February, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 621—626 (1986)* 621

Solvent Effect on the Liquid-Liquid Partition Coefficients of Dimethyldithiocarbamic Acid and Its Copper(II) Chelate

Hisanori Imura, Satoru Matsumora, and Nobuo Suzuki*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

(Received August 16, 1985)

Partition coefficients of dimethyldithiocarbamic acid and its copper(II) chelate have been determined in various organic solvents -0.10 mol dm^{-3} aqueous perchlorate solution systems at 25 °C. The effects of inert organic solvents are explained with the aid of the regular solution theory. Also, a linear free-energy relationship between the partition coefficient of the copper(II) chelate and that of the reagent is demonstrated. The partition coefficient of the copper(II) chelate is compared with that of bis(2,4-pentanedionato)copper(II) and various factors governing the partition coefficients of these chelates are discussed with the aid of the scaled particle theory.

Dithiocarbamate derivatives are highly versatile chelating agents for the separation and determination of metals by solvent extraction, liquid chromatography, etc. In chelate extraction, the extractability of metal ions can be expressed by the partition coefficients of the reagent and the neutral metal chelate, the acid-dissociation constant of the reagent, and the stability constant of the chelate. The partition coefficients are strongly dependent on organic solvents and are the most important factors affecting the extractability of a metal ion. However, the partition for dithiocarbamate-group reagents and their metal chelates even for a diethyldithiocarbamate reagent which is most frequently used in extraction separation has been scarcely investigated. The effect of organic solvents has not been investigated at all.

In this research, the partition coefficients of dimethyldithiocarbamic acid(Hdmdtc), the most simple compound in the dithiocarbamate group, and its copper(II) chelate (Cu(dmdtc)$_2$) were determined in various organic solvent systems. Here, the relationship between the partition coefficient of the chelate and that of the reagent is theoretically explained. Such a relationship has been thoroughly studied regarding various β-diketone systems in this laboratory.[1–4] The solvent effect has been elucidated with the aid of the regular solution theory and the scaled particle theory. Some factors governing the partition coefficient of the metal chelate are discussed by comparing the partition coefficient of Cu(dmdtc)$_2$ with that of bis(2,4-pentanedionato)copper(II)(Cu(acac)$_2$).[3]

Experimental

Reagents and Apparatus. Sodium dimethyldithiocarbamate dihydrate (Nadmdtc·2H$_2$O) was obtained from Tokyo Kasei Co., Ltd. and was purified by recrystallization from acetone-absolute ether. Bis(dimethyldithiocarbamato)copper(II) (Cu(dmdtc)$_2$) was obtained from Tokyo Kasei Co., Ltd. and purified by vacuum sublimation.

A carrier-free radioisotope, ^{67}Cu, was produced by a photonuclear reaction of ^{68}Zn(γ,p)^{67}Cu. Radioactive copper(II) perchlorate solutions of the desired concentration were prepared as described in a previous paper.[3]

Organic solvents were purified by the usual chemical treatment and distillation. The ionic strength in the aqueous phase was adjusted to 0.10 M (1 M=1 mol dm^{-3}) by the use of sodium perchlorate. Other reagents and equipment were the same as those used previously.[3]

Measurements of Partition Coefficient (P_A) of Hdmdtc by a Kinetic Method. Dithiocarbamate group reagents have a strong tendency to decompose in acidic aqueous solutions. The partition coefficient of dimethyldithiocarbamic acid was determined by utilizing its decomposition reaction in the aqueous phase. The partition coefficient of Hdmdtc between carbon tetrachloride and 0.10—0.03 M perchloric acid solutions with an ionic strength of 0.10 was determined by measuring both the stripping rate of Hdmdtc from the organic to the aqueous phase and the decomposition rate in the aqueous phase. The organic solution of Hdmdtc was prepared by an extraction, as follows: A 1 cm^3 portion of a 0.06 M Nadmdtc aqueous solution was added to 9 cm^3 of 0.03 M perchloric acid and 10 cm^3 of carbon tetrachloride in a centrifuge tube with a ground-glass stopper. Immediately, the contents were shaken for 15 s and centrifuged for 30 s at 4000 rpm. The organic phase was taken out and diluted to about a 5×10^{-4} M Hdmdtc solution with carbon tetrachloride. This working solution of Hdmdtc was prepared just before the following kinetic stripping experiment. This Hdmdtc solution (5 cm^3) was vigorously shaken for various times between 10 and 150 s with an equal volume of 0.10 M or 0.03 M perchloric acid solution. The shaking speed was as high as 430 strokes per min in order to attain a rapid mass transfer of the organic-aqueous interface. Immediately after centrifuging for 30 s, the absorbance of Hdmdtc in the carbon tetrachloride phase was measured at 285 nm. The decomposition of Hdmdtc in the organic phase during the shaking within 150 s could be neglected. The stripping-rate constant of Hdmdtc was calculated from the absorbance measurement at various shaking time intervals.

The decomposition rate of Hdmdtc in an aqueous phase was separately measured by spectrophotometry. The decrease in absorbance at 270 nm was measured as a function of time after an injection of 0.01 cm^3 of a 0.06 M Nadmdtc aqueous solution into an optical cell containing 4 cm^3 of a 0.10 M or 0.03 M perchloric acid solution saturated with carbon tetrachloride. All experiments were carried out in a thermostated room at 25±1 °C.

Measurements of Distribution Ratio (D_A) of Hdmdtc. A 0.1 cm^3 portion of 0.1—0.4 M Nadmdtc in water was added to a centrifuge tube containig 5 cm^3 of an organic solvent, 1 cm^3 of 0.50 M sodium perchlorate, and 3.9 cm^3 of a 0.01

M phosphate buffer solution of pH 5.5—7.0. The contents were shaken for 30 s and centrifuged for 30 s. An aliquot of each phase was pipetted out. The aqueous phase was diluted with 0.1 M sodium hydroxide to about 100-fold and the absorbance was measured at 280 nm. In the alkali solution, dimethyldithiocarbamate was very stable and its molar absorption coefficient was 13800 $M^{-1} cm^{-1}$ at an absorption maximum of 280 nm due to the $dmdtc^-$ anion. To determine the Hdmdtc concentration distributed in the organic phase, the organic phase was shaken with an appropriate volume of a 0.1 M sodium hydroxide solution for 3 min. Dimethyldithiocarbamic acid was back-extracted into the alkaline aqueous solution and determined by measuring the absorbance at 280 nm. The distribution ratio of the dimethyldithiocarbamate was calculated from the concentration of each phase. The equilibrium pH value was measured with a glass electrode just after shaking.

Measurements of Partition Coefficient (P_M) of $Cu(dmdtc)_2$. A small portion (0.01 cm^3) of a 5×10^{-5}—5×10^{-2} M radioactive copper(II) solution was added to a 30 cm^3 centrifuge tube containing 5 cm^3 of an organic solvent and 5 cm^3 of a 1×10^{-4}—1×10^{-2} M Nadmdtc aqueous solution (pH 7—8). The contents were shaken for 15—60 min. After centrifuging, an aliquot (0.1—3 cm^3) was very carefully taken from each phase. The γ-activities of each phase were measured with a well-type NaI(TI) scintillation counter and the partition coefficient of the copper(II) chelate was calculated. The equilibrium pH value was measured with a glass electrode.

A back extraction was performed as follows. An organic phase containing the radioactive copper(II) chelate which was prepared in the forward extraction (as just mentioned above) was shaken with the aqueous phase containing Nadmdtc at pH 7—8. The P_M value was determined by the same manner as that for the forward extraction.

Results

Partition Coefficient of Hdmdtc. Since dimethyldithiocarbamic acid very rapidly decomposes in an acidic aqueous solution, the partition coefficient was determined using the decomposition reation (decomposition rate) of Hdmdtc. When different organic solutions containing Hdmdtc were shaken with the aqueous solutions at pH 1—2, their concentrations in the organic phase decreased with an increase in the shaking time. This decrease was faster in accordance to the following order for organic solvents; benzene< carbon tetrachloride<heptane. This phenomenon seems to be due to the following reactions,

$$\mathrm{Hdmdtc_{org}} \rightleftharpoons \mathrm{Hdmdtc} \qquad (1)$$

$$\mathrm{Hdmdtc} \longrightarrow \mathrm{(CH_3)_2NH + CS_2}, \qquad (2)$$

where the subscript org denotes the species in the organic phase. The equilibrium constant for Eq. 1 corresponds to the partition coefficient of Hdmdtc and the rate constant for Eq. 2 is the decomposition-rate constant (k_d) in the aqueous phase. The decomposition rate of the aqueous phase in a sufficiently low pH region can be written as follows:[5,6]

$$-\frac{d[\mathrm{Hdmdtc}]}{dt} = k_d[\mathrm{Hdmdtc}]. \qquad (3)$$

Table 1. Rate Constants for Stripping (k_{st}) and Decomposition (k_d) and Partition Coefficient (P_A) of Dimethyldithiocarbamic Acid in the Carbon Tetrachloride System at 25 °C

$[H^+]$ / M	k_{st} / $10^{-3} s^{-1}$	k_d [b)] / $10^{-2} s^{-1}$	P_A [c)]
0.10	4.62	6.42±0.22	12.9±0.5
0.030 [a)]	3.85	5.49±0.14	13.3±0.4
0.030 [a)]	3.78	5.49±0.14	13.5±0.4

Average value of P_A: 13.2±0.4.
a) I=0.10 by $NaClO_4$. b) Result for three measurements. c) Calculated from $P_A = k_d/k_{st} - 1$.

On the other hand, the decrease in the Hdmdtc concentration in the organic phase upon shaking is given by

$$-\frac{d[\mathrm{Hdmdtc}]_{org}}{dt} = k_{st}[\mathrm{Hdmdtc}]_{org}, \qquad (4)$$

where k_{st} is the stripping-rate constant. From Eqs. 3 and 4, the following relation is obtained,

$$P_A = \frac{k_d}{k_{st}} - 1. \qquad (5)$$

Respective first-order plots of Eqs. 3 and 4 gave good linear relationships from which the rate constants, k_d and k_{st}, were determined. The results for the carbon tetrachloride-perchloric acid system are shown in Table 1. The P_A values obtained at different perchloric acid concentrations are consistent within experimental error.

The distribution ratio of dimethyldithiocarbamate is expressed by

$$D_A = \frac{[\mathrm{Hdmdtc}]_{org}}{[\mathrm{Hdmdtc}] + [\mathrm{dmdtc^-}]}. \qquad (6)$$

This can be written using P_A and the acid-dissociation constant, K_a,

$$D_A = \frac{P_A}{1 + K_a/[H^+]}. \qquad (7)$$

If $[H^+]$ is much smaller than K_a,

$$D_A = \frac{P_A[H^+]}{K_a}. \qquad (8)$$

Figure 1 shows plots of log D_A vs. pH for various organic solvent systems. Each plot is close to a straight line with a slope of −1; thus, Eq. 8 was found to hold in the pH regions as expected from the pK_a value of

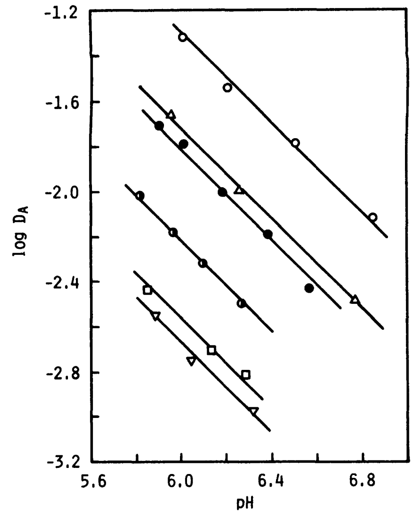

Fig. 1. Distribution ratio of dimethyldithiocarbamate as a function of pH in various organic solvent systems.
○: Benzene, △: isopropylbenzene, ●: carbon tetrachloride, ◑: dibutyl ether, □: heptane, ▽: hexane.

Hdmdtc shown below. The pK_a value of Hdmdtc can be obtained using the P_A value determined for the carbon tetrachloride system (Table 1). The value was determined to be 3.05±0.06 (the activity of hydrogen ions was used in place of the concentration in Eq. 8). This is in agreement with a value of 3.21 for an ionic strength of 0.01.[6] The partition coefficients of Hdmdtc in organic solvent systems other than carbon tetrachloride can be readily determined from Eq. 8 using the K_a value. These date are listed in Table 4.

Partition Coefficient of Cu(dmdtc)$_2$. The distribution ratio of copper(II) is expressed by

$$D_M = \frac{[\mathrm{Cu(dmdtc)_2}]_{\mathrm{org}}}{[\mathrm{Cu^{2+}}] + [\mathrm{Cu(dmdtc)^+}] + [\mathrm{Cu(dmdtc)_2}] + \cdots} \tag{9}$$

and can be written using the partition coefficient of Cu(dmdtc)$_2$ and the overall stability constant (β_n) in the aqueous phase,

$$D_M = \frac{P_M\beta_2[\mathrm{dmdtc^-}]^2}{1 + \beta_1[\mathrm{dmdtc^-}] + \beta_2[\mathrm{dmdtc^-}]^2 + \cdots}. \tag{10}$$

Table 2. Partition Coefficient of Cu(dmdtc)$_2$ at Different Dimethyldithiocarbamate Concentration in the Heptane System at 25 °C

[dmdtc$^-$]/M	pH	log P_M
2.0×10^{-4}	6.37	2.238
2.0×10^{-4}	6.00	2.236$^{a)}$
2.0×10^{-3}	7.18	2.223
2.0×10^{-3}	6.09	2.217$^{a)}$
1.0×10^{-2}	7.65	2.196
1.0×10^{-2}	7.61	2.201$^{a)}$
2.0×10^{-2}	7.71	2.210

Concentration of copper(II): 1.0×10^{-7} M.
a) Obtained from back extraction.

Table 3. Partition Coefficient of Cu(dmdtc)$_2$ at Different Copper(II) Concentrations in the Carbon Tetrachloride System at 25 °C

[Cu(II)]/M	log P_M
5.0×10^{-7}	3.687
5.0×10^{-7}	3.736$^{a)}$
5.0×10^{-7}	3.669$^{a)}$
5.0×10^{-7}	3.787$^{a)}$
1.2×10^{-5}	3.690
1.2×10^{-5}	3.688$^{a)}$
1.2×10^{-5}	3.781$^{a)}$
1.2×10^{-5}	3.788$^{a)}$

Concentration of dmdtc$^-$: 1.0×10^{-2} M.
a) Obtained from back extraction.

If the dimethyldithiocarbamate concentration in the aqueous phase is sufficiently high and the formation of such anionic complexes as Cu(dmdtc)$_3^-$ is negligible, the D_M values become independent of the ligand concentration and are consistent with P_M. To confirm this, P_M was determined at different ligand concentrations (Table 2). The obtained P_M values are thought to be constant within the experimental error when the ligand concentrations are altered by two orders of magnitude. The values obtained by forward extraction of copper(II) are in good agreement with those obtained by back extraction. This result demonstrates the complete attainment of the partition equilibrium of the copper(II) chelate.

The P_M value was measured at different copper(II) concentrations to ascertain the absence of a polymerized species of the chelate in the organic and aqueous phases. The results for the carbon tetrachloride system are shown in Table 3. A constant P_M was obtained within the experimental error when the copper(II) concentration was altered by more than an order of magnitude. The P_M values of Cu(dmdtc)$_2$ in various organic solvent systems are summarized in Table 4.

The partition coefficients of Cu(dmdtc)$_2$ were larger than those of Hdmdtc in all the solvents and the order of the solvents for each solute was the same, i.e., benzene>isopropylbenzene>carbon tetrachloride>dibutyl ether>heptane≈hexane.

Discussion

The partition coefficient of a molar fraction scale can be written using a modified equation based on the regular solution theory,[3]

$$\ln P_2^{\circ} = \frac{V_2}{RT}[C_{ww} - C_{oo} + 2(C_{o2} - C_{w2}')], \tag{11}$$

where V and C are the molar volume and the cohesive energy density, respectively. The subscripts (2, w, and o) denote the solute, water, and organic solvent, respectively. The parameter C_{w2}' expresses the interac-

Table 4. Partition Coefficients of Hdmdtc (P_A) and Its Copper(II) Chelate (P_M) at 25 °C

No.	Organic solvent	δ[b] / $\mathrm{cal^{1/2}\,cm^{-3/2}}$	μ[c] / D	log P_A	log P_M
1	Hexane	7.27	0	0.28±0.05	2.23±0.04
2	Heptane	7.43	0	0.38±0.04	2.21±0.02
3	Carbon tetrachloride	8.58	0	1.12±0.01	3.71±0.05
4	Isopropylbenzene	8.53	0.39	1.22±0.03	4.31±0.03
5	Benzene	9.16	0	1.65±0.04	4.57[a]
6	Dibutyl ether	7.62	1.18	0.73±0.02	3.42±0.02

a) Average of two measurements. b) Solubility parameter calculated from heat of vaporization at 25 °C.[18]
c) Dipole moment ($1\mathrm{D}=3.333\times10^{-30}\,\mathrm{Cm}$).

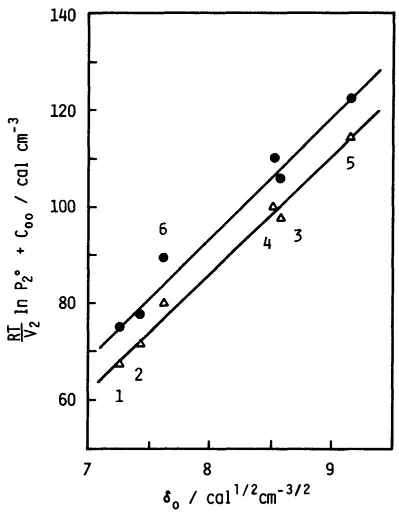

Fig. 2. Evaluation of the partition coefficients based on the regular solution theory. The numbers correspond to those in Table 4.
△: Hdmdtc, ●: Cu(dmdtc)$_2$.

tion between the solute and water involving a specific interaction such as hydrogen and coordination bonding. If a geometric mean approximation for C_{o2} with the solubility parameters, δ, is valid, Eq. 11 can be rewritten as follows,

$$\frac{RT}{V_2}\ln P_2^\circ + C_{oo} = 2\delta_2\delta_o + C_{ww} - 2C_{w2}'. \qquad (12)$$

A linear relationship between the left hand side of Eq. 12 and δ_o is expected. An apparent solubility parameter of the solute(δ_2) and the interaction term with water ($C_{ww}-2C_{w2}'$) can be obtained from the slope and the intercept, respectively. Figure 2 shows plots for Hdmdtc and its copper(II) chelate, where their molar volumes were estimated as follows. The van der Waals volume[7] of Hdmdtc can be calculated to be 62.81 cm^{3}mol^{-1} and is very close to that of enol of 2,4-pentanedione(acetylacetone, Hacac), 60.14 cm^{3}mol^{-1}. Assuming that the ratio of the van der Waals volume to the molar volume of each chelating agent is the same in Hacac (the molar volume; 101.59 cm^{3}mol^{-1}[8]) and Hdmdtc, the molar volume of Hdmdtc (106 cm^{3}mol^{-1}) is obtained. The molar volume of Cu(dmdtc)$_2$ was estimated to be 190 cm^3 mol^{-1} using the relation between the molar volume of acetylacetone and that of its copper(II) chelate.[2] In the plots of Hdmdtc and its copper(II) chelate, good linear relationships are found for non-polar organic solvents, except for dibutyl ether (Fig. 2). It seems that the organic solutions of these solutes can be taken as apparently regular solutions and that the solvent effects can be interpreted according to Eq. 12. The apparent solubility parameters of Hdmdtc and Cu(dmdtc)$_2$ were calculated to be 12.2 and 12.7 cal$^{1/2}$cm$^{-3/2}$ (conversion factor: 1 cal$^{1/2}$cm$^{-3/2}$=2.0455 J$^{1/2}$cm$^{-3/2}$) respectively from the slope of the plots as described above. Since these values were obtained using a limited number of solvents (i.e., hexane and heptane in alkanes, carbon tetrachloride of haloalkanes and benzene and isopropylbenzene of phenyl compounds), it is difficult to precisely determine their magnitudes. However, the value for Cu(dmdtc)$_2$ is larger than those for copper(II) β-diketonates such as acetylacetonate (11.6 cal$^{1/2}$cm$^{-3/2}$), 1,1,1-trifluoro-2,4-pentanedionate (11.2 cal$^{1/2}$cm$^{-3/2}$), and 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedionate (11.0 cal$^{1/2}$cm$^{-3/2}$), which were determined by means of a similar technique.[4] This suggests a somewhat high polarity of the former. Metal dithiocarbamate chelates have lone-pair electrons at nitrogen atoms which are readily released from nitrogen to sulfur atoms.[9–12] This seems to be responsible for the polarity of the dimethyldithiocarbamate molecule and may cause interactions with a solvent having a large dipole moment, such as dibutyl ether. Hence, it follows that a positive deviation for dibutyl ether for Eq. 12 can be observed from Fig. 2.

The parameter, $C_{ww}-2C_{w2}'$, of Cu(dmdtc)$_2$, which indicates the interaction between the solute and water, is the same as that of the reagent, i.e., −110 cal cm^{-3} (convergion factor: 1 cal cm^{-3}=4.184 J cm^{-3}) was obtained from the plots for Eq. 12 (Fig. 2). This result means that Cu(dmdtc)$_2$ has no specific interaction with water (such as coordination bonding to the central metal) and is remarkably different from that in the acetylacetonate system.[3] In fact, the absorption spectrum of the dimethyldithiocarbamate chelate in donor solvents such as dibutyl ether and acetone was almost the same as that in carbon tetrachloride and benzene (the absorption peak was at 435 nm in

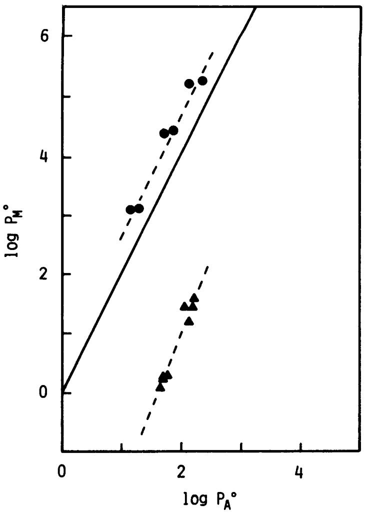

Fig. 3. Relationship between the partition coefficients of the copper(II) chelate and the reagent. ●: Cu(dmdtc)$_2$, ▲: Cu(acac)$_2$.[3]

these solvents) and the change in the absorption spectrum of the acetylacetonate chelate in dibutyl ether and water was observed.[3]

Since Eq. 12 holds for a chelate and a reagent, the following relation can be derived,

$$\log P_M^\circ = \frac{V_M}{V_A}\log P_A^\circ + \frac{2V_M}{2.30RT}(\delta_M-\delta_A)\delta_o + \frac{2V_M}{2.30RT}(C_{wA}'-C_{wM}'). \tag{13}$$

If the difference between δ_M and δ_A as well as between C_{wM}' and C_{wA}' is small, that is, solute-solvent interactions for the chelate are similar to those for the reagent, a plot of log P_M° vs. log P_A° is expected to be a straight line with a slope of two (V_M/V_A is approximately equal two) passing through the origin. Figure 3 shows plots for Cu(dmdtc)$_2$ together with those for Cu(acac)$_2$.[3,4] The plots of Cu(dmdtc)$_2$ are close to a straight line as expected from the preceding discussion; however, those of Cu(acac)$_2$ are in a much lower region. This suggests that the specific solute-water interactions are weak for the dimethyldithiocarbamate chelate but remarkably strong for the acetylacetonate chelate.

As described in a previous paper,[4] it is difficult to discuss the strict physical meaning of the solute–water interaction parameter based on the simple regular-solution concept, but it is worth evaluating a solute–water interaction with the aid of the scaled particle theory(SPT), which is applicable to an aqueous solution without any adjustable parameters.

The partition coefficient can be written using the Gibbs free energy for the cavity formation($\overline{G}_c$) and for an interaction ($\overline{G}_i$) in the organic and aqueous phases,[2,13]

$$\ln P_2 = \frac{\overline{G}_{c,w}-\overline{G}_{c,o}}{RT} + \frac{\overline{G}_{i,w}-\overline{G}_{i,o}}{RT}. \tag{14}$$

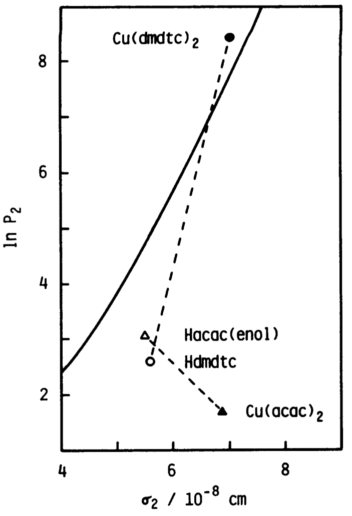

Fig. 4. Comparison of the partition coefficients of dimethyldithiocarbamates and acetylacetonates[3] with those of cavity calculated by the scaled particle theory in the carbon tetrachloride system. Solid line shows the calculated value of $(\overline{G}_{c,w}-\overline{G}_{c,o})/RT$.

The cavity-formation energy can be calculated using the SPT;[14]

$$\overline{G}_c = -RT\ln(1-y) + RT\frac{3y}{1-y}\left(\frac{\sigma_2}{\sigma_1}\right) + RT\left[\frac{3y}{1-y}+\frac{9}{2}\left(\frac{y}{1-y}\right)^2\right]\left(\frac{\sigma_2}{\sigma_1}\right)^2 + \frac{N_A yp}{\rho}\left(\frac{\sigma_2}{\sigma_1}\right)^3 \tag{15}$$

where σ_1 and σ_2 are the molecular diameters of the solvent and solute, N_A is Avogadro's number, p is the pressure, ρ is the number density of the solvent and y is the packing fraction ($y=\pi\rho\sigma_1^3/6$). The molecular diameter of the solute was estimated using an empirical correlation[4] between the molecular diameter of various compounds determined by the SPT[14,15] and their molar volumes. The values for Hdmdtc and Cu(dmdtc)$_2$ are 5.59×10^{-8} and 6.98×10^{-8}cm, respectively. Figure 4 shows the partition coefficients of Hdmdtc, Hacac(enol) and respective copper(II) chelates as a function of the molecular diameter. The solid line indicates the hypothetical partition coefficient of the cavity, which may be considered to be of a solute where $\overline{G}_{i,w}=\overline{G}_{i,o}$. The plots for Hdmdtc and Hacac are similar, but those of both the copper(II) chelates are significantly different. The partition coefficients of Hdmdtc and Cu(dmdtc)$_2$ lie close to a solid line calculated according to the SPT, compared with that of Cu(acac)$_2$. This means that the difference in the interaction energies for solute–carbon tetrachloride and solute–water is not so great for Cu(dmdtc)$_2$ and Hdmdtc. Consequently, the partition coefficient in this system is mainly governed by the difference between the cavity-formation energy in the organic and aqueous phases. On the other hand, the partition coefficient of

$Cu(acac)_2$ is remarkably lower than that of $Cu(dmdtc)_2$ as well as the cavity. This suggests that interactions of $Cu(acac)_2$ with water molecules are much stronger than that with organic solvent molecules.

Such differences regarding dimethyldithiocarbamate and the acetylacetonate chelate in solute–solvent interactions may be ascribed to the nature of their coordination bonds. The dimethyldithiocarbamate chelate involving sulfur donor atoms has a larger effect on ligand field stabilization than the acetylacetonate chelate involving oxygen donor atoms. Hence, the copper(II)–sulfur bonding is more covalent.[16,17] This results in a greater electron transfer from the ligand to the metal. Consequently, in the dimethyldithiocarbamate chelate the ability of the further coordination to the central metal with donor solvents and of the hydrogen bonding to the donor atoms of the ligand is much lower than that in the acetylacetonate chelate.

In conclusion, the partition coefficient of $Cu(dmdtc)_2$ was close to that calculated from the difference of the cavity-formation energy between the organic and the aqueous phase. The partition coefficients of the chelating agents, Hdmdtc and Hacac(enol), did not deviate much from that calculated from the cavity-formation energy. This suggests that specific interactions with water are weak for those solutes, especially for $Cu(dmdtc)_2$. On the other hand, the partition coefficient of $Cu(acac)_2$ was remarkably lower than that calculated from the cavity-formation energy. This suggests that the specific interactions between $Cu(acac)_2$ and water, such as coordination and hydrogen bonding,[3] are strong.

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