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Salt Effect on the Solubility of Copper and Beryllium Chelates of 4,4,4-Trifluoro-1-phenyl-1,3-butanedione

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In order to examine whether the substitution of a trifluoromethyl group for a methyl group in metal chelates of 1-phenyl-1,3-butanedione (BA) affects the salt effect on the solubility of these chelates, the solubility of copper and beryllium chelates of 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BFA) in water and in some aqueous salt solutions was measured at 25 °C. The solubility in water (S_0) was $9.07 \pm 0.22 \times 10^{-7}$ mol dm^{-3} for the copper chelate and $4.85 \pm 0.08 \times 10^{-6}$ mol dm^{-3} for the beryllium chelate. These solubility values are compared with those of the corresponding BA chelates and an influence of fluorination on the solubility of these BA chelates is discussed. It was found that the solubility of the above BFA chelates in the aqueous salt solutions (S) could be expressed satisfactorily by the equation, $\log (S_0/S) = a\sqrt{C_s} + bC_s$, where C_s is the concentration of salt. This result suggests that introduction of CF_3 group brings about a specific interaction between the fluorinated chelates and their surroundings.

In a series of our investigations, the salt effect on the solubility of bis(1-phenyl-1,3-butanedionato)copper(II) (Cu(bzac)$_2$) and bis(1-phenyl-1,3-butanedionato)beryllium(II) (Be(bzac)$_2$) has been studied and a generalized interpretation for the salt effect in the solvent extraction of metal chelates was presented[1,2]. The substitution of a trifluoromethyl group for a methyl group in the metal chelates of β-diketones affects their properties such as volatility.[3] The polarity of the metal chelates of the above fluorinated β-diketones is expected to be higher than that of parent chelates because of the high electronegativity of fluorine atoms.

On the other hand, in our studies on the salt effect on the solubility of BA and BFA, it was suggested that species of the latter was less polar than that of the former in aqueous solutions.[4,5] It is very interesting to see whether fluorination of β-diketone chelates affects the salt effect or not. Thus, in the present study, the solubility of bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)copper(II) (Cu(bfac)$_2$) and bis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)beryllium(II) (Be(bfac)$_2$) in water and in aqueous salt solutions is measured and the salt effect on the solubility of these chelates is compared with that for Cu(bzac)$_2$ and Be(bzac)$_2$.

Experimental

Materials. The copper and beryllium chelates of BFA were prepared and purified by the same procedures as used for Cu(bzac)$_2$ and Be(bzac)$_2$.[1,2] The melting points of these chelates were 239 °C (Ref. 6, 241 °C) and 143 °C (Ref. 6, 143 °C), respectively. Aqueous solutions of LiCl, $NaClO_4$, NaCl, $NaNO_3$, and Na_2SO_4 were also prepared as previously reported.[1,2] Redistilled water was used and heptane was purified by an ordinary method.

Solubility Measurement. The apparatus and procedure used for the solubility measurement were similar to those previously reported,[1] except for the procedure modified to extract completely BFA into heptane. Filtered aliquots of the solution saturated with Cu(bfac)$_2$ or Be(bfac)$_2$ were acidified with one drop of 5 M (1 M = 1 mol dm^{-3}) HCl solution and then exact volume of these acidified solutions (30 cm^3 for Cu(bfac)$_2$ and 10—20 cm^3 for Be(bfac)$_2$) was transferred to 50 cm^3 centrifuge tubes in which Na_2SO_4 was previously placed. As the partition coefficient of BFA between water and heptane is lower than that of BA,[7] Na_2SO_4 was added to the above acidified solutions as a salting-out reagent to extract completely BFA. BFA was completely extracted at the concentrations of Na_2SO_4 over 1.5 M, and so in most cases Na_2SO_4 was added to give the concentration of 2 M. In the cases in which the addition of 2 M Na_2SO_4 results in the precipitation of salts while being extracted, for example, in the solubility measurement for Be(bfac)$_2$ in 3 M salt solutions, Na_2SO_4 concentration was reduced to 1 M. Even in these cases, the complete extraction of BFA was confirmed by stirring again aliquots of the aqueous phases, from which BFA was once extracted, with freshly added heptane. The mixtures of the aqueous solutions prepared as described above and 5 cm^3 of heptane were warmed at 30 °C to dissolve completely added Na_2SO_4 and stirred for 2 h with a magnetic stirrer.

The calibration curve to determine the concentration of BFA extracted into heptane phase was obtained as follows. Three independent series of standard solutions of BFA in heptane were prepared over the concentration range of 6.47×10^{-6}—3.24×10^{-5} M, and 5 cm^3 portions of these standard solutions were stirred for 2 h with 10—30 cm^3 of 2 M Na_2SO_4 acidified with one drop of 5 M HCl. After the heptane phases were separated by centrifugation, the absorbance at 323 nm in the heptane phases was measured, and the least-squares method was applied to these data. The calibration curve is expressed as

$$C = (A + 0.0077)/(1.48 \times 10^4), \tag{1}$$

where C and A are the concentration(M) of BFA, and the absorbance at 323 nm in heptane phases, respectively.

The pH of sample solutions (250 cm^3) to be saturated with Cu(bfac)$_2$ or Be(bfac)$_2$ was adjusted within the ranges described in the following section by adding 0.1—0.4 cm^3 of 0.08 M sodium tetraborate-5 M HCl mixed solution of pH 7.4.

Results and Discussion

Solubility of Cu(bfac)$_2$ and Be(bfac)$_2$ in Water. The results of solubility measurement of Cu(bfac)$_2$ and Be(bfac)$_2$ in water are presented in Tables 1 and 2, respectively, in order to demonstrate influences of pH and equilibration time. The solubility values calculated from the concentration of BFA in heptane phases were practically constant over the pH ranges of 6.9—7.2 for Cu(bfac)$_2$ and 6.2—6.5 for Be(bfac)$_2$. For Be(bfac)$_2$, fairly long equilibration time was required to attain complete saturation.

Table 1. Solubility measurement for $Cu(bfac)_2$ in water at 25 °C

Equilibration time/h	pH[a)]	pH[b)]	Solubility 10^{-7} mol dm^{-3}	Equilibration time/h	pH[a)]	pH[b)]	Solubility 10^{-7} mol dm^{-3}
Run 1				Run 3			
32	7.21	6.99	9.27	42	7.20	7.16	9.59
48	7.01	6.99	9.15	66	7.09	7.01	9.18
54	6.99	7.01	8.93	90	7.06	7.11	9.03
72	7.16	7.09	8.82	114	7.02	6.99	9.01
Run 2							
72	7.19	7.10	9.20	Mean of all data 9.07±0.22			
95	7.01	7.03	8.85				
115	7.02	6.93	8.99				
142	7.00	7.01	8.85				

a,b) The pH of saturated solutions measured before and after being filtered to be equilibrated with heptane, respectively.

Table 2. Solubility measurement for $Be(bfac)_2$ in water at 25 °C

Equilibration time/h	pH[a)]	pH[b)]	Solubility 10^{-6} mol dm^{-3}	Equilibration time/h	pH[a)]	pH[b)]	Solubility 10^{-6} mol dm^{-3}
Run 1				Run 2			
90	6.40	6.40	4.70	235	6.26	6.24	4.86
114	6.49	6.44	4.89	264	6.29	6.23	4.88
138	6.42	6.42	4.84	283	6.24	6.24	4.78
168	6.40	6.38	4.96	314	6.21	6.17	4.81
186	6.48	6.41	4.90	332	6.24	6.22	4.85
210	6.39	6.43	4.84	356	6.30	6.24	4.73
234	6.39	6.43	4.96	380	6.49	6.48	4.96
				Mean of all data 4.85±0.08			

a,b) The pH of saturated solutions measured before and after being filtered to be equilibrated with heptane, respectively.

Table 3. Melting points and solubilities in water (S_0) at 25 °C for Cu and Be chelates with BA and BFA

Chelate	Mp θ_m/°C	S_0/mol dm^{-3}
$Cu(bzac)_2$[a)]	195	1.38×10^{-6}
$Cu(bfac)_2$	239	9.07×10^{-7}
$Be(bzac)_2$[b)]	211	9.98×10^{-7}
$Be(bfac)_2$	143	4.85×10^{-6}

a) Ref. 1. b) Ref. 2.

A comparison of the solubility of $Cu(bfac)_2$ and $Be(bfac)_2$ in water with that of $Cu(bzac)_2$ and $Be(bzac)_2$ is very interesting. As shown in Table 3, the higher the melting points of these chelates are, the smaller their solubilities are. This is a general phenomenon for the solubility of similar solids in their natures.[8)] The extremely low melting point of $Be(bfac)_2$ may be ascribed to a mutual repulsion between molecules in its solid state caused by the introduction of CF_3 group.[6)]

Salt Effect on the Solubility of $Cu(bfac)_2$ and $Be(bfac)_2$. For the solubility measurement in aqueous LiCl, $NaNO_3$, $NaClO_4$, NaCl, and Na_2SO_4 solutions, the pH ranges which gave constant values for BFA concentration in heptane phases were 6.4—6.9 for $Cu(bfac)_2$ and 6.0—6.5 for $Be(bfac)_2$. For each sample solution, the solubility measurement was made independently 4 times for $Cu(bfac)_2$ and 4—7 times for $Be(bfac)_2$ at adequate time intervals (*cf.* Tables 1 and 2). The number of solubility measurement for $Be(bfac)_2$ depends on the volume taken out of the saturated solutions. The standard deviations of these measurements were within 3% in all cases.

In the previous studies, it was confirmed that the solubility of $Cu(bzac)_2$ and $Be(bzac)_2$ in aqueous salt solutions (S) could be expressed by

$$\log S = \log S_0 - k_s C_s, \qquad (2)$$

where S_0, k_s, and C_s were the solubility of these chelates in water, salting coefficient, and the concentration of salts, respectively.[1,2)] For $Cu(bfac)_2$ and $Be(bfac)_2$, as the plot of log (S) *vs.* C_s did not give straight lines, Eq. 2 was not valid.

As shown in Figs. 1 and 2, where log (S_0/S) is plotted against $\sqrt{C_s}$ for $Cu(bfac)_2$ and $Be(bfac)_2$, it was found that the solubility data for these chelates might be expressed by

$$\log (S_0/S) = a\sqrt{C_s} + bC_s \qquad (3)$$

The values for a and b in Eq. 3 obtained by applying the least-squares method to the solubility data are listed in Table 4, where the square root of the dispersions of residues of log (S_0/S), *i.e.*,

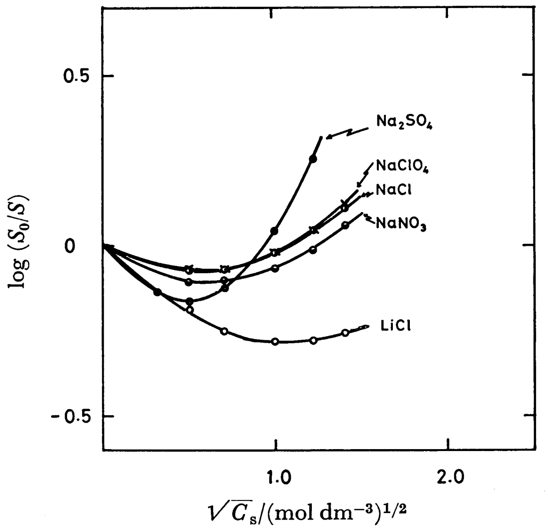

Fig. Plot of log (S_0/S) *vs*. $\sqrt{C_s}$ for Cu(bfac)$_2$. Solid lines are values calculated from log $(S_0/S) = a\sqrt{C_s} + bC_s$ by using the least-squares method.

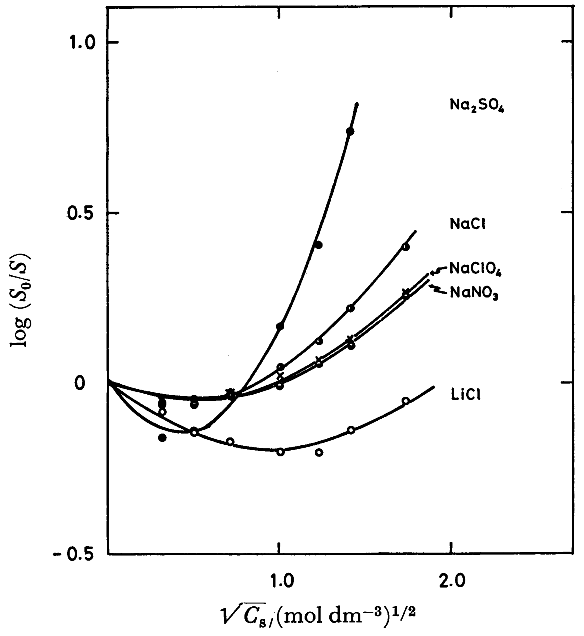

Fig. 2. Plot of log (S_0/S) *vs*. $\sqrt{C_s}$ for Be(bfac)$_2$. Solid lines are values calculated from log $(S_0/S) = a\sqrt{C_s} + bC_s$ by using the least-squares method.

$$\sigma = [\sum_{i=1}^{n} \{\log (S_0/S_i) - (a\sqrt{C_{si}} + bC_{si})\}^2/(n-1)]^{1/2}$$

is also tabulated. The S_0/S term in Eq. 3 represents the ratio of the activity coefficient of chelates in aqueous salt solutions to that of chelates in water.[9]

For all the salts studied in this work, the values for *a*-coefficient were negative and those for *b*-coefficient were positive (see Table 4). In a low region of C_s, the $a\sqrt{C_s}$ term is larger than the bC_s term and the solubility of Cu(bfac)$_2$ and Be(bfac)$_2$ in aqueous salt solutions is higher than the solubility in water. On the other hand, in a high region of C_s, the bC_s term is predominant and the solubility of these chelates decreases with increasing C_s. From a comparison of the salt effect on the solubility of Cu(bfac)$_2$ with that for Be(bfac)$_2$, it seems that the influence of the introduction of CF$_3$ group on the salt effect scarcely varies with the configuration of the chelates.

TABLE 4. *a*- AND *b*-COEFFICIENTS IN $\log(S_0/S) = a\sqrt{C_s} + bC_s$ FOR Cu(bfac)$_2$ AND Be(bfac)$_2$

Salt	a/(mol dm^{-3})$^{1/2}$	b/mol dm^{-3}	σ[a]
	Cu(bfac)$_2$		
LiCl	−0.512	0.232	0.0060
NaNO$_3$	−0.336	0.267	0.0038
NaClO$_4$	−0.259	0.245	0.0040
NaCl	−0.270	0.247	0.0040
Na$_2$SO$_4$	−0.685	0.729	0.0046
	Be(bfac)$_2$		
LiCl	−0.411	0.216	0.0177
NaNO$_3$	−0.206	0.201	0.0097
NaClO$_4$	−0.204	0.206	0.0114
NaCl	−0.236	0.272	0.0099
Na$_2$SO$_4$	−0.707	0.868	0.0262

a) $\sigma^2 = \sum_{i=1}^{n} \{\log (S_0/S_i) - (a\sqrt{C_{si}} + bC_{si})\}^2/(n-1)$.

When the value for *a*-coefficient in Eq. 3 is negligible, Eq. 3 agrees with Eq. 2. Thus, a difference between the salt effect on the solubility of Cu(bfac)$_2$ or Be(bfac)$_2$ and that for Cu(bzac)$_2$ or Be(bzac)$_2$ is attributed to the $a\sqrt{C_s}$ term. Although the $a\sqrt{C_s}$ term must reflect a specific interaction between fluorinated chelates and water molecules or ions, more detailed study is required for clarifying the interaction.

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