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# The Temperature Dependence of the Solubilities of 1-Phenyl-1,3-butanedione and 4,4,4-Trifluoro-1-phenyl-1,3-butanedione in Water and Aqueous Electrolyte Solutions[1]

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The temperature dependence of the solubilities of 1-phenyl-1,3-butanedione (benzoylacetone) and 4,4,4-trifluoro-1-phenyl-1,3-butanedione (benzoyltrifluoroacetone) in water and in 1.0 mol l$^{-1}$ aqueous solutions of $HClO_4$, HCl, $NaClO_4$, KCl, NaBr, NaCl, $BaCl_2$, and $Na_2SO_4$ was determined over the temperature ranges of 20 to 45 °C for benzoylacetone and of 15 to 30 °C for benzoyltrifluoroacetone. From these data, the thermodynamic quantities associated with the dissolution in water and with the transfer from water to the aqueous electrolyt solutions were estimated. Both the enthalpy and the entropy of solution of benzoyltrifluoroacetone in water were much smaller than those for benzoylacetone. This was interpreted by assuming a higher hydrophobic hydration for the less polar benzoyltrifluoroacetone. The thermodynamic quantities of the transfer of benzoyltrifluoroacetone from water to the aqueous perchloric acid solution showed characteristic features compared with those of the other electrolyte solutions. The overall salt effect on the dissolution of benzoylacetone and benzoyltrifluoroacetone is discussed in terms of the change in the thermodynamic quantities.

As the first step in clarifying the salt effect in the solvent extraction of metal chelates, we have investigated the salt effect on the liquid-liquid distribution of 1-phenyl-1,3-butanedione (benzoylacetone, abbreviated as BA) and 4,4,4-trifluoro-1-phenyl-1,3-butanedione (benzoyltrifluoroacetone, abbreviated as BFA).[2,3] They are frequently used as extraction agents for various metal ions.[4]

In the systems of the metal-chelate extraction, a system consists of an organic phase and an aqueous phase. Accordingly, in a thermodynamic study of the solvent extraction of metal chelates, it seems that the thermodynamic quantities of the dissolution of metal chelates in water give fundamental and important information. Because the solubilities of metal chelates in water are generally very low and metal chelates dissociate in water, few papers on the thermodynamic quantities of the dissolution of metal chelates in water have been published.

In view of the above points, in the present study the temperature dependence of the solubilities of BA and BFA in water and in several aqueous electrolyte solutions was measured. From the consequent data, the thermodynamic quantities of the dissolution of these $\beta$-diketones in water and of the transfer of these $\beta$-diketones from water to the aqueous electrolyte solutions were estimated. Such thermodynamic quantities of the transfer seem to give useful information relating to the salt effect.[5]

## Experimental

*Materials.* The benzoylacetone and BFA were purified as previously described.[2,3] The stock solutions of the eight electrolytes used in this study were also prepared as previously described.[2,3] The electrolytes used were as follows: perchloric acid, hydrochloric acid, sodium perchlorate, sodium chloride, sodium bromide, potassium chloride, barium chloride, and sodium sulfate. Redistilled water was used.

*The Temperature Dependence of the Solubilities of Benzoylacetone and Benzoyltrifluoroacetone in Water and in 1.0 mol l$^{-1}$ Aqueous Electrolyte Solutions.* The solubility determination was made as follows: about 1—2 ml of a saturated solution of BA or BFA equilibrated with each solid phase at a desired temperature was transferred into a 25-ml volumetric flask which had been exactly weighed preliminarily ($w_1$ g). The saturated solution in the flask was allowed to stand for about 30 min at the constant room temperature of 25 °C, and then the total weight of the saturate solution and the flask was exactly weighed ($w_2$ g).

In an experiment at a temperature higher than room temperature, a modified procedure was applied to avoid any error due to recrystallization on standing in order to measure the weight. In this case, recrystallized BA or BFA was completely dissolved by adding 5 or 2.5 ml of 99.5% ethanol. Water was added to the mark, and then the absorbance was measured, if necessary, after appropriate dilution. To avoid any error due to the dissociation of BA and BFA, which are weak acids, the final solution was acidified to pH 3 with hydrochloric acid.

The addition of ethanol brought about a change in the content of the enol tautomer of BA in the solution; this was ascertained from the apparent extinction coefficient at 312 nm assigned to the enol tautomer of BA.[6] Accordingly, in the case of the experiment for BA, the ethanol content in the final solution was adjusted to 20% (vol) by the further addition of ethanol. The concentration of BA in the equilibrated solution was then calculated from the absorbance at 312 nm. The apparent extinction coefficient of BA at 312 nm in the solution with the ethanol content of 20% (vol) was thus found to be 6860±27 l mol$^{-1}$ cm$^{-1}$ at 25 °C. This value was not affected by the electrolytes below 0.1 mol l$^{-1}$.

On the other hand, the extinction coefficient of BFA at the maximum absorption wave length of 249.5 nm was not affected by ethanol at contents below 10% (vol). In the case of BFA, the ethanol content in the final solutions was below 1% (vol), and so the concentration of BFA was simply determined as has previously been described.[3] In the experiments at temperatures lower than room temperature for both BA and BFA, the addition of ethanol was not needed. Therefore, in these cases, too, the concentration of BA or BFA in the final sample solutions was measured as previously described.[2,3]

The solubilities of BA and BFA in terms of the mole number in the saturate solution (1000 g), $S$, were calculated from

$$S = \frac{C \times (1/V_{\text{dil}}) \times 25}{w_2 - w_1}, \tag{1}$$

where $C$, $V_{\text{dil}}$, and $w_2 - w_1$ denote the measured concentration of BA or BFA in the final sample solution (mol $l^{-1}$), the degree of dilution, and the weight of the saturated solution taken (g) respectively. The solubility measurements were made over the temperature ranges of 20 to 45 °C for BA and of 15 to 30 °C for BFA, and were made 4—8 times for the saturated solutions taken independently. The temperatures were kept at the desired temperatures within 0.2 °C.

*The Temperature Dependence of the Keto-Enol Tautomerism Constants of Benzoylacetone in Water and in 1.0 mol $l^{-1}$ Aqueous Electrolyte Solutions.* The keto-enol tautomerism constants of BA at all the temperatures where its solubility was measured were estimated from the temperature dpendence of the apparent extinction coefficients at 310 nm of BA in water and in 1.0 mol $l^{-1}$ aqueous electrolyte solutions.

The apparent extinction coefficients of BA in terms of the molarity at 310 nm in the respective solutions at 25 °C, which were measured in a previous work,[2)] were converted into values in terms of molarity, $\varepsilon_{(m)}$, from the densities of the water and the 1.0 mol $l^{-1}$ aqueous electrolyte solutions at 25 °C. The extinction coefficients for the enol tautomer, $\varepsilon_{(m)}$, were obtained from the above $\varepsilon_{(m)}$ and the enol contents estimated in the previous work.[2)] The values for $\varepsilon_{(m)}$ estimated were as follows: 15058±69 (kg $mol^{-1}$ $cm^{-1}$) in water (acidified to 0.001 mol $l^{-1}$ HCl solution); 14787±87 in 1.0 mol $l^{-1}$ HCl; 14276±140 in 1.0 mol $l^{-1}$ $HClO_4$; 14775±10 in 1.0 mol $l^{-1}$ NaCl, and 14458±91 in 1.0 mol $l^{-1}$ $NaClO_4$.

The apparent extinction coefficients, $\varepsilon_{(m)}$, of BA at each temperature except 25 °C were determined as has been described above. In these measurements, the standard solutions of BA were immersed for about 30 min in a water bath kept at the desired temperature within 0.1 °C before the absorbance measurements at 310 nm. It was confimed from a pre-experiment that the keto-enol tautomeric equilibrium of BA in an aqueous solution was attained within 10 min at a given temperature.

The keto-enol tautomerism constants of BA, $K_{aq}$, which were defined as the concentration ratios of the keto to the enol tautomers, were calculated by means of

$$K_{aq} = \frac{1-(\varepsilon_{(m)}/\varepsilon_{e(m)})}{\varepsilon_{(m)}/\varepsilon_{e(m)}}, \qquad (2)$$

where it was postulated that the values for $\varepsilon_{(m)}$ in the respective solutions were independent of the temperature.

*The Densities of 1.0 mol $l^{-1}$ Aqueous Electrolyte Solutions at 25 °C.* The densities of 1.0 mol $l^{-1}$ HCl, $HClO_4$, NaCl, KCl, NaBr, $BaCl_2$, and $Na_2SO_4$ solutions at 25 °C were obtained as follows. The densities of these aqueous electrolyte solutions at 25 °C have been listed in an earlier article as functions of the weight percent concentrations of these electrolytes.[7)] For the respective electrolyte solutions, the plots of $W \times d$ against $d$, where $W$ and $d$ denote the weight-percentage concentrations of the electrolytes and the densities of the electrolyte solutions with the concentrations of $W$ at 25 °C respectively, gave straight lines. Therefore the best-fit equations for these straight lines were obtained by the method of least squares. The densities of the above electrolyte solutions at 25 °C were calculated from the best-fit equations as has been described in the literature.[7)]

The densities of aqueous $NaClO_4$ solutions at 25 °C have not yet been reported. Therefore, the density of the 1.0 mol $l^{-1}$ $NaClO_4$ solution was measured with a pycnometer. The densities of the 1.0 mol $l^{-1}$ aqueous electrolyte solutions at 25 °C thus obatined were as follows: HCl, 1.0145 (g $ml^{-1}$); NaCl, 1.0368; KCl, 1.0426; $HClO_4$, 1.0455; NaBr, 1.0746; $NaClO_4$, 1.0754; $Na_2SO_4$, 1.1149; $BaCl_2$, 1.1741.

In the solubility experiments for the neutral electrolytes, the aqueous electrolyte solutions were acidified with HCl (0.001 M) to prevent the dissociation of BA and BFA. Therefore, contribution of added HCl to the densities of these solutions may be small enough to be neglected because of its low concentration.

## Results and Discussion

*The Thermodynamic Quantities of the Dissolution of Benzoylacetone and Benzoyltrifluoroacetone in Water.*

*(i) The Calculation of the Thermodynamic Quantities of the Dissolution in Water:* The solubilities obtained by Eq. 1 were convereted to the value in terms of molality by using the densities of the respective electrolyte solutions at 25 °C.

The solubilities in terms of molality at different temperatures, $S_{(m)}$, are listed in Table 1 for BA and in Table 2 for BFA. In these tables, the addition of such small amounts of acids as 0.001 M to prevent the dissociation of BA and BFA does not introduce any error into the solubility determination.[2,3)] The values quoted are the means of 4—8 independent experiments, and the deviations of the listed values denote mean errors;** in most cases, the relative mean errors did not exceed 0.6%.

In the case of BA, the solubilities tabulated in Table 1 are the apparent values for the mixtures of the enol and keto tautomers. The solubilities of the enol tau-

TABLE 1. TEMPERATURE DEPENDENCE OF THE SOLUBILITY OF BENZOYLACETONE IN WATER AND 1.0 mol $l^{-1}$ AQUEOUS ELECTROLYTE SOLUTIONS ($S_{(m)} \times 10^3$/mol $kg^{-1}$)

| Electrolyte | Temperature (°C) | | | | | |
|---|---|---|---|---|---|---|
| | 20 | 25 | 30 | 35 | 40 | 45 |
| Water[a)] | $1.89_6 \pm 0.01_2$ | $2.43_2 \pm 0.00_8$ | $3.13_7 \pm 0.00_9$ | $4.02_1 \pm 0.01_0$ | $5.13_8 \pm 0.00_3$ | $6.58_8 \pm 0.02_3$ |
| HCl | $2.04_3 \pm 0.00_5$ | $2.58_9 \pm 0.00_5$ | $3.28_7 \pm 0.01_0$ | $4.17_2 \pm 0.00_5$ | $5.32_4 \pm 0.01_6$ | $6.81^8 \pm 0.03_4$ |
| $HClO_4$ | $3.73_6 \pm 0.00_6$ | $4.68_1 \pm 0.00_9$ | $5.99_6 \pm 0.01_2$ | $7.67_4 \pm 0.03_6$ | $9.91_7 \pm 0.06_1$ | $12.8_3 \pm 0.0_5$ |
| NaCl[a)] | $1.33_1 \pm 0.00_5$ | $1.69_5 \pm 0.00_5$ | $2.12_9 \pm 0.00_3$ | $2.69_2 \pm 0.01_4$ | $3.50_1 \pm 0.02_2$ | $4.47_9 \pm 0.00_7$ |
| $NaClO_4$[b)] | $2.45_2 \pm 0.01_0$ | $3.12_1 \pm 0.00_1$ | $3.99_0 \pm 0.00_6$ | $5.12_9 \pm 0.01_9$ | $6.60_1 \pm 0.01_0$ | $8.52_9 \pm 0.01_1$ |

a) Contains $10^{-3}$ mol $l^{-1}$ HCl. b) Contains $10^{-3}$ mol $l^{-1}$ $HClO_4$.

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** The mean error, $a$, is given by

$$a = \frac{\sum_{i=1}^{n} |d_i|}{\sqrt{n(n-1)}},$$

where $n$ and $d$ indicate the times of measurement and the residue respectively.

Table 2. Temperature dependence of the solubility of benzoyltrifluoroacetone in water and 1.0 mol l$^{-1}$ aqueous electrolyte solutions ($S_{(m)}\times 10^3$/mol kg$^{-1}$)

| Electrolyte | Temperature (°C) | | | |
|---|---|---|---|---|
| | 15 | 20 | 25 | 30 |
| Water[a)] | $12.8_9\pm0.0_1$ | $13.6_7\pm0.0_2$ | $13.8_3\pm0.0_3$ | $14.1_2\pm0.0_3$ |
| $HClO_4$ | $14.7_0\pm0.1_3$ | $15.1_7\pm0.0_5$ | $15.7_3\pm0.0_1$ | $16.4_0\pm0.0_5$ |
| HCl | $10.6_2\pm0.0_2$ | $10.6_4\pm0.0_2$ | $10.8_7\pm0.0_4$ | $11.1_5\pm0.0_4$ |
| $NaClO_4$[a)] | $10.2_8\pm0.0_4$ | $10.6_8\pm0.0_3$ | $11.0_2\pm0.0_7$ | $11.4_1\pm0.0_2$ |
| KCl[a)] | | $8.92_3\pm0.02_8$ | $8.94_3\pm0.02_7$ | $9.19_7\pm0.03_1$ |
| NaBr[a)] | | $8.34_2\pm0.02_2$ | $8.44_5\pm0.01_2$ | $8.65_6\pm0.01_8$ |
| NaCl[a)] | $7.24_9\pm0.01_9$ | $7.28_0\pm0.02_1$ | $7.43_4\pm0.02_0$ | $7.66_1\pm0.02_6$ |
| $BaCl_2$[a)] | | $4.71_6\pm0.01_2$ | $4.73_4\pm0.00_6$ | $4.83_5\pm0.00_7$ |
| $Na_2SO_4$[a)] | | $2.86_9\pm0.00_9$ | $2.94_7\pm0.00_9$ | $3.07_0\pm0.00_4$ |

a) Contains $10^{-3}$ mol l$^{-1}$ HCl.

Table 3. Temperature dependence of the keto-enol tautomerism constant, $K_{aq}$,[a)] of benzoylacetone in water and 1.0 mol l$^{-1}$ aqueous electrolyte solutions

| Electrolyte | Temperature (°C) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 | 20 | 25 | 30 | 35 | 40 | 45 |
| Water[b)] | 1.70±0.01 | 1.80±0.01 | 1.93[d)] | 2.20±0.01 | 2.13±0.01 | 2.23±0.01 | 2.35±0.02 |
| HCl | | 1.92±0.01 | 2.07±0.02 | 2.13±0 | 2.23±0.01 | 2.35±0.01 | 2.45±0.02 |
| $HClO_4$ | | 2.08±0.02 | 2.20±0.04 | 2.27±0.02 | 2.38±0.02 | 2.47±0.01 | 2.57±0.01 |
| NaCl[b)] | | 2.16±0.02 | 2.32±0.01 | 2.38±0.02 | 2.50±0 | 2.61±0.01 | 2.72±0.01 |
| $NaClO_4$[c)] | | 2.32±0.01 | 2.45±0.02 | 2.54±0.01 | 2.65±0.01 | 2.75±0.01 | 2.87±0.01 |

a) Estimated from the apparent extinction coefficient of BA at 310 nm measured at the respective temperature and defined as the concentration ratio of the keto to the enol tautomers. b) Contains $10^{-3}$ mol l$^{-1}$ HCl. c) Contains $10^{-3}$ mol l$^{-1}$ $HClO_4$. d) Literature value (M. L. Eidinoff, *J. Am. Chem. Soc.*, **67**, 2073 (1945); M. Bergon and J. P. Calmon, *Bull. Soc. Chim. Fr.*, **1972**, 1020).

tomer, $S_{e(m)}$, and those of the keto tautomer. $S_{k(m)}$, were estimated by using the keto-enol tautomerism constants of BA listed in Table 3.[2)]

On the other hand, the solubilities of BFA tabulated in Table 2 can be regarded as those for the hydrate form of BFA previously reported.[3)] Accordingly, in the following discussion of BFA, only the hydrate form will be considered.

Generally, the temperature dependence of the solubility of a solid nonelectrolyte can be written by

$$\ln S_{(m)} = -\frac{\Delta H_{soln}}{RT} + \text{const}, \tag{3}$$

where $\Delta H_{soln}$ indicates the heat of solution. The plots of $\ln S_{(m)}$ against $1/T$ grounded on Eq. 3 gave straight lines, as is shown in Fig. 1(a) for the enol tautomer of BA, in Fig. 1(b) for the keto tautomer of BA, and in Fig. 2 for BFA. The heats of solution in water, $\Delta H^\circ_{soln}$, were obtained from the slopes of the straight lines for the solubilities in water by the least-squares method. The free energies of solution in water, $\Delta G^\circ_{soln}$, were calculated by means of

$$\Delta G^\circ_{soln} = -RT\ln X^\circ_{sat}, \tag{4}$$

where $X^\circ_{sat}$ represents the solubilities in water in terms of the mole fraction. The values for $\ln X^\circ_{sat}$ were calculated from $\ln S^\circ_{(s)}$ at 25 °C obtained from the above straight lines. The entropies of solution in water, $\Delta S^\circ_{soln}$, were calculated from $\Delta H^\circ_{soln}$ and $\Delta G^\circ_{soln}$. The activity coefficients of the enol and keto tautomers of BA, and of BFA in the saturated solutions are regarded as unity because of their quite low solubilities in water.[2,3)] These results are tabulated in Table 4.

Table 4. Thermodynamic quantities of the dissolution of benzoylacetone and benzoyltrifluoroacetone at 25 °C in water

| | $\Delta G^\circ_{soln}$[a)] cal mol$^{-1}$ | $\Delta H^\circ_{soln}$[b)] cal mol$^{-1}$ | $\Delta S^\circ_{soln}$[c)] cal mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| Benzoylacetone (enol from) | 6566±6 | 7913±5 | 4.5 |
| Benzoylacetone (keto form) | 6182±5 | 9840±4 | 12.2 |
| Benzoyltrifluoroacetone (hydrate form) | 4908±7 | 991±5 | −13.1 |

a) Calculated by $\Delta G^\circ_{soln} = -RT\ln X^\circ_{sat}$. b) Obtained from the slopes of the plots of $\ln S^\circ_{(m)}$ *vs.* $1/T$. c) $\Delta S^\circ_{soln} = (\Delta H^\circ_{soln} - \Delta G^\circ_{soln})/T$.

*(ii) A Comparison between the Thermodynamic Quantities of the Dissolution of Benzoylacetone and Those of Benzoyltrifluoroacetone*: It has been confirmed by X-ray crystallography that BA exists in the enol form in the crystal.[8)] Accordingly, it may be concluded that the thermodynamic quantities of the dissolution for the keto tautomer of BA are summations of those for the enol tautomer and the thermodynamic quantities of the ketonization in the saturated solution of BA.

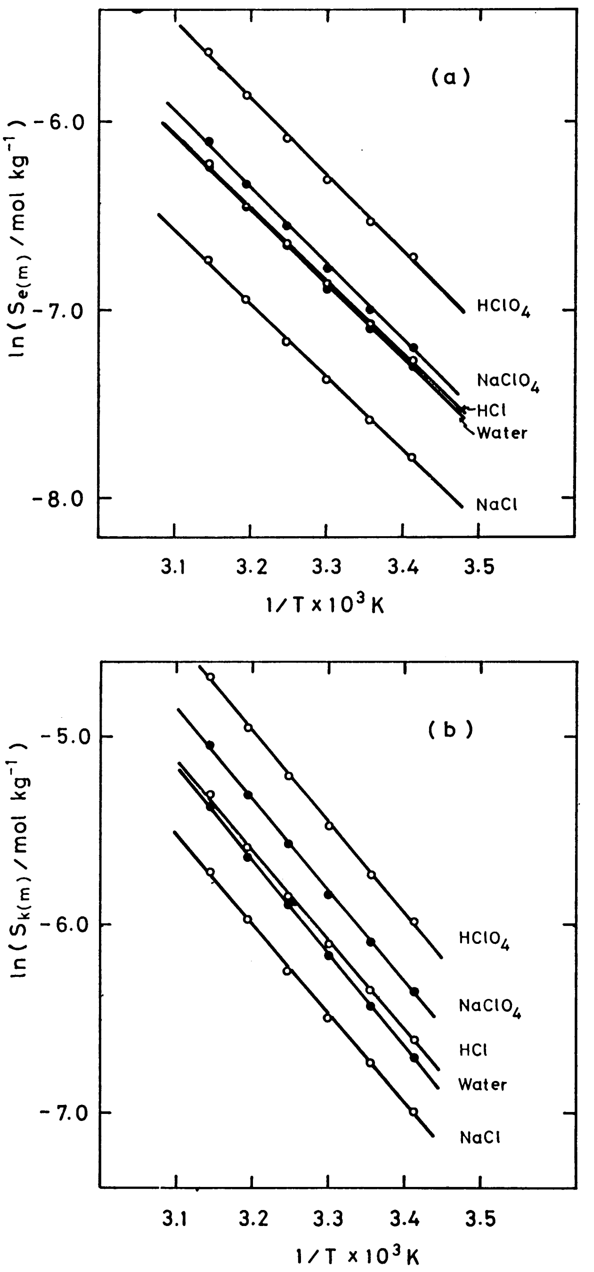

Fig. 1. Plot of ln $S_{(m)}$ *vs.* $1/T$ for the solubilities of the respective tautomers of benzoylacetone in water and 1.0 mol l$^{-1}$ aqueous electrolyte solutions.
Straight lines are drawn by method of least squares.
(a) For the enol tautomer,
(b) for the keto tautomer.

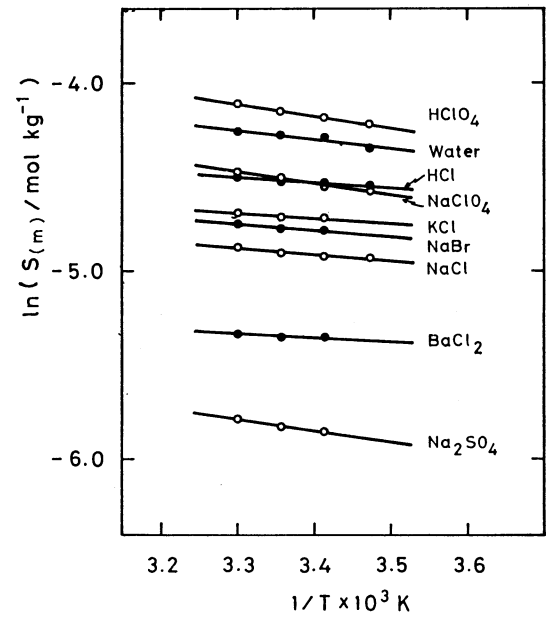

Fig. 2. Plot of ln $S_{(m)}$ *vs.* $1/T$ for the solubilities of the hydrate form of benzoyltrifluoroacetone in water and 1.0 mol l$^{-1}$ aqueous electrolyte solutions.
Straight lines are drawn by method of least squares.

Therefore, in the case of BA, the values for the enol tautomer ought to be discussed.

On the other hand, the reaction of 2-thenoyltrifluoroacetone (TTA) with water yields the crystal of its hydrate form.[9] Similarly, the solid phase of BFA equilibrated with its saturated solution seems to take the hydrate form. Thus, the solution equilibrium of BFA in the saturated solution may be established between the hydrate form in the aqueous phase and that in the solid phase. Therefore, the thermodynamic quantities of the dissolution of BFA do not involve the thermodynamic quantities of the hydrate formation.

The thermodynamic quantities of the dissolution of BFA in water are much smaller than those of BA. The smaller enthalpy of solution for BFA contributes to its smaller free energy of solution, and this results in its larger solubility in water. These results may be explained as follows, by assuming nearly identical volatilities for BA and BFA.[10] In water, the hydrophilic groups, such as the carbonyl and hydroxyl groups, can interact with water molecules through the electrostatic force and the hydrogen bond. On the other hand, the hydrophobic groups such as the alkyl group cause the formation of an "iceberg" structure of the water around them (hydrophobic hydration).[11] Our previous study suggests that the two hydroxyl groups and trifluoromethyl group in the hydrate form of BFA may behave as the hydrophobic groups rather than as the hydrophilic groups in its aqueous solution.[3] Thus, the higher hydrophobic hydration for BFA may cause a greater decrease in both the enthalpy and the entropy.

The above results give a useful suggestion regarding the dissolution behavior of metal chelates of BA and BFA in water. In these chelates, the hydrophilic parts in BA and BFA—that is, both the carbonyl group and the hydroxyl group—combine with the central metal ions, while the hydrophobic parts in BA and BFA mainly came in contact with water molecules in their aqueous solutions. This suggests that the hydrophobic hydration for their metal chelates may be higher than that for BA and BFA. This hydrophobic hydration of their chelates may contribute considerably to their thermodynamic quantities upon dissolution in water and a non-polar organic solvent.

*The Thermodynamic Quantities of the Ketonization of Benzoylacetone in Water.* The heat of ketoni-

TABLE 5. THERMODYNAMIC QUANTITIES OF THE KETONIZATION OF BENZOYLACETONE AND ACETYLACETONE AT 25 °C IN WATER

| | $\Delta G^\circ_T$ a) kcal mol$^{-1}$ | $\Delta H^\circ_T$ b) kcal mol$^{-1}$ | $\Delta S^\circ_T$ c) cal mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| Benzoyl- acetone | $-0.383\pm0.003$ | $1.947\pm0.002$ | 7.8 |
| Acetyl- | $-0.9$ | 1.5 | 8 |

a) Calculated by $\Delta G^\circ_T = -RT\ln K^\circ_{aq}$. b) Obtained from the slope of the plot of $\ln K^\circ_{aq}$ *vs.* $1/T$. c) $\Delta S^\circ_T = (\Delta H^\circ_T - \Delta G^\circ_T)/T$. d) Literature values (Ref. 12).

TABLE 6. THERMODYNAMIC QUANTITIES OF THE TRANSFER OF BENZOYLTRIFLUOROACETONE FROM WATER TO 1.0 mol l$^{-1}$ AQUEOUS ELECTROLYTE SOLUTIONS AT 25 °C

| Electrolyte | $\Delta G_{tr}$ a) cal mol$^{-1}$ | $\Delta H_{tr}$ b) cal mol$^{-1}$ | $T\Delta S_{tr}$ c) cal mol$^{-1}$ |
|---|---|---|---|
| $HClO_4$ | $-67$ | 270 | 337 |
| $NaClO_4$ | 144 | 202 | 58 |
| HCl | 150 | $-413$ | $-563$ |
| KCl | 263 | $-462$ | $-725$ |
| NaBr | 300 | $-343$ | $-643$ |
| NaCl | 374 | $-347$ | $-721$ |
| $BaCl_2$ | 641 | $-553$ | $-1194$ |
| $Na_2SO_4$ | 922 | 197 | $-725$ |

a) Calculated by $\Delta G_{tr} = RT\ln(X^\circ_{sat}/X_{sat})$. b) $\Delta H_{tr} = \Delta H_{soln} - \Delta H^\circ_{soln}$. c) $T\Delta S_{tr} = \Delta H_{tr} - \Delta G_{tr}$.

TABLE 7. THERMODYNAMIC QUANTITIES OF THE TRANSFER OF BENZOYLACETONE FROM WATER TO 1.0 mol l$^{-1}$ AQUEOUS ELECTROLYTE SOLUTIONS AT 25 °C

| Electrolyte | $\Delta G_{tr}$ a) cal mol$^{-1}$ | $\Delta H_{tr}$ b) cal mol$^{-1}$ | $T\Delta S_{tr}$ c) cal mol$^{-1}$ |
|---|---|---|---|
| | | Enol form | |
| $HClO_4$ | $-327$ | 189 | 516 |
| $NaClO_4$ | $-39$ | 202 | 241 |
| HCl | $-1$ | $-202$ | $-201$ |
| NaCl | 299 | $-128$ | $-427$ |
| | | Keto from | |
| $HClO_4$ | $-405$ | $-209$ | 196 |
| $NaClO_4$ | $-181$ | $-194$ | $-13$ |
| HCl | $-38$ | $-397$ | $-359$ |
| NaCl | 195 | $-410$ | $-605$ |

a) Calculated by $\Delta G_{tr} = RT\ln(X^\circ_{sat}/X_{sat})$. b) $\Delta H_{tr} = \Delta H_{soln} - \Delta H^\circ_{soln}$. c) $T\Delta S_{tr} = \Delta H_{tr} - \Delta G_{tr}$.

zation of BA in water, $\Delta H^\circ_T$, was obtained from the plot of $\ln K^\circ_{aq}$ against $1/T$. $K^\circ_{aq}$ is the keto-enol tautomerism constant of BA in water. This plot gave a good straight line. The free energy, $\Delta G^\circ_T$, and the entropy of ketonization, $\Delta S^\circ_T$, were obtained in the ordinary manners. These results are listed in Table 5, along with the literature values[12] for those of acetylacetone (AA).

The entropies of ketonization for BA and AA are nearly identical, but the heat of ketonization of BA is larger than that of AA. It is this that mainly contributes to the smaller negative free energy of the ketonization of the former, that is to the higher enol content of the former in water. The difference in the heats of ketonization of BA and AA may be attributed mainly to a difference in the enthalpies of the enol tautomer of BA and AA; that is, the enthalpy of the enol tautomer of BA is lowered due to the resonance energy between the phenyl group and the enol ring.

*The Thermodynamic Quantities of the Transfer of Benzoylacetone and Benzoyltrifluoroacetone from Water to 1.0 mol $l^{-1}$ Aqueous Electrolyte Solutions.* The free energies, $\Delta G_{tr}$, and the enthalpies, $\Delta H_{tr}$, of the transfer of one mole of BA or BFA from water to 1.0 mol l$^{-1}$ aqueous electrolyte solutions at hypothetically identical solute concentrations were obtained by means of the following equations:[5)]

$$\Delta G_{tr} = RT\ln(X^\circ_{sat}/X_{sat}), \tag{5}$$

$$\Delta H_{tr} = \Delta H_{soln} - \Delta H^\circ_{soln}. \tag{6}$$

In Eq. 5, $X_{sat}$ indicates the solubilities in a mole fraction of BA or BFA in the 1.0 mol l$^{-1}$ aqueous electrolyte solutions at 25 °C. The values for $\ln X_{sat}$ were calculated from $\ln S_{(m)}$ at 25 °C obtained from the best-fit equations for the plots shown in Figs. 1 and 2. The values for $\Delta H_{soln}$ in Eq. 6, which indicates the heats of solution in the aqueous electrolyte solutions, were also calculated from the slopes of the above best-fit equations. The entropies of transfer, $\Delta S_{tr}$, were calculated from $\Delta H_{tr}$ and $\Delta G_{tr}$. These results are listed in Table 6 for the hydrate form of BFA and in Table 7 for the enol and keto tautomers of BA.

Very few inorganic electrolytes are known to exhibit a so-called "salting-in" effect on non-polar nonelectrolytes. Table 6 shows that the thermodynamic quantities of the transfer of BFA to the aqueous perchloric acid solution show a characteristic feature in comparison with those to the other electrolyte solutions studied. That is, though the enthalpy of transfer to the perchloric acid solution is positive, the positive entropy contributes to the negative free energy, which results in the salting-in effect.

The salt effect of tetraalkylammonium salts has been quite well studied,[13–17)] and both the enthalpies and the entropies of transfer of various nonelectrolytes from water to the aqueous solutions of these ammonium salts have been found to be positive.[17,18)] These results have been interpreted in terms of a so-called "hydrophobic interaction" between the nonelectrolyte solutes and the tetraalkylammonium cations.[17,19)]

The positive enthalpy and entropy of transfer of BFA to the aqueous perchloric acid solution may also be interpreted in a similar way as follows. The perchlorate anion destroys the iceberg structure of water,[20)] which may bring about the hydrophobic interaction with BFA, and this interaction in turn weakens the hydrophobic hydration for BFA. Thus, the decrease in the enthalpy and entropy of BFA through the hydrophobic hydration in the perchloric acid solution becomes smaller than that in water. This argument on the role of the perchlorate anion may offer a possible explanation of the well-known phenomenon that the perchlorate anion is markedly extracted into organic solvents as ion pairs with large hydrophobic cations.[21)]

For the transfer of BFA to the sodium sulfate solution, a negative entropy and a positive enthalpy are observed. This results in the largest positive free energy among the electrolytes studied. Both the enthalpies and the entropies of transfer to all the other electrolyte solutions, except for $HClO_4$, $NaClO_4$, and $Na_2SO_4$, are negative. Moreover, the larger negative entropies bring about positive free energies of transfer. However, it is very difficult at present to interpret the above results thoroughly.

The thermodynamic quantities of the transfer for the enol tautomer of BA in Table 7 show the same tendency as those for BFA. For all the electrolytes studied, the thermodynamic quantities of the transfer for the keto tautomer of BA are smaller than those for its enol tautomer. Probably these results may be ascribed to the stronger interaction between the more polar keto tautomer and its surroundings, such as water molecules and the electrolytes.

Very few papers on the salt effect in the solvent extraction of metal chelates have referred to the thermodynamic quantities. To clarify the very complicated salt in the solvent extraction of metal chelates, we consider the overall salt effect by dividing it into two stages, that is, the salt effect in chelate formation in the aqueous phase and that in the distribution of the metal chelates between aqueous and organic phases. In the former stage, the chemical reactions of metal ions with salt components must be taken into account; for example, the coordination of such anions as chloride and bromide ions to metal ions[22,24)] and ion-pair formation between charged metal chelates and counter ions such as perchlorate anions[23,24)] *etc.* Thus, the salt effect in this stage is very particular, and so it seems to be difficult to generalize about it. On the other hand, in the latter stage, the metal chelates distributed may be regarded as nonelectrolytes. Accordingly, the salt effect in this stage may described by analogy from the present results for the chelating agents. Thus, the present study gives useful suggestions for the generalized interpretation of the salt effect in the distribution of metal chelate compounds in the solvent extraction.

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