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STUDIES ON ION-SOLVENT INTERACTIONS III. NOTE ON THE COMPLEX FORMATION OF SILVER AND SODIUM IONS IN ACETYLACETONE WITH OTHER SOLVENTS

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Abstract : The complex formation constants of silver and sodium ions in acetylacetone with other solvents have been determined potentiometrically at 25°C. The solvent effect on the complex formation was discussed in connection with the donor number of solvents.

INTRODUCTION

Acetylacetone (2, 4-pentanedione, Hacac) is one of β-diketones and has widely been used as a chelating reagent. As a solvent, it is a protic and less basic solvent with a relatively high dielectric constant (27.2), and most of the 1-1 electrolytes in Hacac are fairly well dissociated.

The authors have studied the dissociation equilibria of 1-1 electrolytes (tetraalkylammonium and alkali metal salts, and some weak acids such as *p*-toluenesulfonic and methanesulfonic acids) in Hacac by conductometry and potentiometry, and reported the results as follows[1-4].

(1) The ion association constants (K_A) of alkali metal salts in Hacac decrease as well as in acetone with increasing crystallographic radii of cations, while in acetonitrile (AN) and alcohols the K_A values increase with increasing cation sizes. The solvating ability of Hacac towards cations, that is, the basicity of Hacac is weaker than that af AN and alcohols.

(2) The anion dependence of the K_A values of tetraalkylammonium halides and the limiting molar conductivities of halide ions in Hacac is similar to that in alcohols which can interact effectively with anions through hydrogen bonding. This anion dependence in Hacac is in contrast with that in acetone, and indicates the hydrogen bonding ability of Hacac based on the enol form of the solvent.

(3) The homoconjugation constants in Hacac, however, are nearly equal to those in aprotic solvents such as AN and propylene carbonate. The intramolecular hydrogen bonding in the enol form of Hacac appreciablly reduces the solvating ability towards anions, that is, the acidity of the solvent as well as the basicity. Consequently, the acidity of

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Hacac is not so strong as to stabilize anions by hydrogen bonding to a great extent.

In this note is reported the complex formation of silver and sodium ions in Hacac with such solvents as AN, acetone, water, methanol(MeOH), ethanol(EtOH), dimethylformamide(DMF), dimethylacetamide(DMA) and dimethylsulfoxide(DMSO), and is discussed the solvent effect on the complexing.

RESULTS AND DISCUSSION

Potentiometric determination of the complex formation constants

The emf of the following cell (1) was measured at 25°C for the complexing of silver ion, with a digital potentiometer (Orion Research model 701A), to ±0.1 mV. In the cell (1),

$$\begin{array}{c|c||c||c|c}
\mathrm{Ag} & 0.01\ \mathrm{mol\ dm^{-3}} & 0.1\ \mathrm{mol\ dm^{-3}} & 0.001\ \mathrm{mol\ dm^{-3}} & \mathrm{Ag} \quad (1) \\
 & \mathrm{AgClO_4} & \mathrm{Bu_4NClO_4} & \mathrm{AgClO_4} & \\
\end{array}$$

(Hacac) (Hacac) (Hacac+S)

[reference electrode] [salt bridge] [test solution] [indicator electrode]

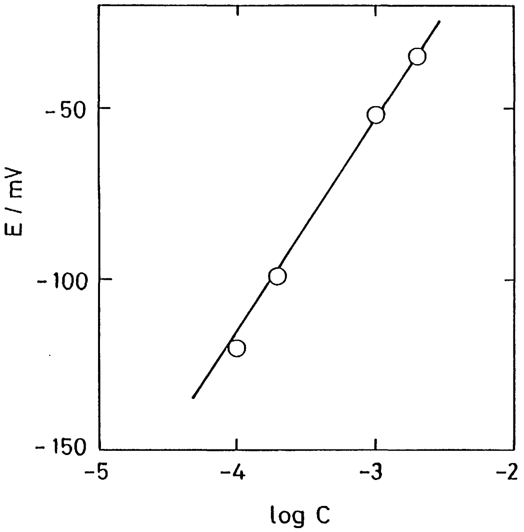

Fig. 1 Relation between the potentials of silver wire electrode (E) and log C in acetylacetone

$$\begin{array}{c|c||c||c|c}
\mathrm{Ag} & 0.01\ \mathrm{mol\ dm^{-3}} & 0.1\ \mathrm{mol\ dm^{-3}} & \mathrm{Sample} & \mathrm{Ag} \\
 & \mathrm{AgClO_4} & \mathrm{Bu_4NClO_4} & & \\
\end{array}$$

Sample ; $C=10^{-4}\sim 2\times 10^{-3}$ mol dm^{-3} $AgClO_4$, Slope ; 62 mV.

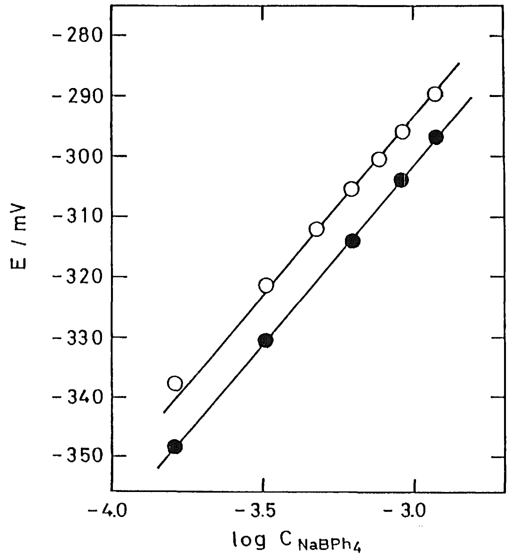

Fig. 2 Relation between the potentials of sodium ion sensitive glass electrode (E) and log C in acetylacetone

$$\begin{array}{c|c||c||c|c}
\mathrm{Ag} & 0.01\ \mathrm{mol\ dm^{-3}} & 0.1\ \mathrm{mol\ dm^{-3}} & \mathrm{C\ mol\ dm^{-3}} & \mathrm{Na^+\text{-}glass} \\
 & \mathrm{AgClO_4} & \mathrm{Et_4NPic} & \mathrm{NaBPh_4} & \mathrm{electrode} \\
\end{array}$$

(○) ; without supporting electrolyte,
(●) ; with 0.01 mol dm^{-3} Bu_4NClO_4,
Pic ; picrate, BPh_4 ; tetraphenylborate
slope ; 59 mV.

S denotes a solvent added little by little to the test solution. The liquid junction potential between the salt bridge and the test solution was assumed to be constant upon the addition of a solvent S. For the complexing of sodium ion, a sodium ion sensitive glass electrode (Orion Research model 97-11) was used as the indicator. The Nernstian response of the Ag wire electrode and the Na^+ ion sensitive glass electrode to each ion is shown in Figs. 1 and 2.

The complex formation equilibrium of M^+ ion in Hacac with other solvents S is expressed as follows,

$$M^+ + nS \overset{\beta_n}{\rightleftharpoons} M^+(S)_n \qquad (2)$$

$$\beta_n = \frac{[M^+(S)_n]}{[M^+][S]^n} = K_1K_2\cdots\cdots K_n \qquad (3)$$

where M^+ is the ion solvated only by Hacac, n the number of solvating S molecule(s). β_n is the over-all complex formation constant, while K_i the successive one. As is constant the analytical concentration of M^+, the next relation holds.

$$R \equiv \left\{\frac{[M^+]_{Hacac}}{[M^+]_{Hacac+S}} - 1\right\}/[S]$$
$$= \beta_1 + \beta_2[S] + \cdots\cdots\cdots + \beta_n[S]^{n-1} \qquad (4)$$

Here, $[M^+]_{Hacac}$ and $[M^+]_{Hacac+S}$ denote the M^+ ion solvated only by Hacac in pure Hacac and that in Hacac+S mixture, respectively. The R values can be obtained from the emf of cell (1) in pure Hacac and Hacac+S mixture as presented in equation (5),

$$R[S] + 1 = \frac{[M^+]_{Hacac}}{[M^+]_{Hacac+S}}$$
$$= 10^{(E_{Hacac} - E_{Hacac+S})/0.059} \qquad (5)$$

where E_{Hacac} and $E_{Hacac+S}$ are in V.

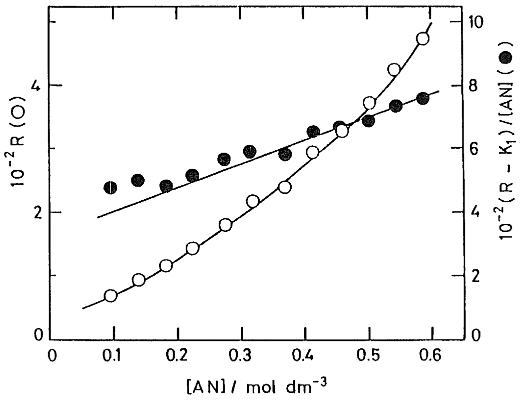

Fig. 3. R vs. [AN] and (R-K_1)/[AN] vs. [AN] plots for the complexing of silver ion in acetylacetone (AN= acetonitrile)

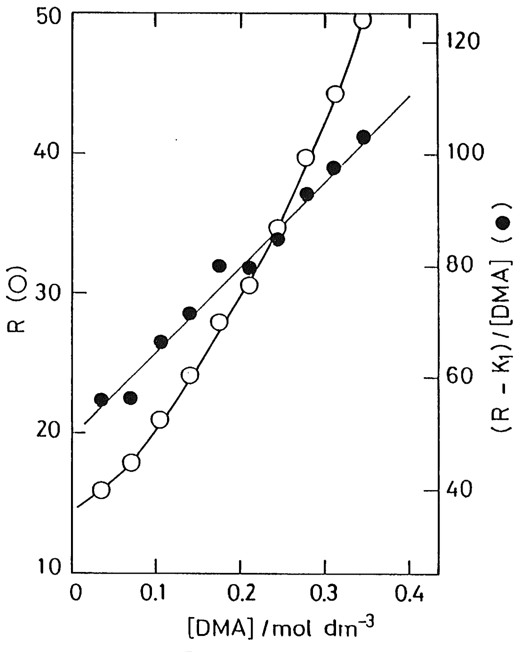

Fig. 4. R vs. [DMA] and (R-K_1)/[DMA] vs. [DMA] plots for the complexing of sodium ion in acetylacetone (DMA =dimethylacetamide)

The typical applications of the graphical analysis for equation (4) are shown in Figs. 3 and 4.

Solvent effect on the complex formation

The over-all complex formation constants of silver ion in Hacac with other solvents are summarized in Table 1. Only mono-solvated ions were formed for acetone, while mono- and di-solvated ions were formed for MeOH and EtOH. Tri-solvated species were also detected for AN, water, DMF and DMA. For DMSO, a complexing up to four solvent molecules is observed. The complexing of silver ion in Hacac becomes easier with the increase in the basicity of the solvent added in the order of acetone<MeOH ~EtOH<DMF<DMA<DMSO. This order is consistent with that of stability of silver ion in pure solvents5). Hydration is stronger than expected from the donor number6) of water. The abnormally strong complexing of silver ion with AN is attributed to the back bonding interaction of silver ion with the nitrile group of AN7). The relation between log K_1 of sodium ion and the donor number of solvents is shown in Fig. 5, which also indicates an important role of the solvent basicity in the complexing. Figure 6 represents the distribution of ionic

Table 1. Over-all complex formation constants (β_n) of silver ion in acetylacetone with other solvents

Solvent	(DN)	β_1	β_2	β_3	β_4
AN	(14.1)	3.4×10	3.2×10^2	7.1×10^2	
Acetone	(17.0)	1.3			
H_2O	(18.0)	4.3	5.5	9.1	
MeOH	(19.0)	2.0	0.3		
EtOH	(20.0)	2.1	2.1		
DMF	(26.6)	1.8×10	3.6×10	1.4×10^2	
DMA	(27.8)	3.8×10	3.1×10^2	1.8×10^3	
DMSO	(29.8)	1.1×10^2	1.6×10^2	1.6×10^4	3.5×10^4

DN; donor numbers of the solvents, AN; acetonitrile, DMF; dimethylformamide, DMA; dimethylacetamide, DMSO: dimethylsulfoxide.

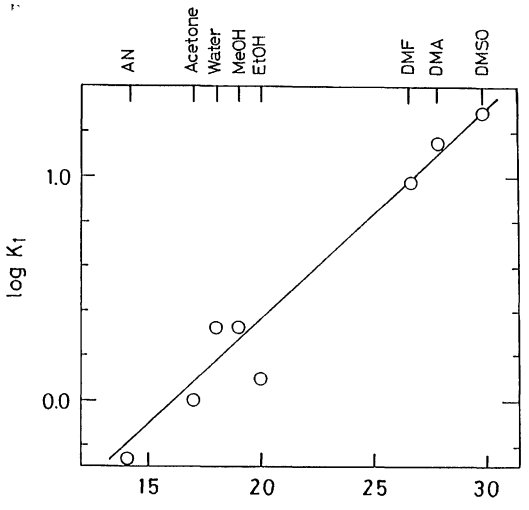

Fig. 5. Relation between log K_1 and donor numbers of solvents (DN) in the complexing of sodium ion in acetyl acetone

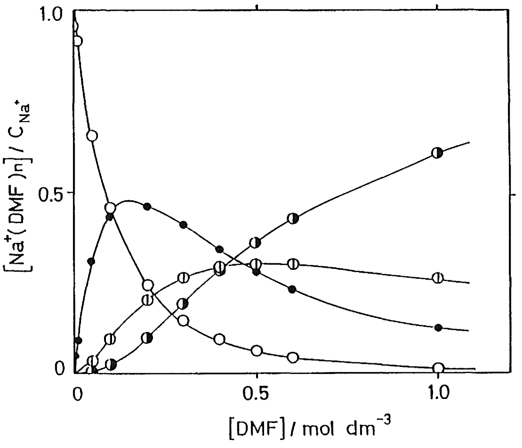

Fig. 6. Distribution of ionic species of sodium ion in acetylacetone + dimethylformamide (DMF) mixture (○); n=0, (●); n=1, (◐); n=2, (◑); n=3, C_{Na^+}; 0.001 mol dm^{-3} (the total concentration of sodium ion)

species of sodium ion in Hacac+DMF mixture. The values of $\beta_1=9.5$, $\beta_2=20$ and $\beta_3=48$ were used in the calculation of concentration ratios.

The complexing of alkali metal, ammonium and thallium(I) ions in AN with various solvents was comprehensively studied by Izutsu et al.[8] by using a cation sensitive glass electrode. To elucidate quantitatively the solvation phenomena in Hacac, the authors have been investigating the ionic free energies of transfer from Hacac to other solvents. Above discussions will be extended later in detail in connection with the results reported in literatures and from the viewpoint of transfer energies.

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