July, 1986] *Bull. Chem. Soc. Jpn.*, *59, 2135—2140 (1986)* 2135

Partial Molar Enthalpy of Solution for Tris(2,4-pentanedionato)cobalt(III) in Mixed Solvents of Water and Dimethyl Sulfoxide

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(Received January 16, 1986)

The solubility (X_s) of tris(2,4-pentanedionato)cobalt(III) ([Co(acac)$_3$]) in mixed solvents of water and dimethyl sulfoxide (DMSO) with various compositions was determined over the temperature range 20—60 °C. It was found that the experimental values of X_s could be satisfactorily fitted to $\ln X_s = A(1/T) + B\ln T + C$ and the partial molar enthalpy of solution ($\Delta\bar{H}_s$) at 25 °C for [Co(acac)$_3$] was estimated from slopes of the solubility curves. When $\Delta\bar{H}_s$ was plotted against the mole fraction of DMSO (X_{DMSO}), a clear maximum was found at about $X_{\mathrm{DMSO}}=0.3$. This composition profile of $\Delta\bar{H}_s$ is discussed in connection with the internal pressure of a mixture of water and DMSO. A method to estimate an approximate value of the partial molar enthalpy of hydrophobic hydration ($\Delta\bar{H}_h$) in an aqueous DMSO mixture of [Co(acac)$_3$] is also presented by using the solubility data in mixtures with a lower X_{DMSO} than 0.14.

In studies on the solvent extraction of various metal chelates, it has been found that the role of organic solvents can be successfully interpreted by the aid of the regular solution theory in terms of the solubility parameters of organic solvents.[1] However, an application of the regular solution theory to the aqueous phase in solvent-extraction systems is unreasonable because of strong interactions between solutes and water molecules such as the hydrogen bonding and association of water molecules due to hydrogen bonding among them.

Recently, Yamamoto applied a scaled particle theory to an interpretation of the thermodynamic properties of tris(2,4-pentanedionato)chromium(III) ([Cr(acac)$_3$]) in an aqueous solution.[2] Awano et al.[3] have found that the composition dependence of the partition coefficients of some tris(2,4-pentanedionato) chelates between heptane and mixed solvents of water and dimethyl sulfoxide (DMSO) can be explained in terms of the internal pressure of aqueous DMSO mixtures.

The thermodynamic properties of tetraalkylammonium salts[4—10] and some nonelectrolytes[11—14] in mixtures of water and aprotic solvents have been investigated rather extensively. Especially, Somsen et al.[7,9,10] have shown that the composition dependence of the enthalpy of solution for tetraalkylammonium salts in mixtures of water and aprotic solvents, such as DMSO and *N*,*N*-dimethylformamide (DMF), can be interpreted in terms of an effect of the organic solvents on the hydrophobic hydration of the solutes in the mixtures.

In tris(2,4-pentanedionato) chelates, central metal ions are octahedrally surrounded by three 2,4-pentanedionate anions and two oxygen atoms of the anion combine with the central metal ions. Since six methyl groups reside on the periphery of the chelates, these chelates may be expected to exhibit a hydrophobic property. In connection with the solvent extraction of metal chelates, it is interesting to examine the behavior of such chelates both in water and in mixtures of water and organic solvents such as DMSO.

Thus, in this study, tris(2,4-pentanedionato)cobalt(III) ([Co(acac)$_3$]), which is inert to exchange or substitution reactions of ligands and is fairly soluble in water,[15] was chosen as a model chelate and its solubility in water and in aqueous DMSO mixtures was determined over the temperature ranges 5—60 °C and 20—60 °C, respectively. From these data, the partial molar enthalpy of solution ($\Delta\bar{H}_s$) for [Co(acac)$_3$] was estimated and the effect of DMSO on $\Delta\bar{H}_s$ and on the hydrophobic hydration of [Co(acac)$_3$] is discussed.

Experimental

Materials. [Co(acac)$_3$] was obtained from Dojin Chemical Laboratories Ltd. and recrystallized from a water–acetone mixture (60% acetone by volume). The ultraviolet and visible absorption spectrum of the purified [Co(acac)$_3$] in ethanol agreed with values found in the literature.[16]

Commercial DMSO (spectrophotometric grade reagent, Dojin Chemical Laboratories Ltd.) was dried over calcium hydride for a week and distilled under reduced pressure. Middle fractions were collected and stored over a molecular sieve (type 4A). The water content in the purified DMSO, measured by Karl Fischer titration, was about 0.06% by weight. The purified DMSO was placed in a dry box whose humidity was kept below 20% with silica gel. Mixtures of water and DMSO were prepared by weight; preparations were carried out in the dry box. Redistilled water was used.

Solubility Measurement. The apparatus shown in Fig. 1 was used to saturate a given sample solution with [Co(acac)$_3$]. A sufficient amount of [Co(acac)$_3$] and about 50 cm^3 of a sample solution were placed in the apparatus, which was thermostated at the desired temperatures to within ±0.1 °C. The mixture was stirred with a magnetic stirrer for about 48—72 h at each temperature. At appropriate time intervals, the saturated solution was passed through an absorbent cotton filter by injecting dry air. A volume of the saturated solution suitable for subsequent spectroscopic measurements was transferred by pipette into a 5 or 10 cm^3 volumetric flask which had been previously weighed. The total weight of the flask and the saturated solution was weighed. If [Co(acac)$_3$] precipitated during weighing, 1 cm^3 of DMSO was added to the saturated solution in order to dissolve the precipitation. After letting the flask stand for 30 min in an incubator kept at 25±0.5 °C, water was added to the mark at 25 °C; this solution was further diluted with water to give an absorbance between 0.2 and 0.6 at 324 nm.

The concentration (C mol dm^{-3}) of [Co(acac)$_3$] in the above final solution was calculated by using the absorbance at 324 nm (A) from

$$C = (A - 0.0011)/\varepsilon d, \tag{1}$$

where εd was 8.37×10^3 mol^{-1} dm^3. The solubility in molality units (S_m mol kg^{-1}) was calculated from the weight of the saturated solution, the degree of dilution, and C.

The absorbance of [Co(acac)$_3$] at 324 nm was not entirely affected by the presence of 5% DMSO by volume. Since in all cases, the volume fraction of DMSO in the final solution for measuring A was less than 1%, Eq. 1 settled in water was used throughout.

The temperature of the saturated solution was increased from 20 to 60 °C (from 5 to 60 °C for water) at 5 °C intervals. It was found that [Co(acac)$_3$] attained equilibrium within 24 h at each temperature. Solubility measurements were carried out at least 3 times for equilibration times of 48—72 h at each temperature.

In solubility measurements for mixtures with a DMSO content of $X_{DMSO}\geq0.4$ (X_{DMSO} is mole fraction of DMSO), the saturated solution could not be passed rapidly through a cotton filter at the increased temperature because of the adhesion of a solid [Co(acac)$_3$] to the cotton filter. In this case, a further measurement was not carried out.

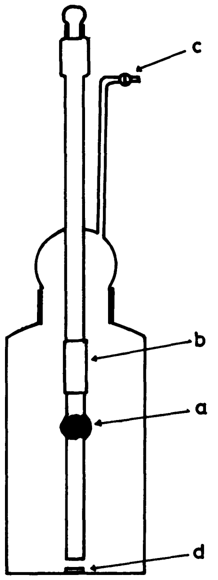

Fig. 1. Apparatus for solubility measurement. a: Filter filled with absorbent cotton, b: Silicone tube, c: Stop-cock for injecting air, d: Magnetic stirring bar.

Results

The S_m values of [Co(acac)$_3$] in water are listed in Table 1. Errors denote deviations at a 95% confidence level and are less than 2%. In order to confirm whether [Co(acac)$_3$] is hydrolyzed in water or not, independent measurements were carried out for two saturated solutions. The solubility was obtained from the absorbance at 324 nm in one measurement and from that at 593 nm in the other. The separately obtained S_m values closely agreed with each other (see Table 1). Furthermore, when the saturated solution equilibrated at 60 °C was allowed to attain equilibrium again at 25 °C, the solubility value at 25 °C was reproducible within the experimental error (see the lowest line in Table 1). These results show that [Co(acac)$_3$] is not decomposed over the temperature range studied.

The S_m values in mixtures of water and DMSO are given in Table 2. The solubility data at 25 °C were reproducible within the experimental error when the solutions at the end of experiment at the highest temperature were allowed to attain equilibrium at 25 °C. This result shows that the evaporation of water or DMSO during the equilibration produced no detectable effect.

Discussion

Partial Molar Enthalpy of Solution of [Co(acac)$_3$] ($\Delta\bar{H}_s$). The S_m values of [Co(acac)$_3$] were converted to solubility in mole fraction (X_s) and then $\ln X_s$ was plotted against $1/T$. In Fig. 2 typical plots are

Table 1. Solubility of [Co(acac)$_3$] in Water ($S_m\times10^3$/mol kg^{-1})$^{a)}$

Temperature/°C	$S_m$$^{b)}$	$S_m$$^{c)}$
5	6.93±0.05	6.85±0.02
10	5.70±0.04	5.64±0.02
15	4.86±0.03	4.82±0.03
20	4.27±0.02	4.25±0.01
25	3.82±0.05	3.83±0.01
30	3.52±0.02	3.53±0.01
35	3.29±0.04	3.32±0.02
40	3.13±0.01	3.09±0.02
45	3.04±0.02	3.02±0.01
50	3.02±0.02	2.97±0.02
55	3.00±0.02	2.99±0.01
60	3.06±0.02	3.05±0.01
25	3.79±0.02$^{d)}$	

a) Error denotes deviation at 95% confidence level. b, c) Solubility values obtained from absorbance at 324 nm and 593 nm, respectively. d) Value obtained by the experiment that the solution equilibrated at 60 °C is allowed to attain equilibrium again at 25 °C.

Table 2. Solubility of [Co(acac)$_3$] in Aqueous DMSO Mixtures ($S_m \times 10^3$/mol kg^{-1})[a)]

Temperature /°C	Mole Fraction of DMSO (X_{DMSO})						
	0.0160	0.0272	0.0587	0.0957	0.1400	0.1940	0.2644
20	3.81±0.02	3.43±0.06	2.62±0.02	2.00±0.01	1.50±0.01	1.25±0.01	1.32±0.01
25	3.50±0.01	3.25±0.07	2.67±0.02	2.13±0.01	1.68±0.01	1.45±0.01	1.58±0.01
30	3.29±0.05	3.16±0.03	2.72±0.01	2.28±0.03	1.90±0.01	1.70±0.01	1.89±0.01
35	3.18±0.01	3.12±0.01	2.83±0.02	2.45±0.01	2.18±0.01	2.01±0.02	2.28±0.01
40	3.13±0.02	3.12±0.02	2.97±0.02	2.69±0.03	2.47±0.04	2.38±0.04	2.74±0.02
45	3.13±0.01	3.17±0.01	3.15±0.01	2.97±0.03	2.82±0.02	2.80±0.01	3.31±0.01
50	3.17±0.01	3.28±0.02	3.37±0.01	3.29±0.04	3.26±0.01	3.31±0.02	3.99±0.05
55	3.25±0.02	3.44±0.04	3.66±0.01	3.64±0.04	3.72±0.02	3.91±0.07	4.83±0.02
60	3.33±0.02	3.64±0.03	3.96±0.07	4.11±0.08	4.32±0.07	4.62±0.07	5.76±0.17

	X_{DMSO}						
	0.3503	0.4309	0.4986	0.5690	0.6849	0.8555	1.0000
20	1.99±0.02	3.29±0.01	5.19±0.02	7.81±0.02	14.6±0.1	29.0±0.1	42.4±0.2
25	2.37±0.01	3.86±0.02	6.03±0.03	8.91±0.13	16.6±0.1	32.5±0.2	46.9±0.5
30	2.83±0.02	4.58±0.04	7.04±0.01	10.1±0.2	18.8±0.2	36.5±0.4	52.7±0.2
35	3.39±0.03	5.41±0.07	8.22±0.07	11.6±0.1	21.4±0.3	40.7±0.9	59.0±0.2
40	4.07±0.01	6.50±0.12	9.61±0.04	13.3±0.2	24.4±0.1	46.2±0.7	65.4±1.1
45	4.98±0.11	7.94±0.11	11.3±0.2	15.4±0.3	27.7±0.7	52.0±0.5	72.9±1.0
50	6.16±0.13	9.50±0.20	13.2±0.2	17.9±0.4	31.8±0.4	58.9±0.7	81.8±0.8
55	7.21±0.01		15.5±0.3	20.1±0.4	36.3±1.2	66.3±1.0	91.3±0.3
60	8.45±0.20						

a) Error denotes deviation at 95% confidence level.

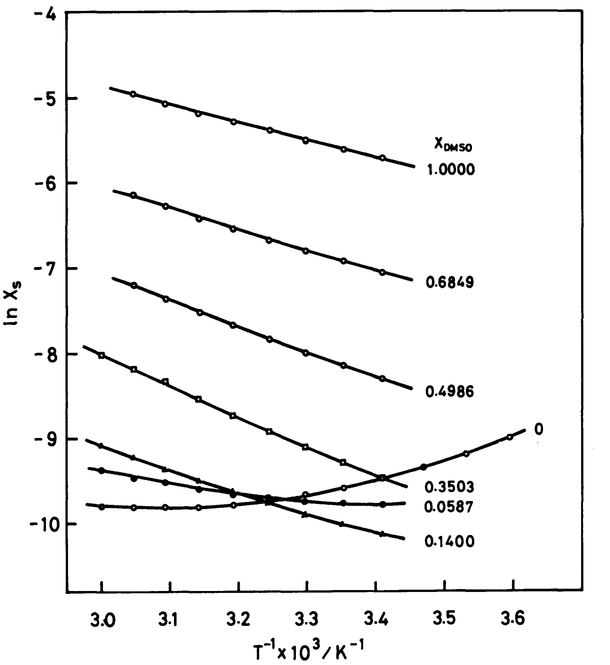

Fig. 2. Typical plot of ln X_s vs. $1/T$ for [Co(acac)$_3$] in water–DMSO mixture.
Solid lines are solubility curves calculated by Eq. 2.

shown. The solubility curve in water passed through a minimum at about 55 °C. Yamamoto has also found a similar minimum in the solubility curve of [Cr(acac)$_3$] in water.[2)]

The minima of the solubility curves in aqueous DMSO mixtures are obviously shifted to lower temperatures with increases in X_{DMSO} (40—45°C for $X_{\mathrm{DMSO}}=0.0160$; 35 °C for $X_{\mathrm{DMSO}}=0.0272$). In mixtures with a composition $X_{\mathrm{DMSO}} \geqq 0.0587$, the minimum was no longer distinct over the temperature range studied.

For representing solubility curves, all experimental values were fitted to

$$\ln X_s = \mathrm{A}(1/T) + \mathrm{B} \ln T + \mathrm{C}, \tag{2}$$

where A, B, and C are fitting parameters. Equation 2 could reproduce the X_s values within errors of ±1% in all cases. In Table 3 the values of the fitting parameters in Eq. 2 are given. The values of $\Delta \bar{H}_s$ at 25 °C can be estimated by combining Eq. 2 with

$$\Delta \bar{H}_s = RT^2(\mathrm{d} \ln X_s/\mathrm{d}T). \tag{3}$$

The upward curvature in the low-temperature region of the solubility curves in water and in mixtures with a lower DMSO content might be related to the hydrophobic hydration of [Co(acac)$_3$]. (A discussion on hydrophobic hydration will be presented subsequently.) In order to confirm whether the solubility curves can be regarded as straight lines or not, an attempt was also made to fit the solubility data in mixtures of $X_{\mathrm{DMSO}} \geqq 0.1940$ to the

Table 3. Values of Fitting Parameters in Solubility Equation ($\ln X_s = \mathrm{A}(1/T) + \mathrm{B} \ln T + \mathrm{C}$) of [Co(acac)$_3$]

X_{DMSO}	A/K	B	C
0	21073.338	64.845187	−449.72031
0.0160	18589.15	58.591129	−405.79352
0.0272	18278.294	59.000034	−407.11899
0.0587	12723.832	43.984506	−303.04912
0.0957	10944.5	40.641577	−278.15726
0.1400	6750.5504	29.867697	−202.83097
0.1940	4896.2513	25.950222	−174.32384
0.2644	4557.4002	26.138173	−174.04164
0.3503	3373.9398	22.317148	−147.75569
0.4309	9302.5399	41.138091	−274.26891
0.4986	4331.113	23.717577	−157.80623
0.5690	3225.146	18.900721	−126.17903
0.6849	3831.2347	20.375146	−135.86458
0.8555	3806.3492	19.595031	−130.50695
1.0000	2199.2121	13.871775	−92.01784

Table 4. Partial Molar Enthalpy of Solution for [Co(acac)$_3$] at 25 °C$^{\mathrm{a)}}$

X_{DMSO}	$\Delta\bar{H}_s$/kJ mol^{-1} $^{\mathrm{b)}}$	$\Delta\bar{H}_s$/kJ mol^{-1} $^{\mathrm{c)}}$
0	−14.5±0.4	
0.0160	−9.3±1.8	
0.0272	−5.7±1.6	
0.0587	3.2±1.2	
0.0957	9.8±1.2	
0.1400	17.9±1.0	
0.1940	23.6±0.9	26.7±1.2
0.2644	26.9±0.8	30.0±1.2
0.3503	27.3±2.3	29.9±1.3
0.4309	24.6±2.1	27.8±2.0
0.4986	22.8±0.9	25.1±1.1
0.5690	20.0±1.4	21.9±0.9
0.6849	18.7±0.7	20.6±0.9
0.8555	16.9±0.8	18.8±0.9
1.0000	16.1±0.7	17.7±0.6

a) Error was estimated from deviation at 95% confidence level of the fitting parameters in Eq. 2 or Eq. 4. b) Values estimated from slopes at 25 °C of curves obtained by fitting solubility data to Eq. 2. c) Values estimated from slopes of straight lines obtained by fitting solubility data to Eq. 4.

following equation over the whole temperature range studied.

$$\ln X_s = \mathrm{a}(1/T) + \mathrm{b} \tag{4}$$

The correlation coefficients (γ)** were higher than 0.998.

The values of $\Delta\bar{H}_s$ estimated by combining Eqs. 4

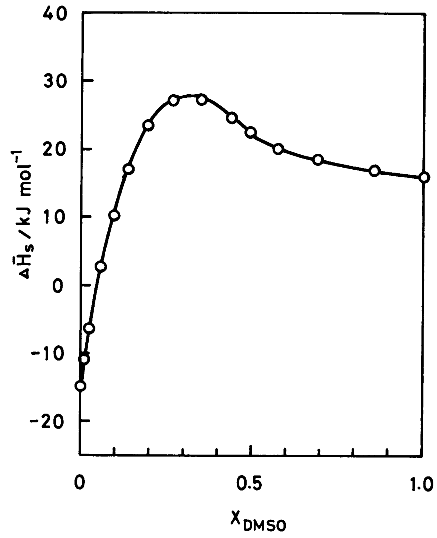

Fig. 3. Composition profile of $\Delta\bar{H}_s$ for [Co(acac)$_3$] in water–DMSO mixture.

and 3 agreed fairly well with the values obtained using Eq. 2 (see Table 4). While this result shows that the solubility curves in these mixtures are practically straight, in the subsequent discussion, $\Delta\bar{H}_s$ estimated by Eq. 2 is used from the standpoint of consistency.

Effect of DMSO on $\Delta\bar{H}_s$ of [Co(acac)$_3$]. When $\Delta\bar{H}_s$ was plotted against X_{DMSO}, a clear maximum was observed at about X_{DMSO}=0.3 (Fig. 3). A similar maximum has been found for various properties of aqueous DMSO mixtures such as the enthalpy of mixing,[17] the viscosity,[18] and the internal pressure.[19] The maximization recognized for these properties has been interpreted in terms of a strong interaction between water and DMSO[18,19] or a marked rigidifying effect of DMSO on the water structure.[17,20,21] However, the cause of the maximization seems not to have been definitely established. Thus, in this discussion, an attempt is made to relate the composition profile of $\Delta\bar{H}_s$ to a certain property of the aqueous DMSO mixtures; also, the appearance of a maximum in Fig. 3 is not discussed in detail.

The composition dependence of the enthalpy of transfer of a hydrophobic solute from water to aqueous mixed solvents can be attributed to the enthalpy of cavity formation.[22] The partial molar enthalpy of cavity formation ($\bar{H}_c$) is related to the internal pressure (P_i) by[23]

$$\bar{H}_c = (\bar{V}_c - a^3N\pi/6)(R/82.05)P_i, \tag{5}$$

where $\bar{V}_c$ and a are the partial molar volume of cavity formation and the hard-sphere diameter of the solute, respectively, N is Avogadro's number, and R is 8.314×10^{-3} kJ mol^{-1} K^{-1}.

Since data for P_i of aqueous DMSO mixtures are available,[19] it is significant to relate the composition

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** The correlation coefficient is given by

$$\gamma = \Sigma\{(x_i-\bar{x})(y_i-\bar{y})\}/\sqrt{\Sigma(x_i-\bar{x})^2\Sigma(y_i-\bar{y})^2},$$

where $\bar{x}$ and $\bar{y}$ are means of x_i and y_i, respectively.

profile of $\Delta\bar{H}_s$ to that of P_i. First, the deviation of $\Delta\bar{H}_s$ from the ideal behavior in aqueous DMSO mixtures ($\delta\Delta\bar{H}_s$) can be defined as

$$\delta\Delta\bar{H}_s = \Delta\bar{H}_s - \{X_{DMSO}\Delta\bar{H}_s(\mathrm{DMSO}) + (1-X_{DMSO})\Delta\bar{H}_s(\mathrm{H_2O})\}, \quad (6)$$

where (DMSO) and (H_2O) denote the values of $\Delta\bar{H}_s$ in DMSO and in water, respectively. Second, if it is assumed that $\bar{V}_c$ is approximately constant over the whole composition range, on the basis of Eq. 5, $\delta\Delta\bar{H}_s$ can be represented by

$$\delta\Delta\bar{H}_s = (\bar{V}_c - a^3N\pi/6)(R/82.05)\delta P_i, \quad (7)$$

where

$$\delta P_i = P_i - \{X_{DMSO}P_i(\mathrm{DMSO}) + (1-X_{DMSO})P_i(\mathrm{H_2O})\}.$$

Figure 4 shows the good linear correlation between $\delta\Delta\bar{H}_s$ and δP_i which is expected from Eq. 7 (γ=0.980). Values of δP_i were calculated from values found in the literature for P_i[19] and $\delta\Delta\bar{H}_s$ values were read from a smooth curve of $\delta\Delta\bar{H}_s$ vs. X_{DMSO} which is not shown in the figure. Thus, the composition profile of $\Delta\bar{H}_s$ of [Co(acac)3] can be linearly related to the composition dependence of P_i of aqueous DMSO mixtures. A definite explanation of the maximization observed in the composition profile of P_i can also be expected to clarify the cause of the maximum of $\Delta\bar{H}_s$.

The above assumption concerning $\bar{V}_c$ is not strictly valid since $\bar{V}_c$ is usually calculated using Eq. 5 with an $\bar{H}_c$ value estimated on the basis of the scaled particle theory.[23] However, the linear correlation between $\delta\Delta\bar{H}_s$ and δP_i in Fig. 4 shows that the influence of a change in $\bar{V}_c$ with the solvent composition on Eq. 7 is negligible.

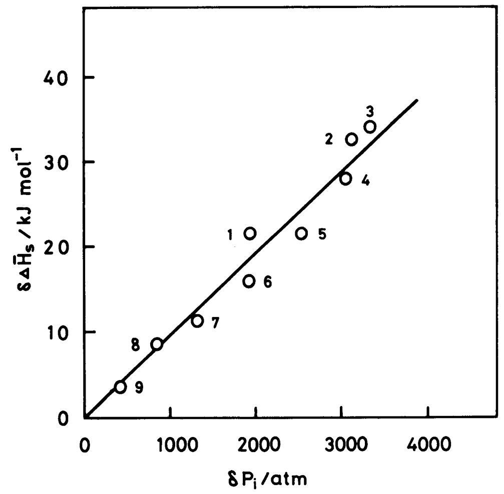

Fig. 4. Correlation between $\delta\Delta\bar{H}_s$ of [Co(acac)3] and δP_i in water–DMSO mixture.
$\delta\Delta\bar{H}_s$ denotes deviation of $\Delta\bar{H}_s$ from ideal behavior defined by Eq. 6. X_{DMSO} is as follows: 1) 0.1; 2) 0.2; 3) 0.3; 4) 0.4; 5) 0.5; 6) 0.6; 7) 0.7; 8) 0.8; 9) 0.9.

In the derivation of Eq. 7, the partial molar enthalpy of interaction ($\bar{H}_i$) is not taken into account; that is, the contribution of $\delta\bar{H}_i$ to $\delta\Delta\bar{H}_s$ is ignored ($\delta\bar{H}_i$ is also defined by a similar equation to Eq. 6). The type of interaction between [Co(acac)3] and water seems to differ from that between [Co(acac)3] and DMSO. While an estimation of $\bar{H}_i$ is difficult, the result in Fig. 4 suggests that a change in $\bar{H}_i$ with solvent composition is approximately proportional to the solvent composition, that is, $\delta\bar{H}_i \fallingdotseq 0$.

Estimation of the Partial Molar Enthalpy of Hydrophobic Hydration ($\Delta\bar{H}_h$) for [Co(acac)3]. The upward curvature at the low-temperature region of the solubility curves in Fig. 2 can be attributed to the hydrophobic hydration of [Co(acac)3].[24] Shinoda has pointed out that the plot of ln X_s against $1/T$ for a hydrophobic solute in water gives a straight line at sufficiently high temperatures because of a disappearance of hydrophobic hydration.[24] The present observation that the minimum in the solubility curves is shifted to lower temperatures with increasing X_{DMSO} suggests that DMSO weakens the hydrophobic hydration of [Co(acac)3].

In an attempt to estimate $\Delta\bar{H}_h$, the straightening of the solubility curve was regarded as an indication of the disappearance of hydrophobic hydration. Thus, the solubility data in aqueous DMSO mixtures with $X_{DMSO} \leq 0.14$ were fitted to Eq. 4 in limited temperature regions and the partial molar enthalpy of solution without hydrophobic hydration ($\Delta\bar{H}'_s$) was estimated from the slopes. The values of $\Delta\bar{H}_h$ were obtained by subtracting $\Delta\bar{H}'_s$ from $\Delta\bar{H}_s$.

In Table 5, $\Delta\bar{H}'_s$ and $\Delta\bar{H}_h$ are listed. For $X_{DMSO} \leq 0.0272$, errors of $\Delta\bar{H}'_s$ estimated from deviations at the 95% confidence level of the slopes in Eq. 4 were extremely large because of the narrow temperature region in which $\Delta\bar{H}'_s$ was estimated; hence, the $\Delta\bar{H}_h$ values should be regarded as being

Table 5. Partial Molar Enthalpy of Solution without Hydrophobic Hydration ($\Delta\bar{H}'_s$) and Partial Molar Enthalpy of Hydrophobic Hydration ($\Delta\bar{H}_h$) at 25 °C of [Co(acac)3]

X_{DMSO}	$\Delta\bar{H}_s'$/kJ mol^{-1} a)	$\Delta\bar{H}_h$/kJ mol^{-1} b)
0.0160	4.4±2.8 (50—60 °C)	−13.7
0.0272	9.4±5.6 (50—60 °C)	−15.1
0.0587	13.5±1.8 (45—60 °C)	−10.3
0.0957	18.2±2.1 (40—60 °C)	−8.4
0.1400	23.3±1.5 (35—60 °C)	−5.4

a) Values were estimated from slopes of straight lines obtained by fitting solubility data to Eq. 4 in the temperature regions given in parentheses and errors were estimated from deviation at 95% confidence level of the slopes. b) $\Delta\bar{H}_h = \Delta\bar{H}_s - \Delta\bar{H}_s'$. The values of $\Delta\bar{H}_s$ are given in Table 4.

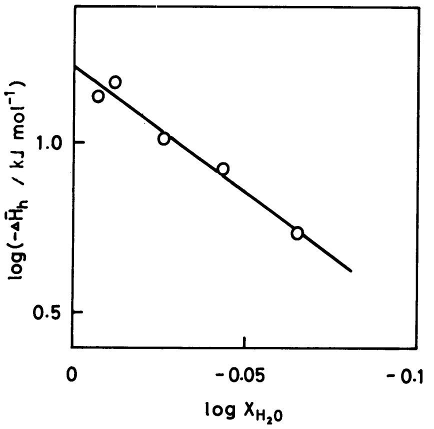

Fig. 5. Correlation between $\log(-\Delta\bar{H}_\mathrm{h})$ of [Co(acac)$_3$] and $\log X_{\mathrm{H_2O}}$ in water–DMSO mixture.

approximate. Nevertheless, it is worth noting that the differences between $\Delta\bar{H}_\mathrm{s}$ and $\Delta\bar{H}'_\mathrm{s}$ for mixtures with a lower X_DMSO than 0.14 are beyond the experimental errors. Therefore, the $\Delta\bar{H}_\mathrm{h}$ values in Table 5 are significant.

According to Somsen et al.,[7,9,10] $\Delta\bar{H}_\mathrm{h}$ in aqueous DMSO mixtures can be expressed by

$$\Delta\bar{H}_\mathrm{h} = \Delta\bar{H}_\mathrm{h}(\mathrm{H_2O})X^n_{\mathrm{H_2O}}, \qquad (8)$$

where $\Delta\bar{H}_\mathrm{h}(\mathrm{H_2O})$ and $X_{\mathrm{H_2O}}$ are $\Delta\bar{H}_\mathrm{h}$ in water and the mole fraction of water, respectively. In an earlier paper of Somsen et al.,[7] n was considered to denote the number of water molecules forming clathrate-like cages around hydrophobic sites or parts of a solute molecule. However, in a later paper, it was shown that n is not unambiguously defined by their model.[9] We consider that n is a measure of the magnitude of the decrease in $\Delta\bar{H}_\mathrm{h}$ with $X_{\mathrm{H_2O}}$. The values of $\log(-\Delta\bar{H}_\mathrm{h})$ are plotted against $\log X_{\mathrm{H_2O}}$ in Fig. 5, which shows the validity of Eq. 8 (γ=0.984).

The value of $\Delta\bar{H}_\mathrm{h}(\mathrm{H_2O})$ for [Co(acac)$_3$], obtained from the intercept, is -16.7 ± 1.2 kJ mol^{-1}. Shinoda has estimated the $\Delta\bar{H}_\mathrm{h}(\mathrm{H_2O})$ of benzene, methylbenzene, and ethylbenzene to be −31.5, −36.1, and −42.3 kJ mol^{-1}, respectively.[24] At present, the validity of $\Delta\bar{H}_\mathrm{h}(\mathrm{H_2O})$ for [Co(acac)$_3$] can not be discussed in terms of values from the literature for various compounds because of the difficulty in estimating $\Delta\bar{H}_\mathrm{h}(\mathrm{H_2O})$. The present result suggests that the adoption of mixed solvents is useful for an estimation of $\Delta\bar{H}_\mathrm{h}(\mathrm{H_2O})$. A further examination in mixed solvents of water and various organic solvents will be carried out.

The authors wish to thank Dr. Toshiki Wakabayashi for his valuable discussions and useful suggestions during this work.

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