adduct formation constant,  $\ln \beta_s^o$ , is calculated to be 12.29 from eqn. (13), so that  $\beta_s^x$  in various organic solvents can be readily calculated by the following equation, derived from eqns. (13) and (15):

$$\ln \beta_s^x = 12.29 + \frac{V_{\text{M}}}{RT} (\delta_{\text{M}} - \delta_{\text{o}})^2 + \frac{V_{\text{S}}}{RT} (\delta_{\text{S}} - \delta_{\text{o}})^2 - \frac{V_{\text{MS}}}{RT} (\delta_{\text{MS}} - \delta_{\text{o}})^2 \quad (21)$$

The calculated values of  $\ln \beta_s^x$  are summarized in Table I and compared with the experimental constant. A good agreement is again clear except for the chloroform system. The present approach is effective in predicting the adduct formation constants in other organic solvent systems which have no specific solute–solvent interaction.

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