1264 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (5), 1264—1267 (1979) [Vol. 52, No. 5

ESR Spectrum of Bis(dibenzoylmethanato)oxovanadium(IV) Dissolved in Molten and Crystalline Charge Transfer Complexes

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(Received August 18, 1978)

The ESR spectrum of bis(dibenzoylmethanato)oxovanadium(IV) dissolved in a number of pyrene and fluoranthene complexes with aromatic polynitro compounds just above their melting points indicates that the motion of the spin probe is more or less restricted. In some favorable cases, the high effective viscosity of the melts can be partially attributed to the association of the electron donor and acceptor molecules. No abrupt change in the ESR spectral pattern is noted upon solidification and the motion of the probe gradually ceases upon lowering the temperature. Therefore, the lattice appears to be not rigid in these crystalline complexes. On the other hand, the ESR spectrum observed in the molten naphthalene–dinitrophenol complex is not far from isotropic at the melting point. Because of the segregation of the probe upon solidification, the measurements on this solid complex could not be made.

When a phase diagram indicates the formation of a 1 : 1 complex with a congruent melting point, it does not necessarily follow that the complex is stable in the molten state. The greater the extent of dissociation, the more flat the curve for the region between the eutectic points is expected, in general, to be.[1–3] However, nothing more can be safely inferred in the absence of any definite information regarding the dissociation of the complex in the molten state. As reported by one of the present authors,[4] all the patterns from the isotropic ESR spectrum to the anisotropic one of oxovanadium chelates can be recorded by employing molten *o*-terphenyl as a solvent. The observed anisotropic molecular motion of the spin probe has been speculated to be evidence for the restricted motion of the host molecules, in other words, the formation of clusters. Therefore, one may hope that the ESR spectral measurement of oxovanadium chelates is equally capable of detecting molecular association in molten charge-transfer complexes. The larger the chelate molecule, the more difficult the motion; thus bis(dibenzoylmethanato)oxovanadium(IV) may be the probe which is effective in the widest temperature range among the three chelates examined before. As will be described below, this chelate was found to be incorporated into the crystalline pyrene, fluoranthene, and phenanthrene complexes with aromatic polynitro compounds and to be a probe for the molecular motion in solids as well.

Experimental

Materials. The bis(dibenzoylmethanato)oxovanadium(IV) (VO(dbm)$_2$) was prepared following the procedure reported by Selbin *et al.*[5] The donors employed were pyrene, fluoranthene, phenanthrene, and naphthalene and the acceptors were *m*-dinitrobenzene (DNB), 2,4-dinitrofluorobenzene (DNF), 2,4-dinitrochlorobenzene (DNC), 2,4-dinitrotoluene (DNT), 2,4-dinitrophenol (DNP), 2,4,6-trinitrochlorobenzene (TNC), and 2,4,6-trinitrotoluene (TNT). The pyrene, Eastman white label, and TNT, Eastman yellow label, were recrystallized from appropriate solvents. The phenanthrene, Eastman white label, was boiled with maleic anhydride in xylene to remove any anthracene.[6] The other reagents were used without further purification. The complexes were prepared by melting mixtures of equimolar amounts of the component compounds. Their melting points were read from calorimetric curves recorded on a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, at a heating rate of 3 °C min^{-1}. As the paramagnetic probe is not very stable above 150 °C, the complexes with relatively low melting points were selected for the present work.

Measurements. The ESR spectra were recorded on a JEOL model JES-ME-3X (X-band) spectrometer with 100 kHz modulation in the range from temperatures well above the melting point of each complex to the temperature where the probe precipitates from the solid complex. The magnetic-field scan was calibrated with Mn^{2+}-doped MgO powder.

Results and Discussion

The ESR spectra of VO(dbm)$_2$ recorded in most of the pyrene complexes kept just above their melting points deviate markedly from the isotropic one. For example, the first derivative of the spectrum in pyrene–DNC (mp 87 °C) recorded at 88.5 °C is shown in Fig. 1. In this spectrum one may locate more lines than the eight expected for the isotropic spectrum. Thus it is apparent that the motion of the probe is restricted. The parameter, *S*, defined by

$$S = (A_{\parallel}' - a)/(A_{\parallel} - a)$$

will be employed as a measure of the molecular motion of VO(dbm)$_2$. Here, $A_{\parallel}$ is the component parallel to the V=O bond direction of the approximately axial hyperfine tensor of the spin probe, *a* is the iso-

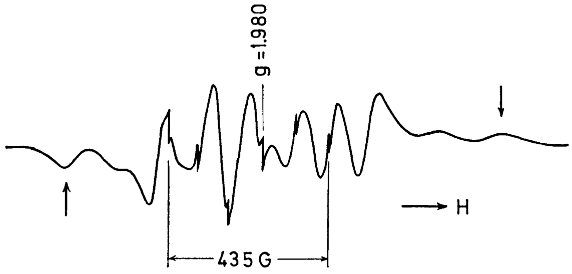

Fig. 1. ESR spectrum of bis(dibenzoylmethanato)-oxovanadium(IV) observed at X-band in pyrene–dinitrochlorobenzene at 88.5 °C. The superimposed small signals are due to the marker, Mn^{2+}-doped MgO powder.

tropic hyperfine constant, and $A_{\parallel}'$ is one-seventh of the separation of the outer hyperfine extrema (these are indicated by arrows in Fig. 1). They are signals from the ensemble of the probe molecules oriented with the applied field, on the average, parallel to the V=O bond direction. The parameter is equal to zero if the probe molecules are tumbling rapidly and unity if they are immobilized in a medium. With the values of $A_{\parallel}$ and a observed in molten *o*-terphenyl, namely, 188 and 108 G (1G=10^{-4} T), the S value for the spectrum in Fig. 1 is estimated to be 0.71. The spectra recorded at higher temperatures indicate a shorter distance for $7A_{\parallel}'$. This means an increased molecular motion. It was not possible to locate the corresponding signals above 114 °C. The probe was found to be dissolved even in the crystalline complex. The spectra recorded below the melting point are still intermediate between the anisotropic and isotropic ones. In this way, the plots given in Fig. 2 were obtained. The open and shaded circles are for two runs with independently-prepared solutions. It must be noted that no discontinuity in the S value is found at the melting point of the complex. This observation may imply that the change of the motional behavior upon solidification is not large or that the motion is slow on an ESR time scale in both the phases. From the macroscopic standpoint, the restriction may be attributed to the high viscosity of the medium, η. Assuming that the η/T value of the medium can be approximated by that of molten *o*-terphenyl at the same S value, the effective viscosity of the molten complex was estimated as 12.2 cP (1cP=10^{-3} Pa s) at the melting point. The viscosity value of *o*-terphenyl required for this estimation was calculated by means of the equation of Greet and Turnbull.[7] It must be added that, if special interactions are conceivable between the probe and solvent molecules, viscosity alone may not account for the deviation from the isotropic ESR spectrum. Therefore, the effective viscosity estimated here may be larger than the actual one.

The S values observed with solidified samples are not very reproducible. In Fig. 3, two independent measurements with the DNT complex are plotted against the temperature. Both the measurements give the same S value, 0.67, at the melting point, 92.5 °C. The open and shaded circles fit on to one curve above this temperature but not below it, suggesting the absence of supercooling of the molten complex. It is unlikely that the difference observed below the melting point arises from a small deviation from the 1 : 1 stoichiometry in the complex for which the lower S values were found. When the complex contains an excess of one of the components, the solid 1 : 1 complex and a liquid coexist in the temperature range from the melting point to the eutectic point. As the probe is generally more soluble in the liquid than in the solid, the observed S value may be largely of the probe in the former phase. If this happens, one expects, in contrast to the observation, that the open circles would lie on the extrapolation of the S-t relation above the melting point. When the temperature is lowered still further, the probe will be more concentrated, eventually leading to the segregation at the eutectic point. As the matter of fact, the segregation was observed at 43 °C, far below the eutectic points, which are 89 °C in the hydrocarbon-rich region and 57.5 °C in the DNT-rich region.[8] Consequently, the large difference in the S values given by these two measurements can be best interpreted in terms of the degree of disorder surrounding the VO(dbm)$_2$ molecules in the solid.

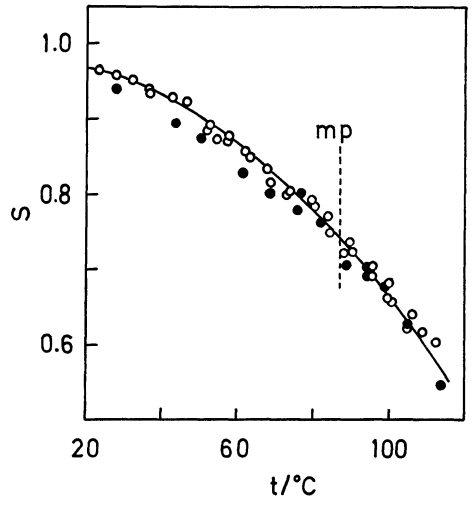

Fig. 2. Temperature dependence of the parameter S in pyrene–dinitrochlorobenzene. The open and shaded circles are for two independent runs.

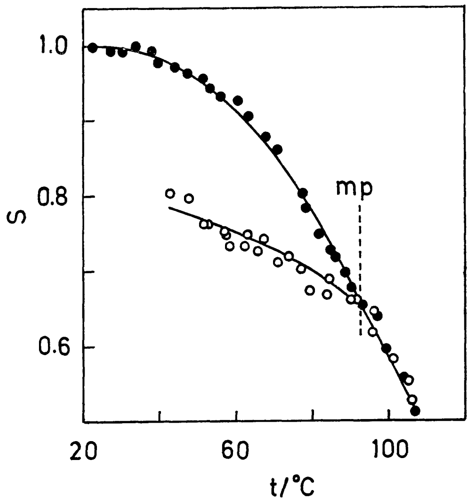

Fig. 3. Temperature dependence of the parameter S in pyrene–dinitrotoluene. The open and shaded circles are for two independent runs.

It is well known that dislocations function as a natural haven for solid-state impurities.[9] The large probe molecules may be more satisfactorily accommodated in the expanded region of the dislocation cores and more mobile than elsewhere in the host lattice. On the other hand, Möhwald and Böhm have shown that various guest acceptor molecules can be accommodated in the naphthalene-tetracyanobenzene complex assuming the same very homogeneous orientation as the host donor molecules.[10] In this situation, the motion of the probe molecules does not always occur readily, unless the neighboring host molecules have a large degree of motion. Thus, the motional behavior of the probe may be dependent upon where the molecules are accommodated which, in turn, may depend on how the melt is quenched.

In addition to the 1 : 1 complex with a congruent melting point, four more pyrene–TNC complexes with mole ratios of 4 : 3, 2 : 1, 3 : 1, and 4 : 1 are known to be formed.[11] The 4 : 3 and 2 : 1 complexes decompose to the solid 1 : 1 complex and a liquid at 136 °C, and the 3 : 1 and 4 : 1 complexes decompose to the solid 2 : 1 complex and a liquid at 126 °C, which is practically the same as the eutectic point. The results obtained with the 1 : 1 and 2 : 1 complexes are illustrated in Fig. 4. The S value at the melting point of the former complex (154.5 °C) is 0.53 and that at the decomposition point of the latter, 0.59. However, the value observed with the 2 : 1 complex at a given temperature above 100 °C is consistently lower than that with the 1 : 1 complex. Thus, the probe molecules are made more mobile as a result of the presence of an excess pyrene in both the molten and solid states. The same tendency was observed with the other TNC complexes containing more pyrene than the 1 : 1 mole ratio. Around 100 °C the S value in the 2 : 1 complex abruptly increases and then becomes almost the same as the value in the 1 : 1 complex. On raising the temperature, a change in the reverse direction occurs between 118 and 125 °C. This change may be associated with the solid-solid transition which was reported earlier to take place at 126 °C.

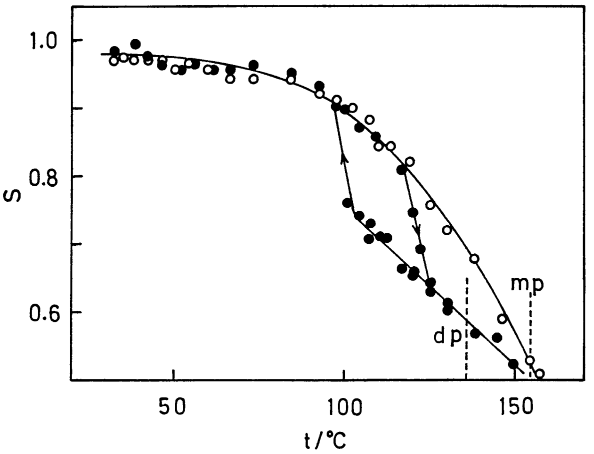

Fig. 4. Temperature dependence of the parameter S in pyrene–trinitrochlorobenzene, the 1 : 1 complex (open circles) and the 2 : 1 complex (shaded circles).

The pyrene complexes with all the aromatic polynitro compounds examined are listed in Table 1 with the S values observed at their melting points. In no case does the value change discontinuously upon solidification. When the molten DNP and TNT complexes are employed as solvents, the outer hyperfine extrema cannot be detected in the ESR spectra near their melting points; however, the extrapolation of the S-t relation obtained with the solid complexes indicates that the required S values are not far from 0.50. Thus, the rapid tumbling of VO(dbm)$_2$ occurs in none of these molecular assemblages at their melting points. The parameter S measures the motion around two axes lying in the flat plane including the vanadium atom. When the probe is dissolved in a liquid, this motion is largely governed by the volume of the solvent to be displaced by the probe molecule.[12] The ESR spectrum of VO(dbm)$_2$ dissolved in molten pyrene is essentially isotropic, that is, $S \fallingdotseq 0$. Therefore, the restricted motion in the TNC and TNT complexes, which have melting points a little higher than that of the hydrocarbon, may be considered as evidence for the association of the electron donor and acceptor molecules in the melts. The magnitude of the S value may depend not only on the size of such clusters but also on the concentration. When the melting point of a pyrene complex is much lower than 150 °C, we must deal with the question of how large the temperature dependence of the viscosity is for each complex. As the answer is not available at present, it is difficult to say in such cases whether the effect of cluster formation is really large enough to increase the S value or not. Nevertheless, if two complexes with nearly the same melting points show significantly different S values, the extent of molecular association may be larger in the complex with a larger S value. Three pyrene complexes have their melting points near 90 °C (363 K). Among them the DNC complex exhibits a much larger S value than those of the other two. Furthermore, the viscosity value estimated for the DNF complex is as large as that for the DNC complex, in spite of the melting point being higher by 32 °C. These observations lead qualitatively to the suggestion that the molecular association in these two complexes is considerable.

Table 1. The S values of VO(dbm)$_2$ dissolved in the 1 : 1 molecular complexes at their melting points (Mp), the effective viscosities (η_{eff}) at the same temperatures, and Shinomiya's melting point elevations (τ) (1 cP = 10^{-3} Pa s)

Complex	Mp/K	S	η_{eff}/cP	τ/K
Pyrene-DNB	366	0.68	9.4	−27
Pyrene-DNF	392	0.71	12.1	31
Pyrene-DNC	360	0.73	12.2	−15
Pyrene-DNT	365.5	0.67	9.0	−18
Pyrene-DNP	417	<0.5	5.6	12
Pyrene-TNC	427.5	0.53	6.1	38
Pyrene-TNT	435	<0.5	5.8	46
Fluoranthene-DNB	349.5	0.68	9.0	−23
Fluoranthene-DNF	361	0.71	11.2	9
Fluoranthene-DNC	316	0.90	43.6	−38
Fluoranthene-DNT	346	0.78	15.8	−17
Fluoranthene-DNP	364.5	0.73	12.4	−20
Fluoranthene-TNC	394	0.70	11.1	25
Fluoranthene-TNT	407	<0.5	5.5	39
Phenanthrene-TNC	361	0.78	16.5	−4

With the exception of the DNB complex, the pyrene complexes employed here are known to show rather small enthalpies of melting.[13,14] The broad-line NMR measurements clearly indicate the onset of a large degree of thermal motion in the crystalline complexes upon polymorphic transitions.[14] The motion of VO-$(dbm)_2$ observed in these complexes seems to be consistent with these earlier results. The enthalpy of melting for the DNB complex not included in our previous work was determined to be 29 kJ mol^{-1} which is slightly larger than the others.[15] Except in the case of the 2 : 1 TNC complex shown in Fig. 4, the solid-solid transition could not be detected by the variation of S with temperature. This observation is probably due to the fact that the high-temperature forms can be readily supercooled.[13]

The ESR measurements were extended to the fluoranthene complexes where the donor molecule is isomeric to pyrene. Their enthalpies of melting are as low as those of the pyrene complexes; namely, 18 to 35 kJ mol^{-1}.[15] The S values measured at the melting points and the effective viscosities at the same temperatures are summarized in Table 1. The fluoranthene complexes melt at lower temperatures by 16 to 52 °C compared with the corresponding pyrene complexes. The difference in the melting point is especially large when the acceptors are DNC and DNP. Since the DNC complex melts at an exceptionally low temperature and gives an unusually high S value and effective viscosity, measurements can be made over a wide temperature range for this particular melt. The composition of the clusters was assumed to be determined by locating the maximum in the S-composition isotherms; therefore, the mixtures with mole ratios of 3 : 2 and 2 : 3 were also examined for this interesting combination. Unfortunately, no deviation from the curve for the 1 : 1 complex could be established. This complex provides a further clue as to the possible molecular association. Fig. 5 shows a plot of the logarithm of effective viscosity against the reciprocal temperature for the 1 : 1 complex. The exponential temperature dependence can be noted above 60 °C, but the increase of the viscosity is considerably greater on approaching and passing the melting point. This behavior may be considered as an indication that molecules pack into clusters, following the argument by Ubbelohde *et al.* made for molten *o*-terphenyl.[16,17]

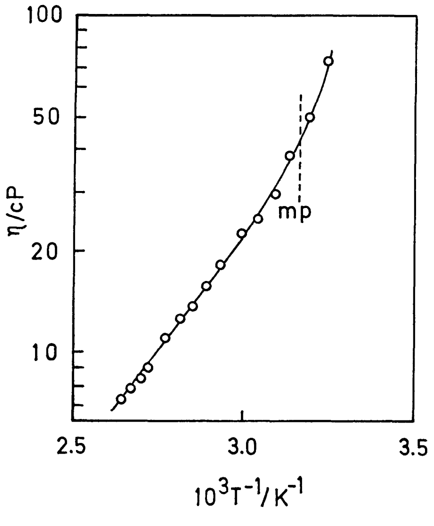

Fig. 5. Temperature dependence of the effective viscosity in fluoranthene-dinitrochlorobenzene.

Nevertheless, it must be emphasized that the high viscosity is largely due to the low melting point and that the value at the melting point may be as large as 36 cP even if the molecular association is absent.

If a complex composed of smaller molecules is selected, the molecular motion above the melting point may be fast enough on an ESR time scale to produce an abrupt increase of the S value upon solidification. With the hope of fulfilling this condition, we examined the ESR spectra of $VO(dbm)_2$ dissolved in the phenanthrene–TNC complex melting at 88 °C and the naphthalene-DNP complex melting at 95 °C. The S value in the former complex varies continuously through the melting point. In the melt of the latter, the ESR spectrum of the probe is essentially isotropic at 106 °C, but slightly deviates from it below this temperature. The value in the crystalline state could not be measured because of the segregation of the probe upon solidification.

As we mentioned already, the congruent melting point of a 1 : 1 complex is expected to be lowered when the association in the melt is less extensive. In order to compare the sequence of the complex formation, Shinomiya defined the melting point elevation for a 1 : 1 complex by

$$\tau = t_C - (t_D + t_A)/2,$$

where t_C is the melting point of the complex and t_D and t_A are the melting points of the donor and acceptor compounds respectively.[18] As we have seen, the large S value of a complex with a low melting point is mostly attributable to the exponential temperature dependence of the viscosity of the medium; therefore, no correlation between the parameters τ and S could be found.

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