Solubility of Tris(acetylacetonato)chromium(III) in Aqueous Alcohol Mixtures

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From the temperature dependence of the solubility of tris(acetylacetonato)chromium(III) in aqueous *t*-butyl alcohol mixtures and in aqueous methanol mixtures, thermodynamic parameters of the solution were calculated. The solubility and these parameters in aqueous *t*-butyl alcohol mixtures could be explained qualitatively by the cavity formation terms of the scaled particle theory. It was suggested that tris(acetylacetonato)chromium(III) is in water microphases at $X_{\mathrm{BuOH}} \leqq 0.04$ and in *t*-butyl alcohol microphases over this region.

2,4-Pentanedione (acetylacetone) is one of the most useful reagents in analytical chemistry to separate a particular metal ion from various matrixes. Besides the analytical purpose, acetylacetonato complexes such as tris(acetylacetonato)chromium(III) ($Cr(acac)_3$), and tris(acetylacetonato)cobalt(III) ($Co(acac)_3$) seem to be useful model compounds in solution chemistry to clarify solute-solvent interactions of metal chelates as they are stable, large, spherical and rigid solutes.[1,2]

In a previous study,[1] the solubility of $Cr(acac)_3$ was measured from 5 to 75 °C in water, which shows a characteristic feature of a hydrophobic solute with a solubility minimum at 45 °C. With a hard sphere diameter of 8.97 Å for $Cr(acac)_3$, a cavity formation term was calculated by the scaled particle theory (SPT),[3,4] and it was shown that the aqueous solubility of $Cr(acac)_3$ could be explained qualitatively by the cavity formation term.

In the present study, the solubility of $Cr(acac)_3$ was measured in aqueous *t*-butyl alcohol and a few of aqueous methanol mixtures, and the dependences of the solubility on the temperature and concentrations of alcohols were examined in connection with the structural properties of the solvents.

Experimental

A preparation of $Cr(acac)_3$ was given in the previous paper.[1] *t*-Butyl alcohol (*t*-BuOH) was a special grade and methanol (MeOH) was a liquid chromatography grade. The procedure for the solubility measurement followed that of the previous study.[1] Solubility measurements were performed from 5 to 60 °C for X_{BuOH} of 0.005 to 0.015 and X_{MeOH} of 0.025 to 0.05, and from 5 to 45 °C for the other mixtures. The solubility was determined spectrophotometrically by the following equation,

$$\varepsilon = am + bm^2, \tag{1}$$

where ε is the absorbance at 380 nm at 25±1 °C, m is the concentration in mol/kg. Parameters a and b for each solvent were given in Table 1. Solubility measurements were repeated at appropriate intervals until the concentrations agreed within ±1%.

TABLE 1. PARAMETERS OF Eq. 1 FOR AQUEOUS ALCOHOL MIXTURES

X_{ROH}	a	b
	t-Butyl alcohol	
0	429	−441
0.005−0.02	423	0
0.03, 0.04	414	0
0.075	411	0
0.1	406	0
	Methanol	
0.025	425	−8328
0.05	422	−4483
0.11	422	−7718
0.2	411	−5926

Results and Discussion

Solubility curves of $Cr(acac)_3$ in aqueous *t*-butyl alcohol are shown in Fig. 1. For the region $X_{\mathrm{BuOH}} < 0.04$, the solubility minimum is observed as in water, but when X_{BuOH} becomes higher than 0.04, the solubility increases monotonically with increasing temperature. A similar trend was observed for the solubility in aqueous methanol, where the solubility curves are like that in water at $X_{\mathrm{MeOH}} \leqq 0.11$.

On the calculation of the thermodynamic parameters of the solution from the temperature dependence of solubility, several equations were examined to represent the solubility curves and equations with three or four parameters were confirmed to be sufficient as found in the previous study for water.[1] In this study the simplest of the following equations were used,

$$\Delta C_p = A, \tag{2}$$

$$\Delta H_{\mathrm{soln}} = \Delta H_0 + AT, \tag{3}$$

$$\ln m = -\Delta H_0/RT + (A/R)\ln T + B/R. \tag{4}$$

The parameters of these equations are given in Table 2. Solubilities calculated by Eq. 4 agreed with experimental ones within the error of less than ±1%. Thermodynamic parameters at 25 °C are

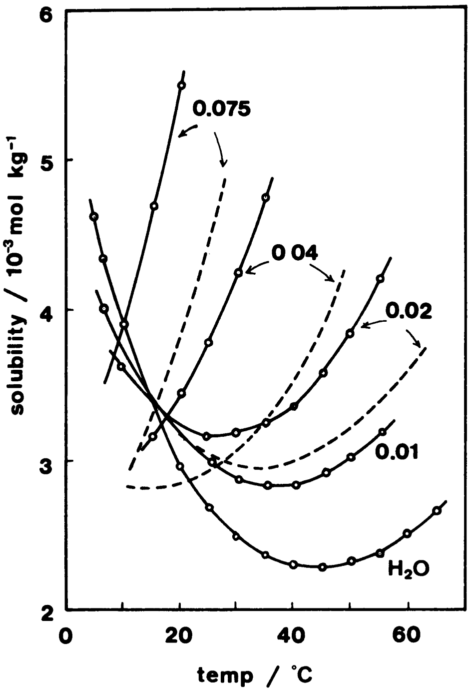

Fig. 1. Solubility of $Cr(acac)_3$ in aqueous *t*-butyl alcohol mixtures.
----: Calculated by SPT.

Table 2. Parameters for solubility equations

X_{ROH}	$A(=\Delta C_p)$ $J\ K^{-1}\ mol^{-1}$	$-B/R$ —	$-\Delta H_0{*}10^{-5}$ $J\ mol^{-1}$
	t-Butyl alcohol		
0	638.1	524.89	2.0253
0.005	620.5	509.67	1.9484
0.01	605.0	496.12	1.8767
0.015	545.0	446.41	1.6640
0.02	556.3	454.18	1.6663
0.03	562.5	456.12	1.6104
0.04	471.8	379.55	1.2552
0.075	85.28	62.688	−0.018289
0.1	47.47	31.552	−0.14025
	Methanol		
0.025	495.4	407.45	1.5417
0.05	437.0	358.17	1.3142
0.11	355.5	287.53	0.95280
0.2	206.3	162.92	0.41424

given in Table 3. ΔH_{soln} changes from exothermic to endothermic with increasing the mole fraction of alcohols, which was accompanied by the change of ΔS_{soln} from negative to positive values.

ΔH-ΔS compensation plots for these two aqueous alcohol mixtures seems to consist of nearly the same line as shown in Fig. 2. The compensation temperature is almost the same, that is, 291±1 *K* for $0 \leq X_{BuOH} \leq 0.04$, and 286±1 *K* for $0 \leq X_{MeOH} \leq 0.11$. Compensation temperatures become higher for both of the mixtures over these regions.

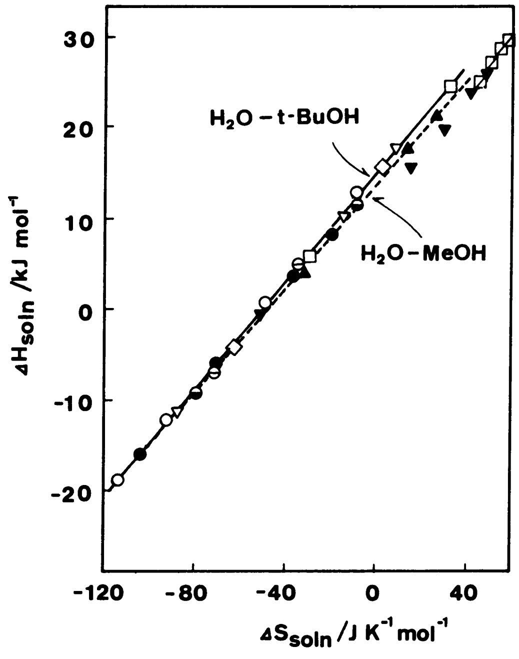

Fig. 2. $\Delta H-\Delta S$ Compensation plots.
X_{BuOH}: ○, 0.0: ⊖, 0.01; ▽, 0.02; ◇, 0.03; □, 0.04; ⧄, 0.075. X_{MeOH}: ●, 0.025; ◒, 0.05; ▲, 0.11; ▼, 0.2.

Table 3. Thermodynamic parameters for the solution of $Cr(acac)_3$ in aqueous alcohol mixtures at 25 °C

X_{ROH}	ΔG_{soln} $kJ\ mol^{-1}$	ΔH_{soln} $kJ\ mol^{-1}$	ΔS_{soln} $J\ K^{-1}\ mol^{-1}$
	t-Butyl alcohol		
0	14.68	−12.30	−92.1
0.01	14.38	−7.28	−71.1
0.02	14.25	−0.79	−50.2
0.03	14.07	6.65	−25.1
0.04	13.82	15.15	4.18
0.075	12.35	27.24	50.21
0.1	11.59	28.20	54.4
		Methanol	
0.05	14.10	−1.13	−50.2
0.11	13.59	10.71	−8.37
0.2	11.92	20.08	29.3

These facts show that the solution process in highly aqueous regions is strongly dependent on the water structure, and then the structural change of water around $Cr(acac)_3$ is reflected on the thermodynamic parameters of the solution of $Cr(acac)_3$ in these solvents.

The deviation of plots from this compensation line with increasing the concentration of alcohols is due to the fact that the structure of the medium changes from water like to organic, and $Cr(acac)_3$ may become to be solvated selectively by alcohols.

In an SPT flame, the free energy of solvation of a gaseous solute (ΔG_{solv}) can be separated into a cavity formation term (G_{cav}) and an interaction term (ΔG_{int}) as Eq. 5,[4]

$$\Delta G_{solv} = G_{cav} + \Delta G_{int} + RT\ln(RT/V), \tag{5}$$

where V is the apparent molar volume of the mixed solvent. The free energy of the solution of a solid solute (ΔG_{soln}) used in the present study could be obtained after a correction of the sublimation energy.[1] The free energy of transfer from water to an aqueous mixture (shown in Fig. 3) does not necessitate such a correction. G_{cav} of Cr(acac)3 in aqueous *t*-butyl alcohol mixtures were calculated by Eq. 6,[4–6]

$$\begin{aligned}G_{cav} = &-RT\ln(1-y_3) + RT[3y_2/(1-y_3)]a_2 \\ &+ RT[3y_1/(1-y_3) + 4.5y_2^2/(1-y_3)^2]a_2^2 \\ &- (1/6)\pi NPa_2^3,\end{aligned} \tag{6}$$

where a_2 is the diameter of the solute molecule, $y_i=(\pi/6)\sum_j\rho_j\sigma_j^i$, $i=1—3$, ρ_j and σ_j are the number density and the hard-sphere diameter of the *j*th component, and P is the pressure. In the following calculation, 9.87 Å,[1] 2.77 Å,[4] and 5.29 Å[6] were used as hard sphere diameters of Cr(acac)3, water and *t*-butyl alcohol, respectively. Densities of aqueous *t*-butyl alcohol mixtures were from Desnoyers *et al.*[7]

A free energy of transfer (ΔG_{tr}) and a free enrgy of transfer of cavity formation ($\Delta G_{cav,tr}$) are given in Fig. 3. Corresponding to the ΔH–ΔS compensation, ΔG_{tr} is only a little negative or positive in a highly aqueous region. Upon increasing the temperature, and upon increasing X_{BuOH}, ΔG_{tr} becomes negatively large.

As an example of the dependences of G_{cav} on the hard sphere diameter of *t*-butyl alcohol, $\Delta G_{cav,tr}$ at 25 °C were calculated with different hard sphere diameters of *t*-butyl alcohol. As shown in Fig. 3, the hard sphere diameter of *t*-butyl alcohol is a very important parameter for estimating G_{cav} quantitatively. But these curves indicate that the trend of the transfer function, and therefore the dependence of solubility on the solvent compositions can be represented only by the G_{cav} terms qualitatively.

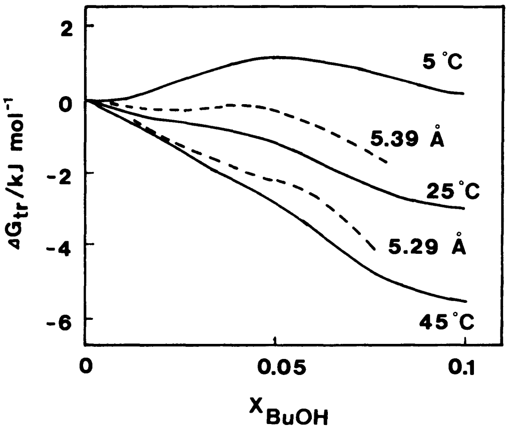

Fig. 3. Free energy of transfer of Cr(acac)$_3$ from water to aqueous *t*-butyl alcohol mixtures.
----: $\Delta G_{cav,tr}$ calculated by SPT for the hard sphere diameter of *t*-butyl alcohol as 5.39 Å and 5.29 Å at 25 °C.

Assuming an interaction term of ΔG_{int} to be constant in the present range and estimating ΔG_{int} from ΔG_{soln} an G_{cav} in water, ΔG_{soln} in aqueous *t*-butyl alcohol mixtures were calculated and solubilities corresponding to these ΔG_{soln} are plotted in Fig. 1. The calculated solubilities for aqueous *t*-butyl alcohol mixtures were lower than the observed ones, though these solubility curves reproduce the presence of the temperature at which solubilities are approximately equal at $X_{BuOH}\leq 0.04$ as observed in the experimental solubility curves. That the cavity formation terms can reproduce such a phenomena means that G_{cav} changes in a similar way. Such a change of G_{cav} may be due to a change in the solvent structure, caused by an equilibrium of the two phases in these solvent mixtures.

For the structure of the aqueous *t*-butyl alcohol mixture, it was proposed that when $X_{BuOH}\leq 0.045$, a clathrate-like species of *t*-BuOH(H$_2$O)$_{21}$ is dispersed in the water and at $X_{BuOH}>0.045$, (*t*-BuOH(H$_2$O)$_{21}$)$_5$ is dispersed in *t*-butyl alcohol.[8] Therefore a fraction of free water available for the hydration of Cr(acac)3 decreases with an increase in the mole fraction of *t*-butyl alcohol at $X_{BuOH}\leq 0.045$. If Cr(acac)3 is considered to dissolve in the aqueous microphase at $X_{BuOH}\leq 0.045$, it is reasonable that the solubility curves in this mole fraction range are like that in water. In this case, it is also expected that the solubility decreases with increasing the concentration of *t*-butyl alcohol at lower temperatures, where the clathrate hydrate is stable. On the other hand, by assuming that Cr(acac)3 dissolves mainly in microphase of *t*-butyl alcohol at $X_{BuOH}>0.045$, the solubility is also expected to increase monotonically with increasing temperature, observed usually on the solubility in organic solvents. The breakdown of the clathrate hydrate-like structure with increasing temperature at $X_{BuOH}>0.045$[8] brings about an increase of the *t*-butyl alcohol available for Cr(acac)3 and then the solubility begins to increase steeply with temperature.

The fact that the ΔH–ΔS compensation curves for propanol mixture was explained in a similar way, that is, benzene is in an aqueous medium when $X_{PrOH}\leq 0.1$, but beyond this region dissolves in the 2-propanol microphases and benzene enhances the formation of 2-propanol microphases.[9]

The fact that the ΔH–ΔS compensation curves for aqueous *t*-butyl alcohol mixtures and aqueous methanol mixtures almost coincide in the highly aqueous region means that regarding the solubility of Cr(acac)3, the difference of chemical interactions of methanol and *t*-butyl alcohol with Cr(acac)3 is only a minor importance compared with the difference of hydrophobicities, or the difference of abilities of these two alcohols to modify the water structure.

The large negative entropy in water, most of which is evaluated as S_{cav},[1] changes from a large negative value to a positive value at $X_{BuOH}=0.04$ at 25 °C. Corresponding to this entropy change, a large ΔC_p in water, most of which is also due to the large C_{cav},[1] decreases only a little in the mole fraction range of 0 to 0.04, and after that it changes suddenly to a very small value (Table 2). Values of ΔC_p include ambiguity when they were obtained as second delivatives of solubility curves. Though it was claimed that ΔC_p is rather independent of temperature for a process where ΔH—ΔS compensation occurs due to the structural change of water.[10] Therefore ΔC_p obtained by Eq. 2 (assuming ΔC_p=constant) may be reliable as a measure of the change of the local structure on the solution of Cr(acac)$_3$ for the highly aqueous region. The dependences of ΔS_{soln} and ΔC_p on the mole fraction of *t*-butyl alcohol also suggest a change in the solvation of Cr(acac)$_3$ from the hydrophobic hydration in a highly aqueous region to selective solvation by *t*-butyl alcohol at $X_{BuOH}>0.04$, by dissolving in *t*-butyl alcohol microphase. The stabilization of Cr(acac)$_3$ observed in ΔG_{tr} at temperatures higher than 25 °C at $X_{BuOH}>0.04$ can also be understood by assuming such a change of solvation.

The difference in the solubilities between the observed and the calculated values may be mainly due to the ambiguity of cavity formation terms by SPT, and also due to the uncertainly of the hard sphere diameter of *t*-butyl alcohol. The solvation schema discussed above tends to change the solubility of Cr(acac)$_3$ in a similar way as expected from the cavity formation terms by SPT. Therefore, the overlap of these two factors, especially selective solvation by *t*-butyl alcohol in the alcohol rich region, may be relevant to the higher solubility compared to the calculated one.

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