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Solvent effects on acetylacetonato iron complexes

Minoru Handa
Graduate School of Science and Technology, Niigata University, 8050 Ikarashi Nino-cho, Niigata 950-21 (Japan)

Yasuhiko Yukawa*
Division of Chemistry, General Education Department, Niigata University, 8050 Ikarashi Nino-cho, Niigata 950-21 (Japan)

Yukio Sasaki
Faculty of Engineering, Tokyo Institute of Polytechnics, 1583 Iiyama, Atsugi, Kanagawa 243-02 (Japan)

Satoshi Igarashi and Hiroshi Miyamoto
Department of Chemistry, Faculty of Education, Niigata University, 8050 Ikarashi Nino-cho, Niigata 950-21 (Japan)

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Abstract

Interactions of various solvents with $Fe(acac)^{2+}$, $Fe(acac)_2^+$ and $Fe(acac)_3$ (the expression represents the solvated species. $acac^-$ is the 2,4-pentanedionate ion, acetylacetonate ion) were investigated through observing ν(Fe–O) and ν(C–O) in resonance Raman spectra. In the $Fe(acac)^{2+}$ system, both ν(C–O) and ν(Fe–O) correlate with donor number (*DN*) the ν(C–O) band shifts toward high frequency with the increase in *DN*, while the ν(Fe–O) band exhibits the inverse trend. The relation between ν(C–O) and ν(Fe–O) in different solvents is a good example of the bond length variation rules (the donor–acceptor concept). In the $Fe(acac)_3$ system, i.e. the non-direct solvation system, ν(C–O) shifts toward low frequency with increase in the relative dielectric constant (ϵ_r) of the solvent, whereas ν(Fe–O) is constant, independent of ϵ_r. These facts indicate that the C–O bond of the $acac^-$ ligand is lengthened by the polarizability effect of the solvents, while the Fe–O bond in the inside of the complex is not influenced. On the other hand, ν(C–O) and ν(Fe–O) do not correlate with ϵ_r in the $Fe(acac)^{2+}$ system. They indicate that the direct effect (donor effect) of the solvent molecules on the metal is larger than macroscopic effects such as polarizability In the $Fe(acac)_2^+$ system, the ν(C–O) shift exhibits a similar trend to that in $Fe(acac)_3$, whereas the shift of ν(Fe–O) is similar to that in $Fe(acac)^{2+}$. The results suggest that $Fe(acac)_2^+$ is influenced by both the macroscopic and direct effects of the solvents. To confirm this in the $Fe(acac)_2^+$ system, solid samples were prepared by freeze drying the solutions and measuring their resonance Raman spectra.

Key words Iron complexes, Bidentate ligand complexes, Chelate complexes

Introduction

β-Diketonato complexes have been widely studied because of their interesting properties and the application of them to catalytic reactions as well as to 2,2′-bipyridine and 1,10-phenanthroline complexes [1, 2]. For example, the substituent effects, which include the good relationship between half-wave potentials and Hammett substituent constants [3, 4], have been studied on many β-diketonato complexes by means of electrochemical techniques [5–8]. Recently a new ligand electrochemical parameter, E_L, has been proposed, which allows one to predict the redox potential of a given metal couple when its structural and spin-state information are available [9]. For those studies, many mixed-ligand complexes were synthesized and their preparation methods have been developed [10–12]. As intermediates for the synthesis of mixed ligand complexes, complexes with solvent molecules have been prepared [13–15]. Sato and co-workers reported methods of preparation of bis(β-diketonato)bis(acetonitrile)ruthenium(III) complexes, which were useful intermediates for the synthesis of mixed-ligand β-diketonato ruthenium(III) complexes of the $[Ru^{III}L_2L']$ type [16, 17]. In our previous work, the inert Ru^{III} system was extended to a labile Fe^{III} system [18]. In the Fe^{III} system, two kinds of species, $Fe(acac)_2^+$ and $Fe(acac)^{2+}$ (the expression represents the solvated species: $acac^-$ is the 2,4-pen-

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*Author to whom correspondence should be addressed.

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tanedionate ion, acetylacetonate ion), were obtained unlike in the Ru^{III} system when only bis(β-diketonato)ruthenium(III) was formed through the reaction of the corresponding tris(β-diketonato)ruthenium(III) with perchloric, sulfuric or hydrochloric acid in acetonitrile [17]

It is important to study solvent effects for acetylacetonato iron complexes in order to obtain basic data about useful intermediates for the synthesis of mixed-ligand β-diketonato iron(III) complexes. In this work, interactions of different solvents with $Fe(acac)^{2+}$, $Fe(acac)_2{}^+$ and $Fe(acac)_3$ were investigated through observing ν(Fe–O) and ν(C–O) in resonance Raman spectra, as well as electronic spectra.

Experimental

Chemicals

Tris(acetylacetonato)iron(III) was prepared as described in the literature [19] and recrystallized from methanol/water. Iron(III) perchlorate was purchased from Kanto Chemical Co. Acetonitrile (AN), acetone (AC), ethyl acetate (EtAc), tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were obtained as high purity solvents for high pressure liquid chromatography. Methyl acetate (MeAc), diethyl ether (Et_2O), dimethyl sulfoxide (DMSO) and propylene carbonate (PC) were special grade quality. All of the solvents were purchased from Wako Chemical Co.

Preparations

Various solvent solutions of $Fe(acac)^{2+}$ and $Fe(acac)_2{}^+$ were prepared by mixing solutions of tris(acetylacetonato)iron(III) and iron(III) perchlorate at the ratios shown in the following equations:

$$Fe(acac)_3 + 2Fe(ClO_4)_3 \longrightarrow 3Fe(acac)^{2+} + 6ClO_4{}^-$$

$$2Fe(acac)_3 + Fe(ClO_4)_3 \longrightarrow 3Fe(acac)_2{}^+ + 3ClO_4{}^-$$

Solutions of $Fe(acac)_3$ were obtained by dissolving $Fe(acac)_3$ in each solvent These complexes were identified by electronic spectra

Solid samples of the $Fe(acac)_2{}^+$–solvents were prepared by freeze drying each solution

Measurements

Resonance Raman spectra were recorded on a Jobin Yvon U-1000 spectrometer with a capillary cell for solutions and a rotated disk for solid samples, the exciting line (514 5 nm, 100 or 50 mW) being provided by an NEC Ar^+ ion laser GLG 3200. Without using the rotated disk, the solid samples photodecomposed and did not exhibit any significant signals. Since almost all the solid samples are extremely hygroscopic, the rotated disk was sealed with a cover glass during the measurement.

Powder diffuse reflection spectra were measured on a Hitachi U-3200 spectrophotometer equipped with a standard Hitachi reflection attachment and magnesium oxide for the standard and a diluent.

Electronic spectra were measured on a Hitachi U-3400 spectrophotometer with a 1 cm quartz cell.

The concentration of the complexes for measuring the resonance Raman and electronic spectra was approximately 0.5 mmol dm^{-3} in all cases.

Results and discussion

The spectrophotometric titration of $Fe(acac)_3$ with $Fe(ClO_4)_3$ in AN shows the formation of $Fe(acac)_2{}^+$ and $Fe(acac)^{2+}$: their spectra agree with those from previous work [18]. The results of the titrations in the different solvents imply the formation of $Fe(acac)_2{}^+$ and $Fe(acac)^{2+}$ in each solvent. Absorption bands of $Fe(acac)_3$, $Fe(acac)_2{}^+$ and $Fe(acac)^{2+}$ in different solvents are shown in Table 1. The band in the visible range is described by a superposition of the ligand-to-metal charge-transfer (LMCT) excited states and the ligand (π,π^*) excited triplets and singlets [18, 20]. The data indicate a correlation between ν_{max} of the absorption spectrum and the number of $acac^-$ ligands in each solvent In other words the solvent has an additive effect. two solvent molecules connect with the iron atom when one $acac^-$ ligand is eliminated, whereas twice as many solvent molecules connect with the metal on removing two $acac^-$, if Fe^{3+} has an octahedral coordination in the solutions From this point of view, it is expected that the peak positions of the spectra of bis- and mono(acac) complexes are correlated with the properties of directly solvated molecules and that of the tris(acac) complex is independent. Figure 1 shows the relation between the donor number (*DN*) and ν_{max}. In the tris(acac) system ν_{max} is constant, whereas the peak positions of both bis- and mono(acac) systems shift toward high frequency with increase in *DN* Therefore $Fe(acac)_2{}^+$ and $Fe(acac)^{2+}$ are influenced by the donor effect of the solvents, while $Fe(acac)_3$ is not influenced by the direct effect of the solvents. The influence on $Fe(acac)^{2+}$ is larger than that on $Fe(acac)_2{}^+$ because $Fe(acac)^{2+}$ is coordinated to more solvent molecules than $Fe(acac)_2{}^+$. The ν_{max} in each species ($Fe(acac)_3$, $Fe(acac)_2{}^+$ and $Fe(acac)^{2+}$) did not correlate with the relative dielectric constants (ϵ_r).

From resonance Raman spectra of the acetylacetonato–Fe^{III} complexes with irradiation of the 514.5 nm Ar^+ ion line, a metal–ligand vibration and an intraligand vibration including a ligating atom can be observed because the irradiation (514.5 nm) overlaps with

TABLE 1 Properties of solvents and absorption bands of $Fe(acac)_3$, $Fe(acac)_2^+$ and $Fe(acac)^{2+}$ in each solvent

Solvent	*DN*	ϵ_r	ν_{max} (10^3 cm^{-1}) (log ϵ (mol^{-1} dm^3 cm^{-1}))		
			$Fe(acac)_3$	$Fe(acac)_2^+$	$Fe(acac)^{2+}$
(A) Acetonitrile (AN)	14.1	35.95	23.00 (3.54)	19.92 (3.34)	16.81 (2.98)
(B) Propylene carbonate (PC)	15.1	64.4	22.96 (3.51)	20.89 (3.34)	18.37 (2.90)
(C) Methyl acetate (MeAc)	16.5	6.7	23.11 (3.56)	20.83 (3.32)	18.42 (2.99)
(D) Acetone (AC)	17.0	20.70	23.02 (3.54)	20.83 (3.38)	19.07 (3.01)
(E) Ethyl acetate (EtAc)	17.1	6.0	23.13 (3.54)	21.17 (3.35)	19.16 (2.99)
(F) Diethyl ether (Et_2O)	19.2	4.3	23.13 (3.59)	21.59 (3.37)	18.95 (2.99)
(G) Tetrahydrofuran (THF)	20.0	7.58	23.02 (3.54)	21.17 (3.34)	19.52 (2.94)
(H) *N*,*N*-Dimethylformamide (DMF)	26.6	36.71	22.96 (3.54)	21.68 (3.34)	20.64 (3.03)
(I) Dimethyl sulfoxide (DMSO)	29.8	46.7	22.83 (3.54)	21.91 (3.30)	21.17 (2.95)

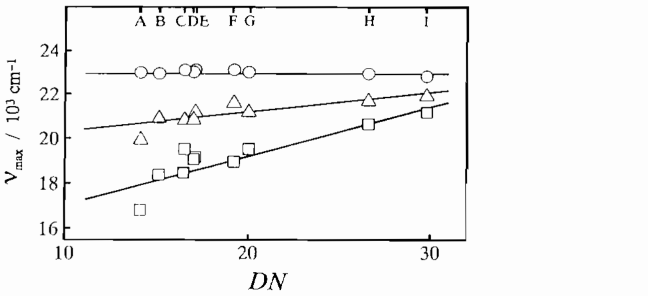

Fig. 1. Relation between the donor number (*DN*) of different solvents and ν_{max} of absorption spectra ○, $Fe(acac)_3$, △, $Fe(acac)_2^+$; □, $Fe(acac)^{2+}$. For explanation of A–I see Table 1.

the region of the LMCT band. Therefore, we can obtain more detailed information of the direct interactions of different solvents with the metal and with the ligand. Resonance Raman shifts, ν(C–O) and ν(Fe–O), of $Fe(acac)_3$, $Fe(acac)_2^+$ and $Fe(acac)^{2+}$ in the various solvents are shown in Table 2. According to the assignment [18, 20–22], the ν(Fe–O) is coupled by a small amount of $\nu(C\text{–}CH_3)$ and the ν(C–O) is coupled by ν(C–C). The shifts of ν(C–O) and ν(Fe–O) are also proportional to the number of coordinated $acac^-$ (N_{acac}) in each solvent, like the relation between the absorption bands and the number of $acac^-$ ligands. However, the relation between N_{acac} and ν(Fe–O) is inverse to that between N_{acac} and ν(C–O).

The relation between *DN* and ν(C–O) and between *DN* and ν(Fe–O) in the $Fe(acac)_3$, $Fe(acac)^{2+}$ and $Fe(acac)_2^+$ systems is shown in Fig. 2. The mono(acac) complex is coordinated to the most solvent molecules, thus the direct solvent effect on the complex is most obvious. In the mono(acac) complex system, both ν(C–O) and ν(Fe–O) correlate with *DN*, whose correlation coefficient (r^2) values are 0.90 (except for diethyl ether) and 0.83, respectively: ν(C–O) shifts toward high frequency with increase in *DN*, while ν(Fe–O) exhibits the inverse trend. The direct solvent effect is ambiguous in the bis(acac) complex and disappears in the tris(acac) complex. Although in the bis(acac) complex the relation between ν(Fe–O) and *DN* has a similar trend to that of the mono(acac) complex ($r^2 = 0.75$), ν(C–O) exhibits no correlation with *DN*. On the other hand, in the tris(acac) complex ν(Fe–O) and ν(C–O) do not show the correlation found for the mono($acac^-$) complex because solvent molecules cannot be coordinated to

TABLE 2. Resonance Raman shifts, ν(C–O) and ν(Fe–O), of $Fe(acac)_3$, $Fe(acac)_2^+$ and $Fe(acac)^{2+}$ in the different solvents

Solvent	ν(C–O) (cm^{-1})			ν(Fe–O) (cm^{-1})		
	$Fe(acac)_3$	$Fe(acac)_2^+$	$Fe(acac)^{2+}$	$Fe(acac)_3$	$Fe(acac)_2^+$	$Fe(acac)^{2+}$
AN	1603	1578 (1577)[a]	1554	451	462 (461)	474
PC	1600	1578 [b]	1555	[c]	[c] [b]	[c]
MeAc	1608	1584 (1576)	1557	448	458 (461)	472
AC	1608	1582 (1577)	1558	449	457 (459)	466
EtAc	1609	1586 (1576)	1560	448	457 (463)	465
Et_2O	1610	1591 (1575)	1572	[c]	[c] (459)	[c]
THF	1608	1584 (1576)	1561	449	454 (460)	468
DMF	1603	1582 (1574)	1563	449	452 (454)	456
DMSO	1602	1581 (1577)	1568	449	453 (451)	457

[a] Solid samples prepared by freeze drying of solutions [b] Not available [c] Overlapped by solvent band

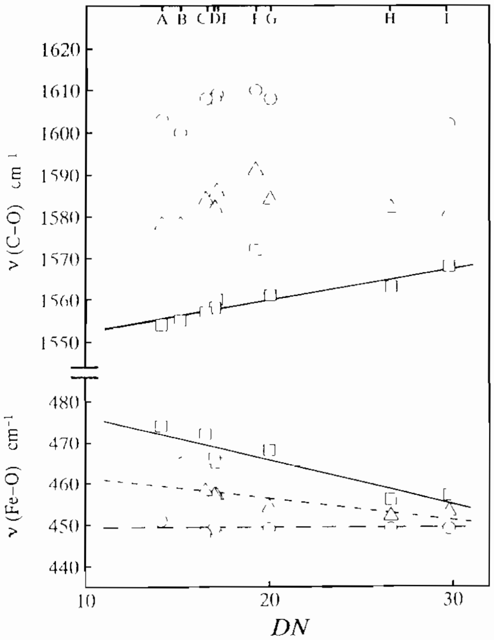

Fig 2 Relation between *DN* and ν(C–O) and between *DN* and ν(Fe–O) in the $Fe(acac)_3$, $Fe(acac)^{2+}$ and $Fe(acac)_2^+$ systems ○, $Fe(acac)_3$, △, $Fe(acac)_2^+$, □, $Fe(acac)^{2+}$ For explanation of A–I see Table 1

the metal in $Fe(acac)_3$. These results are consistent with those from the absorption spectra.

The value of ν(C–O) in the diethyl ether solution deviates toward high frequency from the *DN*–ν(C–O) correlation. This implies that the diethyl ether molecule greatly influences the complex in this solution, though the solvent has a medium grade *DN*. One interpretation may be that the $acac^-$ ligand is pushed out by the steric hindrance of attacking diethyl ether molecules and the Fe–O($acac^-$) bonds stretch: the diethyl ether molecule has only the donor oxygen atom with bulky and flexible substituents (ethyl groups) in the solvent molecules used in this work. Therefore ν(C–O) deviates from the *DN*–ν(C–O) correlation for the reason given below. Unfortunately, it is impossible to confirm this interpretation because ν(Fe–O) perfectly overlaps with the frequencies of the diethyl ether molecule.

The relation between ν(C–O) and ν(Fe–O) in various solvents is a good example of the bond length variation rules (the donor–acceptor concept) given by Gutmann [23]: (i) the smaller the intermolecular distance between the donor and acceptor, the greater the induced lengthening of the adjacent intramolecular bonds in both the donor and acceptor components, (ii) the bond is lengthened when the electron shift takes place from the more electropositive to the more electronegative atom in the uncomplexed species and it is shortened when the electron shift takes place from the more electronegative to the less electronegative atom; (iii) when an adduct is formed, the coordination number (*CN*) is increased both at the donor atom and at the acceptor one and according to rule (i) the bonds originating from these atoms are lengthened irrespective of the state of aggregation. When the bis- or mono(acac) species interacts with the solvent molecules, the *CN* of the species develops a tendency to increase, especially in the large *DN* solvents, and the Fe–O bond is lengthened, i.e. the metal surroundings in $Fe(acac)^{2+}$ or $Fe(acac)_2^+$ approach those in $Fe(acac)_3$, which has the largest *CN* In other words, the strong effect from the large *DN* solvent molecule induces lengthening of the Fe–O bond according to rule (i), and then the charge-density rearrangement takes place throughout the complex, in consequence, the C–O bond is shortened according to rule (ii).

From the point of view of macroscopic properties, the results of the resonance Raman shifts were related to the ϵ_r of the solvents. Figure 3 exhibits the relation between ϵ_r and ν(C–O) and between ϵ_r and ν(Fe–O) of $Fe(acac)_3$, $Fe(acac)_2^+$ and $Fe(acac)^{2+}$ in the various solvents. In the tris(acac) complex, ν(C–O) shifts toward low frequency with increase in ϵ_r ($r^2 = 0.94$), whereas ν(Fe–O) is constant, independent of ϵ_r. This is explained by the fact that the C–O bond in the $acac^-$ ligand is lengthened by the polarizability effect of the solvents, while the Fe–O bond in the inside of the complex is not influenced. The results are consistent with those of $Fe(acac)_3$ and $Ru(acac)_3$ in the acetonitrile–water

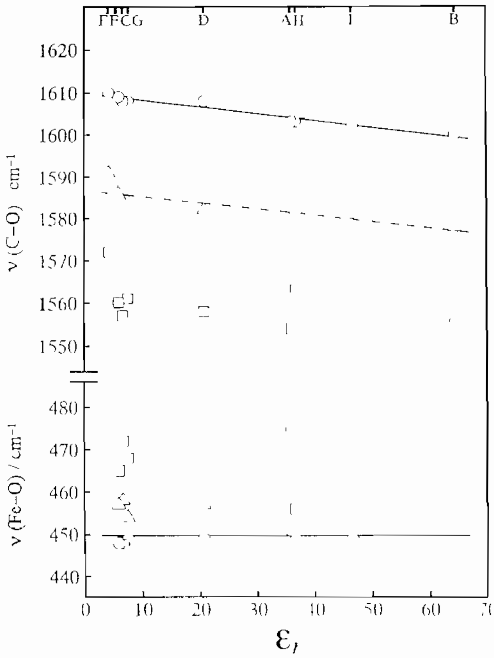

Fig 3 Relation between ϵ_r and ν(C–O) and between ϵ_r and ν(Fe–O) of $Fe(acac)_3$, $Fe(acac)_2^+$ and $Fe(acac)^{2+}$ in the different solvents ○, $Fe(acac)_3$, △, $Fe(acac)_2^+$, □, $Fe(acac)^{2+}$ For explanation of A–I see Table 1

mixed solvent system [24]. On the other hand, neither ν(C–O) nor ν(Fe–O) correlate with ϵ_r in the mono(acac) complex. This indicates that the direct effect of the solvent molecules to the metal is larger than the macroscopic effect such as the polarizability effect in Fe(acac)$^{2+}$. In the bis(acac) complex, ν(C–O) shows a similar trend to that of the tris(acac) complex, although there is not a very good correlation ($r^2 = 0.64$). However, ν(Fe–O) does not correlate with ϵ_r.

To sum up, the Fe–O and C–O bonds in Fe(acac)$^{2+}$ are influenced by the direct effect of the solvent molecules in contrast with Fe(acac)$_3$. On the other hand, the C–O bond in Fe(acac)$_3$ is influenced by the macroscopic solvent effect, though the effect can be disregarded in Fe(acac)$^{2+}$. In Fe(acac)$_2$$^+$, the ν(C–O) shift exhibits a similar tendency to that in Fe(acac)$_3$, whereas the shift of ν(Fe–O) is similar to that in Fe(acac)$^{2+}$ The results show that Fe(acac)$_2$$^+$ is influenced by both the direct and the macroscopic effects of the solvents.

To confirm the influence of the macroscopic and direct effects of the solvents in the Fe(acac)$_2$$^+$ system, solid samples were prepared by freeze drying the solutions and measuring their powder diffuse reflection spectra and resonance Raman spectra. The powder diffuse reflection spectra of some solid bis(acac) samples compared with that of the tris(acac) complex are shown in Fig. 4. Each spectrum of the solid bis(acac) shifts to a higher wavelength region from that of tris(acac). This trend agrees with that found in the solution systems. The resonance Raman shifts of the solid bis(acac) samples are listed in Table 2. Figure 5 shows that the relation between ϵ_r and ν(C–O) and between *DN* and ν(Fe–O) in the solid Fe(acac)$_2$$^+$ system overlapped those in the solution system. The relation between *DN* and ν(Fe–O) in the solid samples shows the same trend as in the solutions, whereas that between ϵ_r and ν(C–O) is different. In the solids, ν(C–O) is constant, independent of ϵ_r. It is suggested that the environment of the acac$^-$ ligand is almost the same in the different solids· the ligand is surrounded by counter anions (ClO$_4$$^-$) and the other acac$^-$ ligands of adjacent complexes Thus the degree of the influence on the C–O bond in the various solids is almost the same, different from that in the solutions. On the other hand, the Fe–O bond in the solids is influenced by the solvent molecules as well as in the solutions because the Fe(acac)$_2$$^+$ forms an adduct with the solvent molecules in both conditions. As a result, the same linear correlation between *DN* and ν(Fe–O) is exhibited both in the solids and in the solutions. Therefore, it is confirmed that Fe(acac)$_2$$^+$ is influenced by both effects, the macroscopic (the polarizability effect) and the direct (the donor effect) effects of the solvents.

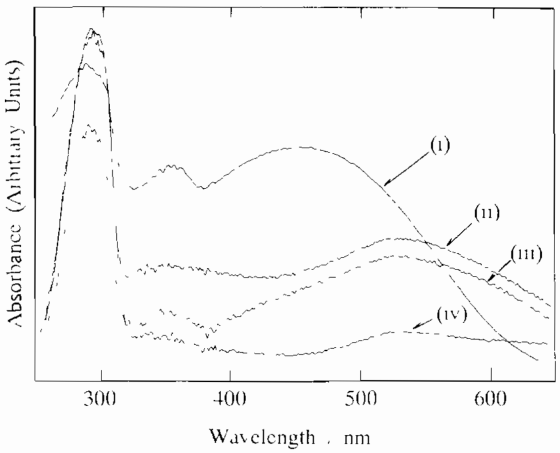

Fig 4 Powder diffuse reflection spectra of Fe(acac)$_3$ ($\lambda_{max} = 462$ nm) (i), and freeze-dried solid samples of Fe(acac)$_2$$^+$ in DMSO (524 nm) (ii), in THF (525 nm) (iii), and in EtAc (529 nm) (iv).

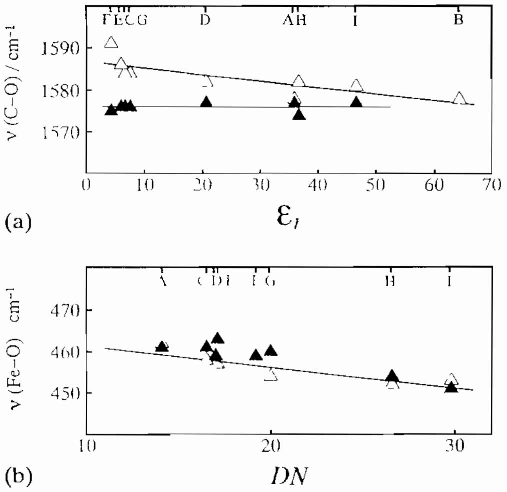

Fig 5 Relation between ϵ_r and ν(C–O) (a) and between *DN* and ν(Fe–O) (b) in the solid Fe(acac)$_2$$^+$ system overlapped those in the solution system. ▲, Solid system, △, solution system For explanation of A–I see Table 1.

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