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Role of the Solvent in the Distribution of the Zinc-TTA Chelate and the Adduct Formation with TBP

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The distributions of the zinc chelate with thenoyltrifluoroacetone (TTA) between an aqueous solution and twelve inert organic solvents were investigated. After it had been confirmed that the distributed species were ZnA_2, the distribution coefficients of the chelate (P_M) and those of TTA (P_{HA}) were compared; it was found that there is a correlation which can be expressed as $\log P_M = n \log P_{HA} + \text{const}$. When TTA and TBP are in the extraction system, the adduct formation constants of chelate were obtained. The activities of all the species which take part in the adduct formation were evaluated on the basis of the regular solution theory. It was found that the adduct formation constant in terms of activity (K_S°) is constant in all the organic solvents; namely, $\log K_S^\circ$ was found to be 4.05. Finally, the role of the solvent in the synergistic extraction system is explained systematically by a combination of the regularity in the distribution and that in the adduct formation.

The extraction processes of metal complexes have been studied qualitatively in several extraction systems, but there have been few works on the role of organic solvents in connection with the physical chemistry of a solution. The properties of solvents governing the distribution coefficient have never been clarified, and the solvents have been chosen empirically without even a qualitative measure.

In the previous papers the relation between the distribution coefficient and the solubility parameter of solvents was examined on the basis of the regular solution theory;[1] the regularities in the distributions of β-diketones and their scandium chelates have thus been explained in the various solvent systems.[2–6] A similar treatment is applicable not only to β-diketone but to a distributed species in general; the distribution coefficients of oxine and its derivatives have been explained in relation to the solubility parameter.[7]

However, the regularity in the distribution can be hardly explained in the same manner when such organic-phase reactions as adduct formation, dimerization, and solvation take place. A synergism on the distribution of the metal chelate has been observed in several extraction systems, but no general explanation of the role of the solvent has

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[1] T. Wakabayashi, S. Oki, T. Omori and N. Suzuki, *J. Inorg. Nucl. Chem.*, **26**, 2255 (1964).

[2] T. Omori, T. Wakabayashi, S. Oki and N. Suzuki, *ibid.*, **26**, 2265 (1964).

[3] N. Suzuki, K. Akiba, T. Kanno and T. Wakabayashi, *ibid.*, **30**, 2521 (1968).

[4] N. Suzuki, K. Akiba, T. Kanno, T. Wakabayashi and K. Takaizumi, *ibid.*, **30**, 3047 (1968).

[5] T. Wakabayashi, K. Takaizumi, K. Seto, N. Suzuki and K. Akiba, This Bulletin, **41**, 1854 (1968).

[6] N. Suzuki, K. Akiba and T. Kanno, *Anal. Chim. Acta*, **43**, 311 (1968).

[7] T. Wakabayashi, This Bulletin, **40**, 2836 (1967).

been given. The physicochemical properties of the solvent will, however, influence both the distribution coefficients and the equilibrium constants of the organic-phase reactions. The synergistic effect should be discussed in relation to not the over-all extraction constant but the equilibrium constants of the organic-phase reactions.

This work was undertaken in order to clarify the role of the organic solvent in the distribution of the chelate and in the adduct formation with a neutral ligand. The distribution coefficients of the zinc-TTA chelate between an aqueous perchlorate medium and several organic solvents are determined, and the relation between the distribution coefficients of TTA is examined. The adduct formation constants of the zinc-TTA chelate with tributyl phosphate (TBP) are obtained by the distribution method.

The activity coefficients of the species related to the organic-phase reaction are estimated with the aid of the regular solution theory,[8] and the adduct formation constants are correlated to changes in the activity coefficients. The role of solvents in synergistic extraction may be explained systematically by the regularity in the distribution and that in the adduct formation.

Experimental

Reagents. The zinc-65 was obtained from the New England Nuclear Corp. (USA) as a hydrochloric acid solution. After a portion of this solution had been dried on a water bath, the tracer was taken in 0.1M perchloric acid; the concentration of zinc ions was controlled by the addition of an inactive zinc solution.

TTA was purified as before.[6]

TBP was refluxed for 5 hr with an equal volume of a 0.5M sodium hydroxide solution on the water bath; the TBP phase was washed with water and dried over anhydrous sodium sulfate, and the washed product was distilled under reduced pressure.

All the solvents were purified by ordinary methods.

The apparatus used was the same as that described previously.[4]

Distribution Ratio of TTA (D_{HA}). The desired organic solution of TTA was shaken for 16 hr with an aqueous perchloric acid solution with an ionic strength of 0.1. After centrifuging, a portion of the aqueous phase was pipetted out, and the concentration of TTA was determined spectrophotometrically. An aqueous solution saturated with an organic solution free from TTA was used as a reference for the measurement of the absorbance.

Distribution Ratio of Zinc (D_M, $D_{M,S}$). An organic solution containing TTA was agitated for 20 hr with an acetate buffer solution (pH 3.5—5.5) containing ^{65}Zn. The ionic strength was adjusted to 0.1 with sodium perchlorate. After the two phases had been separated, the γ-activity of each phase and the pH of the aqueous phase were measured.

All the experiments were carried out at 25°C.

Concentration of Acetate Ions. The distribution ratios of zinc decreased slightly with an increase in the concentration of acetate ions up to about 0.05M, but they were constant below 0.01M. Accordingly, the concentration of acetate ions was kept at 0.002M.

Concentration of Zinc Ions. As the distribution ratios are independent of the zinc-ion concentration below about 5×10^{-6}M, the concentration of zinc was kept at 10^{-6}M. The recovery of the total γ-activity was always checked, and the losses of zinc were found for a few paraffinic solvents. To avoid the loss of zinc, the concentration of zinc was held constant at 10^{-7}M for these solvents.

Results and Discussion

The extraction processes of the zinc-TTA chelate may be expressed as follows:

$$\mathrm{Zn}^{2+}_{\mathrm{aq}} + n\mathrm{A}^-_{\mathrm{aq}} \overset{\beta_n}{\rightleftarrows} \mathrm{ZnA}^{(2-n)+}_{n,\mathrm{aq}} \tag{1}$$

$$\mathrm{ZnA}_{2,\mathrm{aq}} \overset{P_M}{\rightleftarrows} \mathrm{ZnA}_{2,\mathrm{org}} \tag{2}$$

$$\mathrm{ZnA}_{2,\mathrm{org}} + j\mathrm{HA}_{\mathrm{org}} \overset{K_j}{\rightleftarrows} \mathrm{ZnA}_2\cdot j\mathrm{HA}_{\mathrm{org}} \tag{3}$$

$$\mathrm{ZnA}_{2,\mathrm{org}} + m\mathrm{S}_{\mathrm{org}} \overset{K_{S,m}}{\rightleftarrows} \mathrm{ZnA}_2\cdot m\mathrm{S}_{\mathrm{org}} \tag{4}$$

where HA and S stand for the undissociated TTA and the neutral ligand respectively. The subscripts aq and org refer to the aqueous and organic phases.

The distribution of zinc in the absence of the neutral ligand, D_M, is given by:

$$D_M = \frac{P_M\beta_2[\mathrm{A}^-]^2_{\mathrm{aq}}\{1+\sum K_j[\mathrm{HA}]^j_{\mathrm{org}}\}}{1+\beta_n[\mathrm{A}^-]^n_{\mathrm{aq}}} \tag{5}$$

If no mixed adduct complexes, $\mathrm{ZnA}_2\cdot j\mathrm{HA}\cdot m\mathrm{S}$, are formed, and distribution ratio in the presence of the neutral ligand, $D_{M,S}$, is written as:

$$D_{M,S} = \frac{P_M\beta_2[\mathrm{A}^-]^2_{\mathrm{aq}}\{1+\sum K_j[\mathrm{HA}]^j_{\mathrm{org}}+\sum K_{S,m}[\mathrm{S}]^m_{\mathrm{org}}\}}{1+\sum\beta_n[\mathrm{A}^-]^n_{\mathrm{aq}}} \tag{6}$$

The extraction of zinc complexes with the neutral ligand alone is negligibly small. If the undissociated TTA does not react with the chelate and if the only adduct with S is predominant, the following equation is obtained from Eqs. (5) and (6):

$$K_S = \frac{D_{M,S}}{D_M}\cdot\frac{1}{[\mathrm{S}]^m_{\mathrm{org}}} \tag{7}$$

where K_S is the overall adduct formation constant.

Distribution of the Zinc Chelate. The extraction mechanism of the zinc-TTA chelate has been studied for a few solvent systems, and it has been shown that bivalent zinc is extracted into the organic phase as the formally neutral species

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[8] J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3rd Ed., Dover, New York (1964).

ZnA_2.[9-11] In this study it was important to confirm that the distributed species is the same one for all solvents. Plots of $\log D_M$ measured at various pH values against pA ($=-\log[A^-]_{aq}$) gave a series of straight lines with a slope of -2. As an example that for benzene is given in Fig. 1; the same line was obtained at different concentrations of HA. In all cases, the distributed species is ZnA_2 and there is no additive compound with HA. The concentration of the dissociated TTA anion (A^-) in the aqueous phase can be calculated by the following equation:

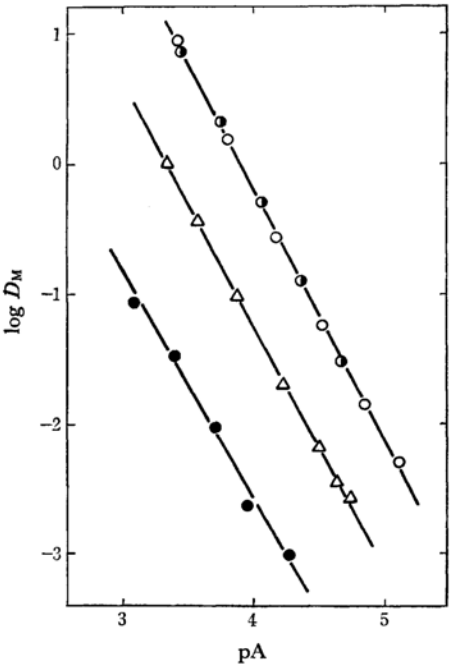

Fig. 1. Distribution ratio of zinc-TTA chelate as a function of pA.
Ionic strength, 0.10; $[HA]_{org,\ init.}=0.1$M
●, *n*-hexane; △, carbon tetrachloride;
○, benzene; ◑, benzene (pH=5.08)

$$[A^-]=\frac{[HA]_{org,init.}}{(P_{HA}+1)[H^+]/K_a+1} \tag{8}$$

where K_a represents the apparent dissociation constant of TTA, $K_a=6\times10^{-7}$,[12] and where P_{HA} is the distribution coefficient of TTA. When the concentration of zinc is over 10^{-6}M, losses of radioactivities were observed in *n*-hexane, *n*-heptane, and cyclohexane. Even in this case, however, the distribution ratios are independent of the zinc concentration and the same straight lines, $\log D_M$ *vs.* pA, are obtained. After the two phases were discarded, the extracting tube was washed with an organic solvent other than the paraffinic solvent or with an acidic aqueous solution; a great portion of the lost activity could be thus recovered. It seems that both the phases were saturated with such complexes as $ZnA_2\cdot nH_2O$ and that a portion of the complexes was removed from the system as a precipitate. The possibility of the formation of the higher complexes, $ZnA_n^{(2-n)+}$ ($n>2$), seems to be eliminated. The measured distribution ratio may be regarded as a contribution of only one species, that shown as ZnA_2. The distribution coefficients of the chelate are too large to be measured experimentally. As the distribution ratio written in Eq. (5) is expressed as a simple function of pA, the distribution ratio is proportional to the distribution coefficient at a definite pA. The distribution ratios at pA 4.0 for each solvent are given in Table 1. The following relation between the distribution coefficients of the chelating agent and those of the metal chelate has been derived from the regular solution theory[2] (the distributions of scandium β-diketonates were satisfactorily explained in the various solvent systems):[2,4-6]

$$\log P_M=\frac{V_M}{V_{HA}}\log P_{HA}+\text{const.} \tag{9}$$

where V_{HA} and V_M denote the molar volume of the chelating agent and that of the metal chelate respectively. This relation is expected to hold for the zinc chelate also. Plots of $\log D_M$ at pA 4.0

TABLE 1. DISTRIBUTION RATIO OF ZINC-TTA CHELATE AND ADDUCT FORMATION CONSTANT WITH TBP AT 25°C, IONIC STRENGTH, 0.10

No.	Solvent	δ	$\log P_{HA}$	$\log D_M$ (pA= 4.0)	$\log K_S$
1	*n*-Hexane	7.3	0.68*	−2.54	5.17
2	*n*-Heptane	7.4	0.57	−2.74	5.26
3	Cyclohexane	8.2	0.56	−2.45	5.01
4	Chloroform	9.3	1.73*	−0.44	2.78
5	Methylene chloride	9.7	1.84*	0.21	3.03
6	Carbon tetrachloride	8.6	1.30*	−1.24	4.43
7	Benzene	9.2	1.62*	−0.23	4.01
8	Monochlorobenzene	9.5	1.65*	−0.30	3.73
9	*o*-Dichlorobenzene	10.0	1.59*	−0.30	3.90
10	Isopropylbenzene	8.5	1·37**	−0.99	4.09
11	Bromoform	10.5			2.84
12	Toluene	8.9	1.60*	−0.32	4.03

* Values from Ref. 1.
** Values from Ref. 2.

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[9] T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 1727 (1964).

[10] H. M. N. H. Irving and D. N. Edgington, *ibid.*, **27**, 1359 (1965).

[11] R. L. Scruggs, T. Kim and N. C. Li, *J. Phys. Chem.*, **67**, 2194 (1963).

[12] J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, **72**, 2948 (1950).

against log P_{HA} give a straight line with a slope of 2.1, as is shown in Fig. 2. It is reasonable that the ratio of the molar volume of the chelate to that of TTA is about two, because two molecules of TTA combine with zinc ion.

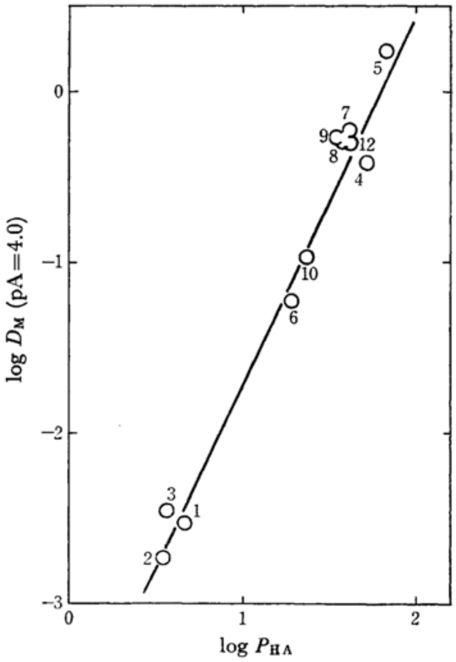

Fig. 2. Correlation between the distribution coefficient of TTA and that of zinc chelate.
The numbers in Figs. 2, 6 and 7 correspond to those in Table 1.

Distribution of Zinc Chelate in the Presence of the Neutral Ligand. When a formally neutral donor (S) is added to the chelate extraction system, the extraction is extremely enhanced.[9–11] The distribution behavior was examined in the presence of TBP in order to obtain a reliable adduct formation constant. At first, the distribution ratio of TTA was measured with the change in the concentration of TBP in order to examine whether or not TBP affects TTA; the results are shown in Fig. 3. The distribution ratios of TTA are independent of the TBP concentration up to 0.01M for *n*-hexane, 0.02M for carbon tetrachloride and benzene, and 0.1M for chloroform. In these concentration ranges of TBP, the UV spectra of TTA are essentially the same as those in the absence of TBP. At higher TBP concentrations, the distribution ratio increases with an increase in the concentration of TBP; the rate of increase is different for each solvent, being especially remarkable for *n*-hexane. It can be considered that the distributed species of TTA is affected by TBP. TTA exists almost entirely as the enol form in the inert solvent or at low TBP concentrations, while the ratio of the keto form increases with an increase in the cocentration of TBP. Therefore, the TBP concentration ranges where there is no effect of TBP were employed. As the distribution coefficients of TBP between the aqueous and the organic phases are very large,[13] the initial concentration of TBP may be regarded as the equilibrium concentration.

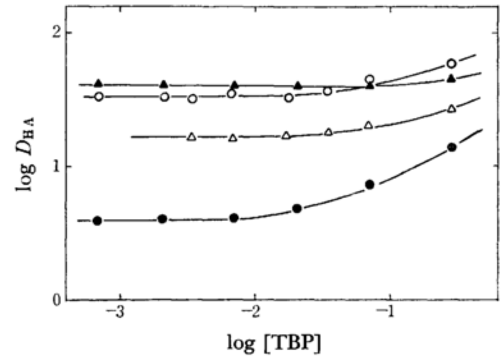

Fig. 3. Distribution ratio of TTA as a function of TBP concentration.
$[HA]_{org,\ init.}$=0.01M; ●, *n*-hexane; △, carbon tetrachloride; ○, benzene; ▲, chloroform

In order to examine the contribution of TBP to the adduct formation, the change in the distribution ratio of zinc ($D_{M,S}$) with the change in the concentration of TBP was examined as in Fig. 4.

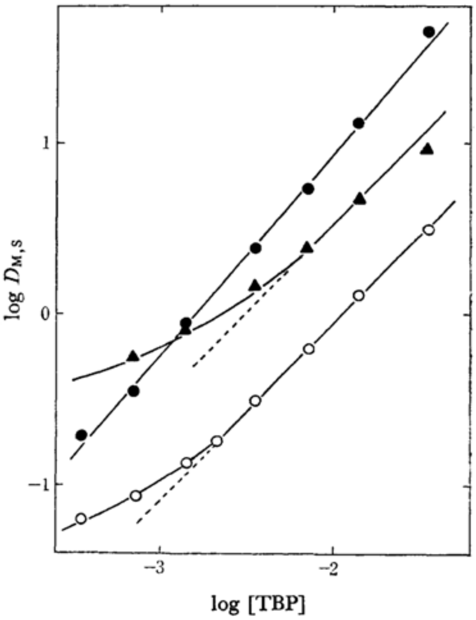

Fig. 4. Distribution ratio of zinc complex as a function of TBP concentration.
$[HA]_{org,\ init.}$=0.01M; ●, *n*-hexane (pA=3.98); ○, benzene (pA=4.82); ▲, chloroform (pA=4.05)

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[13] K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy and H.A.C. McKay, *Trans. Faraday Soc.*, **52**, 39 (1956).

The limiting slope was unity for each solvent. It seems that one molecule of TBP adds to one molecule of chelate; there is no evidence that two or more molecules of TBP add to the zinc chelate. The deviation from the straight line with a slope of 1 is evident at low concentrations of TBP, especially in the case of chloroform, because the assumption that the adduct is predominant is not applicable at low concentrations of TBP.

The plots of log $D_{M,S}$ against pA at a constant [TBP] gave a series of straight lines with a slope of -2, as is shown in Fig. 5. It is clear that the adduct is predominant as compared with the case of no TBP, and that the adduct formation constant can be obtained from D_M and $D_{M,S}$.

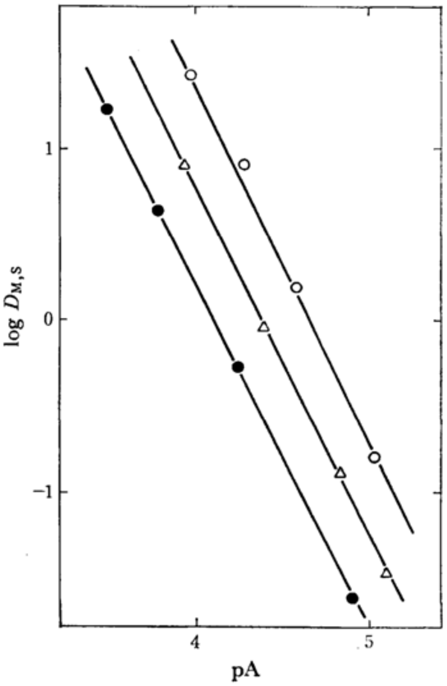

Fig. 5. Distribution ratio of zinc complex in the presence of TBP.
$[HA]_{org, init.}=0.01$ M; [TBP]=0.00366 M;
●, *n*-hexane; △, carbon tetrachloride;
○, benzene

The log K_S values are given in Table 1; they are close to the values obtained by Sekine and Dyrssen, 2.69 for chloroform and 4.34 for carbon tetrachloride.[9] Although there is a tendency toward large K_S values for simple paraffinic solvents and small ones for halogen-substituted solvents, the values of K_S are very different for each solvent. This means that the adduct formation constants are strongly influenced by the nature of the organic solvent, and that the role of the solvent in synergism is complicated. One can not simply relate the K_S values to the physicochemical properties of the solvent. The change in the activity with the solvent nature plays a very important role in the adduct formation. Therefore, the activity coefficients of all the species in the organic phase must be taken into account. Up to the present, it has been sometimes assumed that the activity coefficient of the species in the organic phase is close to unity, and there has been no consideration of the change in the activity with the nature of the solute and/or the solvent.

The interaction among the molecules in the organic solution should be estimated as the activity coefficient for each species. The overall adduct formation constant, expressed in terms of activities defined as K_S°, is:

$$K_S^\circ = \frac{a_{ZnA_2 \cdot mS}}{a_{ZnA_2} a_S^m} = K_S \frac{\gamma_{ZnA_2 \cdot mS}}{\gamma_{ZnA_2} \gamma_S^m} \tag{10}$$

where a represents the activity; γ, the activity coefficient, and the subscripts, chemical species. When the activity coefficient of a pure component is assumed to be unity, as is standard, the K_S° values do not depent on the medium. If the activities of all species can be evaluated in several organic solvents, the applicability of Eq. (10) may be considered. The activities of TBP have been measured in several organic solvents,[13,14] but those of the others have never been established. We have insufficient data on these organic solutions to evaluate the activity.

As the solvents used in this work may be regarded as so-called inert solvents, it seems that there are no specific interactions among the components of the solutions. These solutions are usually considered to be reasonably regular. It is practical to evaluate the activity according to the equation of Hildebrand-Scott:[8]

$$\left\{\begin{aligned} &RT \ln a_A = RT \ln x_A + V_A \varphi_B^2 (\delta_A - \delta_B)^2 && \text{(11a)} \\ &RT \ln a_A = RT\left[\ln \varphi_A + \varphi_B\left(1 - \frac{V_A}{V_B}\right)\right] \\ &\qquad + V_A \varphi_B^2 (\delta_A - \delta_B)^2 && \text{(11b)} \end{aligned}\right.$$

where the subscripts A and B denote the components A and B respectively, and where x represents the mole fraction; V, the molar volume, φ, the volume fraction, and δ, the solubility parameter. If the entropy of mixing is ideal, Eq. (11a) is appropriate. Where the molar volumes of components A and B are quite appreciably different, it seems that Eq. (11b) is more reasonable,[8] so Eq. (11b) is used in this study. The solubility parameters of the solvents have been listed in a monograph, or they can be calculated from the thermodynamic quantity.[8] However, as there are no fundamental data on, *e. g.*, the heat of vaporization and the solubility for the chelate and the adduct, it is difficult to evaluate the solubility parameter.

As for the chelate, the correlation between the

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14) S. Siekierski, *J. Inorg. Nucl. Chem.*, **24**, 205 (1962).

distribution coefficients of TTA and of chelate shown in Fig. 2 would lead us to suppose that the molar volume of the chelate is twice that of TTA and that the solubility parameter of chelate is equal to that of TTA. Consequently, the activity of the chelate may be calculated from the two values V_M 320 ml and δ_{ZnA_2} 9.9. Next, the activity of adduct must be assessed one way or another. Here, taking into account that the concentration of the component A is sufficiently low, A and B represent the molecules of the solute and the solvent respectively in Eq. (11b). If the difference in the ratio of the molar volume of the solute to that of the solvent is small for each solvent, Eq. (11b) can be put into a simpler form:

$$\log \gamma_A = C + D(\delta_A - \delta_B)^2 \qquad (12)$$

where C and D are constants. When the activity coefficients of the component A, γ_A, or the values which are proportional to γ_A are plotted against the solubility parameters of the solvents, δ_B, the curve which indicates a minimum at $\delta_A = \delta_B$ will be drawn. Accordingly, the solubility parameter of the component A can be obtained at the minimum in the curve. Equation (10) can be rewritten as by adopting $m=1$:

$$\gamma_{ZnA_2 \cdot S} = K_S^\circ \cdot \frac{\gamma_{ZnA_2}\gamma_S}{K_S} \qquad (13)$$

The combination of Eq. (12) ($ZnA_2 \cdot S$ was taken as A) and Eq. (13) leads to Eq. (14):

$$\log \frac{\gamma_{ZnA_2}\gamma_S}{K_S} = C' + D(\delta_{ZnA_2 \cdot S} - \delta_B)^2 \qquad (14)$$

where C' is a constant. The values of γ_{ZnA_2} may be calculated as above. Alcock and his co-workers[13] reported that TBP forms an ideal solution up to about a 1% TBP solution with paraffinic solvents and up to 10% with benzene and others. In calculating the activity coefficient of TBP, the experimental data on a 1% solution of TBP were used for n-hexane, n-heptane, and cyclohexane,[13] while those on a 5% solution obtained by Siekierski[14] were used for most of the solvents. The relation of Eq. (14) is shown in Fig. 6. The solubility parameter of the adduct was obtained as 9.4. The molar volume of the adduct may be got from the curvature of Fig. 6, but it is hard to get the accurate value because of an insufficient number of the experimental data on the solvents with large solubility parameters. In the present study the molar volume of the adducts was assumed to be equal to the algebraic sum of the molar volume of the chelate and that of TBP. This seems a reasonable assumption because Eq. (4) is the addition reaction, and, practically, the effect of the small difference in molar volume on the activity coefficient is small except when value of $|\delta_A - \delta_B|$ is large. Accordingly, the activity coefficient of the adduct can also be calculated from the two values $\delta_{ZnA_2 \cdot S}$ 9.4 and $V_{ZnA_2 \cdot S}$ 593 ml.

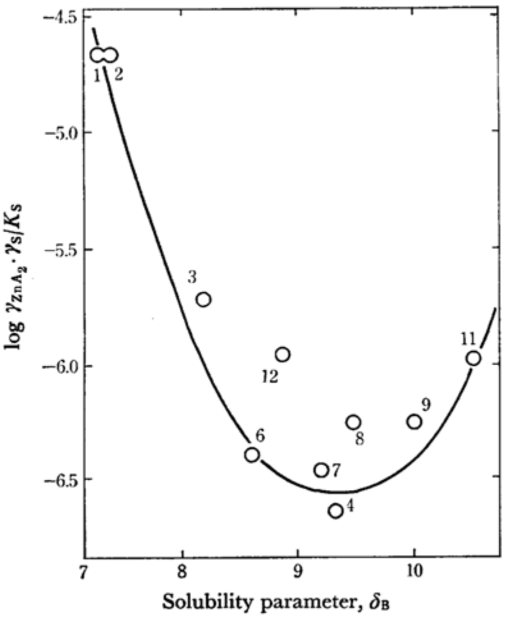

Fig. 6. Relation between the activity coefficient and the solubility parameter of solvent.

Since the activity coefficients of all the species were evaluated, the relation of Eq. (10) is illustrated in Fig. 7. The plots of log K_S against the logarithm of the activity coefficients are close to a straight line with a slope of -1 for most of the solvents, as was to be expected. The deviations from the

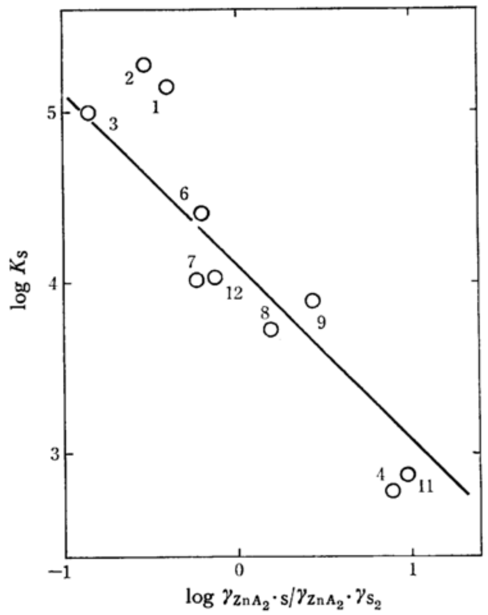

Fig. 7. Relation between the adduct formation constant and the activity coefficients in the organic phase.

line for *n*-hexane and *n*-heptane with large $|\delta_A-\delta_B|$ values appears to be due to the uncertainty concerning the molar volume of adduct. If the molecules of the chelate and TBP form a more compact adduct than the postulated one, the deviations are small. The value of log K_S° was obtained as 4.05. Although the activity coefficients have been estimated on the base of a simplifing assumption, it is significant that the adduct formation constant in terms of activity is constant for each solvent. If the K_S value is measured for one solvent, that for the other can be estimated by considering the activity coefficient of the species.

Eq. (7) can be related to Eq. (10) as follows:

$$D_{M,S} = K_S^\circ D_M[S]_{org}^m \frac{\gamma_{ZnA_2}\gamma_S^m}{\gamma_{ZnA_2\cdot mS}} \qquad (16)$$

The distribution ratio in the presence of a neutral ligand can be pre-estimated from that in the absence of one according to Eq. (16). In this manner the role of the solvent in the synergistic extraction system can be explained systematically by a combination of the regularity as in the distribution of the metal chelate and that in the adduct formation.

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