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Distribution of Thenoyltrifluoroacetone and Its Scandium Chelate in Ketone Solvent System

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The distribution equilibria of thenoyltrifluoroacetone (TTA) and its scandium chelate between aqueous solutions with an ionic strength of 0.1 and ketones at 25°C have been studied. The distribution of TTA was correlated with the solubility parameters of the ketones and the correlation between the distribution coefficients of TTA and those of scandium chelate was confirmed. The characteristic properties of ketones were discussed in comparison with those of other oxygen containing solvents.

The excellent properties of methyl-isobutyl ketone (hexone) as a solvent for solvent extraction, not only in ion association systems but also in chelate systems, have been shown by many authors. However, few systematic studies on ketone solvents are to be found.

In order to clarify the relation between some physico-chemical properties of solvents and the distribution coefficients of extractable species, the authors studied the partition equilibria of some β-diketones and those of scandium chelate in some solvent systems; *i.e.*, so called inert solvents,[1-3] alcohol solvents[4,5] and ester solvents.[6] As a further example, the distribution of oxine in inert solvent systems was also studied.[7] It was shown that solubility parametr theory provides a useful approach to the problem, and that the solubility parameters of solvents are more important factors than other parameters such as dielectric constants and dipole moments, which have often been used to explain the role of solvents, in the case where the specific interaction between solute and solvent is not significant.

The present authors will detemine the distribution coefficients of TTA and its scandium chelate in ketone solvent systems, demonstrate the relation between the distribution coefficients and the solubility parameters of the solvents and discuss the characteristic properties of ketone solvents in comparison with other solvents.

Experimental

Materials. Thenoyltrifluoroacetone was obtained from Dojindo Co., Ltd., and was purified by sublimation. Solvents were purified by distillation. Other chemicals were all GR grade. Scandium-46, obtained from the New England Nuclear Corp. (USA) as chloride in a hydrochloric acid solution, was used as a tracer after substituting perchlorate in a perchloric acid solution. The carrier solution of scandium was prepared from scandium oxide of 99.9% purity.

Determination of Distribution Ratio of TTA. A volume 5 m*l* of a ketone solution containing a known amount of TTA was equilibrated by shaking with an equal volume of aqueous solution with an ionic strength of 0.1 adjusted with sodium perchlorate and perchloric acid in an air thermostat at 25 °C. To minimize the error accompanied by volume

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[1] T. Wakabayashi, T. Omori, S. Oki and N. Suzuki, *J. Inorg. Nucl. Chem.*, **26**, 2255 (1964).

[2] T. Omori, T. Wakabayashi, S. Oki and N. Suzuki, *ibid.*, **26**, 2265 (1964).

[3] S. Oki, T. Omori, T. Wakabayashi and N. Suzuki, *ibid.*, **27**, 1141 (1965).

[4] N. Suzuki, K. Akiba, T. Kanno and T. Wakabayashi, to be published.

[5] N. Suzuki, K. Akiba, T. Kanno, T. Wakabayashi and K. Takaizumi, to be published.

[6] N. Suzuki, K. Akiba and T. Kanno, to be published.

[7] T. Wakabayashi, This Bulletin, **40**, 2836 (1967).

change due to the mutual solubility, both phases were pre-saturated with each other previous to preparing the TTA solution. After centrifuging, the concentration of TTA in the aqueous phase was determined photometrically; an aliquot of the solution was transferred to a constant volume of 0.6 M phosphate buffer of about pH 6.5 and then the absorbance at 337 mμ resulting from the enolate ion of TTA was measured against a blank run at 25°C. It was confirmed by the preliminary experiment that under the conditions the optical density of the solution closely obeys Beer's law. The distribution ratios thus obtained in a pH region below 4 are equal to the distribution coefficients with an error of less than 1 per cent, as previously shown.[1]

Measurement of Absorption Spectra of TTA in Ketone Phase. The spectra of TTA in ketone phases equilibrated with aqueous phase were measured with a Hitachi EPS-3 recording spectrophotometer using a thin layer cell in order to cancel out strong absorption by the solvent in the UV region.

Determination of Enol Content in Ketone Phase. To determine the enol content of TTA, defined as the ratio of the concentration of enol form to the total concentration of TTA in organic phase, the NMR spectrum was measured with a Varian A-60 NMR Spectrometer. The concentration of TTA was about 0.5 M in all solvents. The enol content was determined from the area ratio of the spectrum for the vinyl type protons to that for protons in the thiophen ring.

Determination of Distribution Ratio of Sc. The procedure and experimental conditions were almost the same as TTA. After two phases were separated, γ-activities of each phase were measured by a well-type scintillation counter. The carrier concentration was 10^{-6} M throughout the experiment, except in the case of examining the influence of carrier concentration on the distribution ratio of scandium.

For almost all ketones, complete equilibrium was attained in several hours in a normal extaction; however, a shorter time of 2 hr was required in the back extraction. To confirm the equilibrium, the normal and back extractions were carried out for all solvents. In the case of back extraction, the concentration of TTA in the aqueous phase was determined in the manner described above. The pH of the aqueous phase at equilibrium was measured with a glass electrode pH meter. Although it should be taken into account that the the pH value obtained above for the aqueous solution containing organic solvent is only an apparent one, the value was adopted without any correction because the solubilities of the solvents in water are of the order of a per cent or less.

Results and Discussion

Distribution of TTA. As shown in Fig. 1, TTA is in a keto-enol equilibrium in the ketone phase, while in inert solvents it exists almost completely as the enol form. Taking into account the spectrum of the aqueous solution below pH 4, the peaks at 266 mμ and 292 mμ may be attributed to the ketohybrate.[8] In the case of petanone, the absorption due to the enol form near 320 mμ does not appear as a peak, while in the case of diisobutylketone containing more carbon atoms, the peak at 320 mμ is clearly seen. It was shown that the spectra are independent of hydrogen ion concentration over the pH range 1—4. In a pH region higher then 5, the absorption at 340 mμ in the organic phase increases with pH in the aqueous phase, which corresponds to the absorption at 337 mμ due to the enolate ion in the aqueous phase. At a higher temperature, the peak at 340 mμ becomes stronger.

TABLE 1. DISTRIBUTION RATIOS OF TTA AND ITS SCANDIUM(III) CHELATE IN KETONE-WATER SYSTEMS, 25°C, IONIC STRENGTH, 0.1 ($HClO_4+NaClO_4$)

No	Solvent	δ[a]	δ[b]	$\log D_{HA}$	$\log D_M$ ($pA=8.0$)	r_e
1	Butanone	9.3	9.0	1.37	−2.10[c]	0.18
2	2-Pentanone		8.6_9	2.31	0.31	0.33
3	3-Pentanone	8.8	8.7_6	2.30	0.40	0.32
4	4-Methyl-2-pentanone	8.4	8.3_0	2.30	0,50	0.42
5	Cyclohexanone	9.9	10.0	2.30	0.50	0.23
6	5-Methyl-2-hexanone		8.3_8	2.26	0.25	0.44
7	2-Heptanone		8.4_4	2.28	0.22	0.43
8	3-Heptanone		8.4_4	2.18	0.16	0.50
9	4-Heptanone		8.3_4	2.16	−0.17	0.52
10	5-Methyl-3-heptanone		8.1_7	2.06	−0.40	0.59
11	2,6-Dimethyl-4-heptanone	7.8	7.8_0	1.90	−0.62	0.62
12	2-Octanone		8.3_8	2.20	0.66	0.46
13	2-Nonanone		8.2_6	2.03	−0.23	0.55

a) Found in literature (10).
b) Estimated value by Hildebrand rule.
c) Corrected value considering the contribution of ion associated complex.

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8) E. L. King and W. H. Reas, *J. Am. Chem. Soc.*, **73**, 1806 (1950).

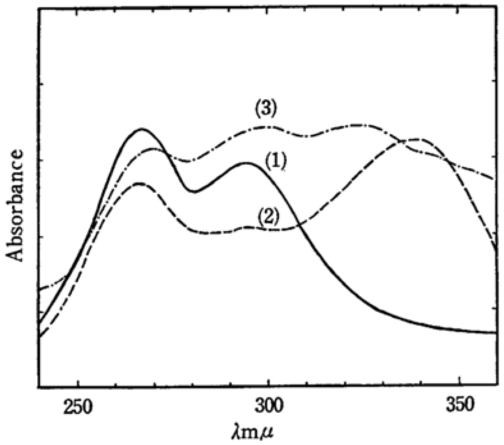

Fig. 1. Absorption spectra of TTA in ketone phase.
(1) 2-Pentanone (below pH 4 in aqueous phase)
(2) 2-Pentanone (pH 7 in aqueous phase)
(3) Diisobutylketone (below pH 4 in aqueous phase)

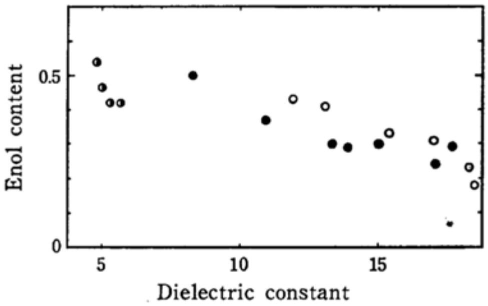

Fig. 2. Enol content of TTA in oxygen containing solvents equilibrated with aqueous solution with pH 2 as a function of dielectric constant of solvent.

● Alcohol, ○ Ketone, ◑ Ester

These facts are common to all the ketones examined. It is, therefore, thought that in the ketone phases, TTA is found as an enolate ion or a sodium salt in a higher pH region.

In the last column of Table 1, the enol contents, r_e, in ketone phases equilibrated with the aqueous phase in a pH range below 4 are summarized. In Fig. 2, the enol contents in oxygen containing solvents under the same conditions are plotted as a function of the dielectric constant of the solvent, though the dielectric constant for the solvent saturated with water should be referred to in order to discuss the influence of dielectric constant on the keto-enol equilibrium. On the whole, there is a trend that the enol content increases with the dielectric constant of solvent.

The distribution ratios of TTA for ketone solvents are shown in Table 1. These values are larger, on the whole, by two or three times than those found in the case of inert solvents, and it is true also in the case of esters.[6] The reason why the distribution coefficients of TTA in the former are larger than those in the latter is understood by considering the fact that in the inert solvents the enol form is almost the only species in the organic phases, while in the case of oxygen containing solvents the enol form is rather a minor species and it is in equilibrium with the keto-hydrate. In alcohol solvents,[4] the distribution ratios are comparable to values in the inert solvents in spite of the similar circumstances to other oxygen containing solvents with respect to the keto-enol equilibrium in the organic phase. In this case, the effect of hydrogen bonding among the solvent molecules should be considered; that is, it may act as if the mole fraction of the solvent were reduced.

As previously reported,[1] the following equation is derived for the distribution coefficient of the enol form of TTA defined as the ratio of the mole fractions in the two phases, P_e,

$$\frac{\log P_e}{\delta_{\mathrm{aq}}-\delta_{\mathrm{solv}}}=\frac{V_e}{2.30\,RT}(\delta_{\mathrm{aq}}+\delta_{\mathrm{solv}}-2\delta_e) \qquad (1)$$

were δ stands for the solubility parameter for the species corresponding to the subscript. Solubility parameters for some ketones have not been reported. It is possible, however, to estimate the values from the boiling point of the solvent according to the Hildebrand rule.[9] In Table 1, the estimated parameters are listed together with the values found in the literature.[10] In order to apply Eq. (1), it is required to know the distribution coefficients of the enol form. The following relation is established between the distribution coefficient of the enol form and that of the overall forms, D_{HA},

$$P_e=D_e\frac{V_{\mathrm{solv}}}{V_{\mathrm{H_2O}}} \quad \text{and} \quad D_e=r_e\frac{K_e}{K_a}D_{\mathrm{HA}} \qquad (2)$$

where K_e, K_a and D_e stand for the dissociation constant of enol, the apparent dissociation constant of TTA and the distribution coefficient of enol form TTA in terms of molarity, respectively. The enol contents of Table 1 are regarded as approximate ones for the present purpose because the values are for a 0.5 M TTA solution, and the values

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[9] J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1962).

[10] J. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," John Wiley and Sons Corp., New York (1957).

required are for more dilute solutions of the order of 10^{-2} M, and because there is considerable error in estimating the areas of NMR spectra. However, since no more accurate data are available, the distribution coefficients for the enol form were estimated using the enol contents of Table 1. An attempt to determine the enol ratios more accurately is now undertaken.

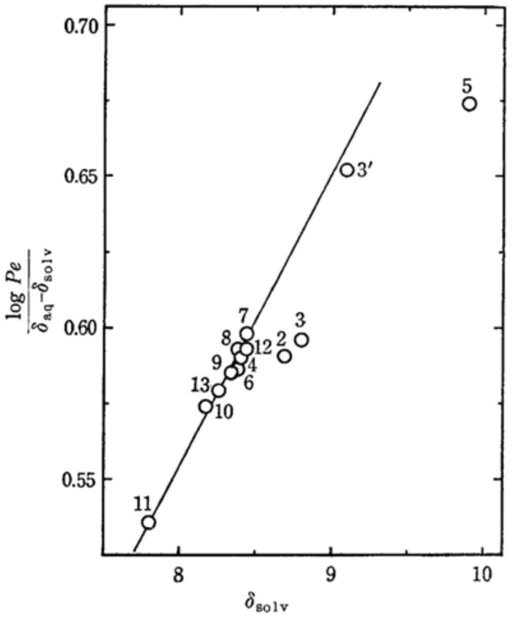

Fig. 3. A relation between distribution coefficients of TTA and solubility parameters of solvents. Numbers refer to Table 1. 3′ is a corrected value of 3 by Eq. (3).

Since the solubility parameters for aqueous solution and for enol in Eq. (1) are considered constant in all present systems, there should be a linear relation between the left-hand side of the equation and the solubility parameters of the solvents, provided that the equation is valid in the present systems. The result is shown in Fig. 3. For some solvents, such as pentanones, cyclohexanone and butanone, are found considerable deviations from the straight line. The fact may be ascribed to the considerable mutual solubility of water and the solvents. If there are data available on the mutual solubility, it may be possible to correct the solubility parameters for the solvents with the following equation, as is the case of 3-pentanone;

$$\bar{\delta}_{solv} = \phi_{solv}\delta_{solv} + \phi_{H_2O}\delta_{H_2O} \qquad (3)$$

where $\bar{\delta}_{solv}$ and ϕ denote the corrected parameter and the volume fraction of each component in the organic phase, respectively. As the solubility parameter for water, the value of 16.3_5 which was obtained previously[1] was used also in the present work. The applicability of Eq. (1) is examined further by the slope of the line which should be related to the molar volume of the reagent. The slope of the line corresponds to a volume of near 140 cc, which is about 10 per cent less than in the previous case.

The reason that the application of the solubility parameter theory is approximately possible even in the present systems may be ascribed to the circumstance that the dispersion effect is dominant among the effects contributing to the cohesive energy, even in polar solvents such as ketones.[11]

Distribution of Scandium. As previously described,[2] the distribution of Sc(III) can be expressed as

$$D_M = \frac{D_{M,0}K_{i=3}[A^-]_{aq}^3\{1+\Sigma K_j[HA]_{org}^j\}}{1+\Sigma K_i[A^-]_{aq}^i}$$

and

$$pA = -\log[A^-]_{aq} = pK_a - pH - \log[HA]_{aq},$$

where K_i is the overall formation constant for $ScA_i^{+(3-i)}$, K_j the overall formation con-

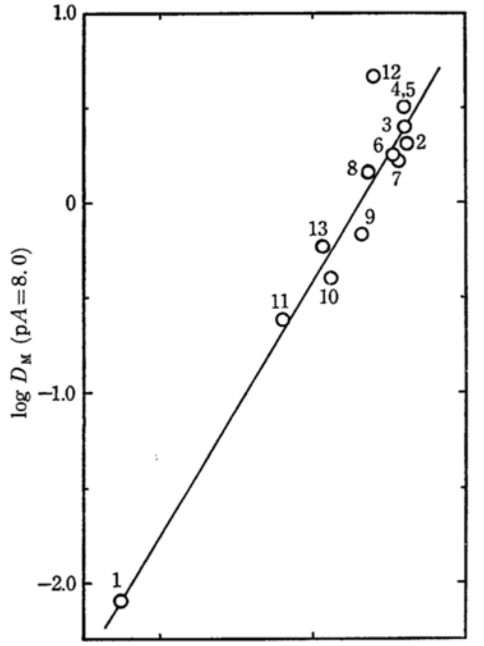

Fig. 4. A correlation between distribution ratios of TTA and those of its scandium chelate in ketone solvent systems.
Numbers refer to Table 1.

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[11] E. F. Meyer and R. F. Wagner, *J. Phys. Chem.*, **70**, 3162 (1966).

stant corresponding to additive compound formation in the organic phase and $[HA]_{aq}$ the total concentration of the reagent in the aqueous phase determined photometrically. For all ketones, the plotting of $\log D_M$ against pA 8. Considering the fact that, so long as the plotting was carried out against pA, the distribution curves for Sc(III) were common to the various runs under different conditions with respect to the concentration of TTA in the organic phase and pH, it is concluded that the extractable species is of the type ScA_3 alone, except in the case of 2-butanone, in which the ion associated complex with perchlorate ion was extracted. In Table 1, the distribution ratios of scandium at a constant pA of 8.0, which are proportional to the distribution coefficients in each solvent, are summarized.

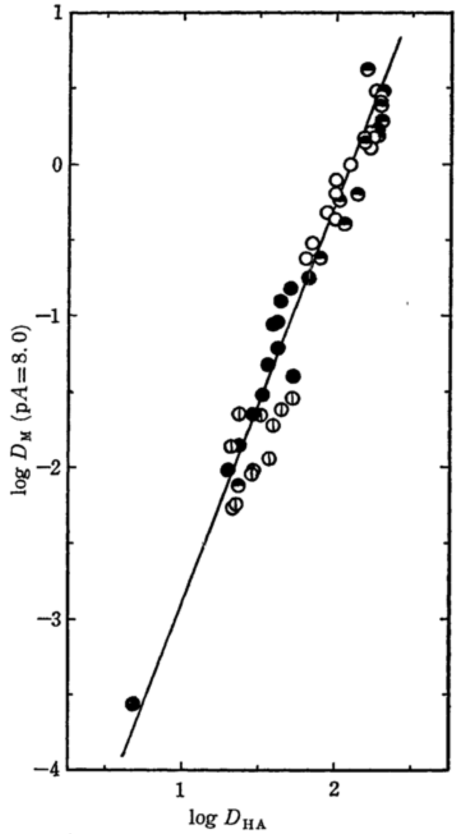

Fig. 5. A correlation between distribution ratios of TTA and those of its scandium chelate in various solvent systems.

● Inert solvent ◓ Ketone
⦶ Alcohol ○ Ester

There is a distinct correlation between the distribution coefficients of the reagents and those of the chelate, as shown in Fig. 4. In Fig. 5, all of the data obtained until now are plotted similarly. Through all of the solvents, a common straight line can be drawn. Although the relation may be ascribed to the similarity, as already discussed,[2,3] of the interactions with solvent molecules in both cases of free TTA and of that bound to scandium, it should be noted that the abscissae in Figs. 4 and 5 express not the distribution coefficients for the enol form but the overall ones. It cannot be asserted that the enol form should be preferable to the other form of TTA in describing the relation, for the relation is only an approximate one and is not so strict that the difference in interactions between the two forms of TTA and solvent molecules can be considered.