Interaction of Vanadyl Acetylacetonate with Solvents: The ^{51}V Hyperfine Interaction in Mixtures of Ethanol and Carbon Tetrachloride

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The ^{51}V hyperfine coupling in vanadyl acetylacetonate has been measured for solutions in mixtures of ethanol and carbon tetrachloride as a function of solvent composition. The results indicate that interaction with at least two solvent molecules determines the hyperfine interaction, and the observations have been characterized quantitatively in terms of two equilibria.

Since Bernal and Rieger [1] first remarked on the sensitivity to solvent of the optical and e.s.r. spectra of vanadyl acetylacetonate there have been several studies of these effects. For example, Walker *et al.*[2] used e.s.r. to investigate the complexing with aza-aromatic bases, and Carlin and Walker [3] used optical spectroscopy and calorimetry to obtain the thermodynamic characterization of assumed equilibria and were able to place the solvents they studied in order of basicity.

All these studies assumed a simple equilibrium of the type

$$V + A \rightleftharpoons VA \qquad (1)$$

(1) where V represents vanadyl acetylacetonate and A the solvent, which was taken to bind at the vacant sixth position of the vanadyl complex, *i.e.* the position *trans* to the vanadyl oxygen. This simple assumption was questioned by Guzy *et al.*[4] who measured the e.s.r. and optical spectra of vanadyl acetylacetonate in a large number of solvents and pointed out that, especially for hydrogen-bonding solvents, there might be significant interaction with the vanadyl oxygen. This point, which does not appear to have been pursued elsewhere, is taken up here.

We have sought to establish whether a simple equilibrium like (1) could always be assumed by measuring the ^{51}V hyperfine coupling in vanadyl acetylacetonate as a function of composition of a two-component solvent. It was necessary to pick a pair of solvents for which the hyperfine couplings were as different as possible and which were miscible over the whole composition range, and ethanol and carbon tetrachloride were selected.

Experimental

The vanadyl acetylacetonate used was prepared by the literature method.[5] Ethanol (B.D.H.) was dried either by refluxing over magnesium and distilling or with molecular sieves. AnalaR carbon tetrachloride was dried using molecular sieves.

Samples were made up and measured in a specially constructed cell. This comprised two vessels of about 50 cm^3 capacity connected by a greaseless stopcock. One vessel was graduated in cm^3, the other had a 4-mm side-arm as an e.s.r. cell. Initially either half of the apparatus could be connected to a vacuum line through B14 cones. When making up samples one of the pure solvents was put into the graduated half of the cell which was then connected to the vacuum line, degassed by repeated freeze–pump–thaw cycles, and sealed off. A weighed amount of vanadyl acetylacetonate was put into the other half of the cell which was thoroughly purged with nitrogen gas; a measured volume of the second solvent, freshly saturated with nitrogen, was added and the solution put on the vacuum line without delay, degassed, and sealed off. Thus, starting from either pure solvent is was possible to make up solutions progressing more than halfway across the solvent-composition scale by successive distillations of small amounts of the second solvent from the graduated half of the cell. Several runs using this system were made. The total solvent volume was generally about 50 cm^3, the vanadyl acetylacetonate concentration being less than 10^{-3} mol dm^{-3}.

E.s.r. measurements were made at room temperature using a Varian New Century spectrometer. The ^{51}V hyperfine coupling was measured as the separation of the $|M_I| = \frac{1}{2}$ hyperfine components.

Results and Discussion

The method of preparing samples described above was evolved after preliminary experiments had shown how sensitive the solutions were to air. Solutions prepared on the open bench had e.s.r. spectra which changed with time, the hyperfine coupling becoming greater than that for either of the pure solvents used. At the same time the solutions became orange and in some cases separation into two liquid phases occurred, indicating the formation of a product rather insoluble in one component. These marked changes provided a useful guide as to whether leaks had occurred when using the special cell and several such runs were aborted on this basis.

The coupling constants for pure ethanol and pure carbon tetrachloride were taken as the averages from many runs. The values of 10.06 ± 0.01 and 10.65 ± 0.02 mT respectively are in accord with the literature.[4] For the analysis of 64 measurements on mixed solvents these values were held constant. The spectra stayed sharp across the whole composition range showing that all exchange processes were fast on the e.s.r. time-scale.

The data were analysed according to two equilibrium schemes. In the first it was assumed that the observed hyperfine coupling is determined by interaction with just one solvent molecule so the appropriate equilibrium is (2) where V, C, and

$$VE + C \rightleftharpoons VC + E; \; K = [VC][E]/[VE][C] \qquad (2)$$

E represent the vanadyl complex, carbon tetrachloride, and ethanol respectively. For fast exchange the observed hyperfine coupling, $\langle a \rangle$, can be written as in (3) where α and γ

$$\langle a \rangle = (Ky\gamma + x\alpha)/(Ky + x) \qquad (3)$$

are the coupling constants in pure ethanol and pure carbon tetrachloride respectively and x and y are the respective mole fractions of the two solvents in mixtures. In deriving (3) it is assumed that the concentration of the paramagnetic species

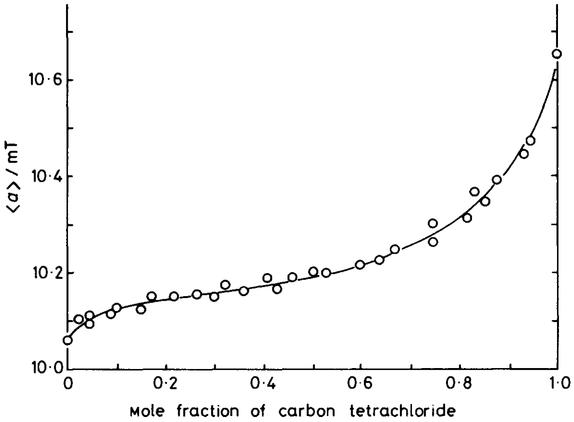

Figure 1. The measured ^{51}V hyperfine coupling as a function of the mole fraction of carbon tetrachloride. The line is the least-squares fit, according to equation (4), through the experimental points

is so small that complexation does not affect the solvent composition. A least-squares fit of the 64 measured $\langle a \rangle$ values to equation (3) yields $K = 0.32$ with $\chi^2 = 5.30$.

For the second analysis it was assumed that interaction with two solvent molecules determines the hyperfine splitting, so it is appropriate to use the double equilibrium scheme (4). It is convenient to define the equilibrium quotients as in (5) so that

$$\mathrm{VE_2 + 2C \rightleftharpoons VEC + C + E \rightleftharpoons VC_2 + 2E} \quad (4)$$

$$K_1 = [\mathrm{VE_2}][\mathrm{C}]/[\mathrm{VEC}][\mathrm{E}];\ K_2 = [\mathrm{VC_2}][\mathrm{E}]/[\mathrm{VEC}][\mathrm{C}] \quad (5)$$

the expression for the observed coupling takes the symmetrical form (6) where β denotes the hyperfine coupling for

$$\langle a \rangle = \frac{K_1x^2\alpha + xy\beta + K_2y^2\gamma}{K_1x^2 + xy + K_2y^2} \quad (6)$$

VEC. A least-squares fit of the data to equation (6) yields $K_1 = 0.04$, $K_2 = 0.13$, and $\beta = 10.14$ mT, with $\chi^2 = 1.16$.

Figure 1 shows a plot of a representative selection of some of the data together with the least-squares line. It is clear that equation (6) describes the observations significantly better than does equation (3). In fact, even qualitative inspection of the data shows that equation (3) can never be wholly satisfactory for in the plot of $\langle a \rangle$ against composition it is evident that the curvature changes sign and equation (3) can never predict this feature.

Figure 2 shows the calculated fractional equilibrium concentrations of the variously solvated vanadyl species across the solvent-composition range. One can imagine that in pure ethanol the vanadyl acetylacetonate interacts with solvent both at the sixth co-ordination position and through hydrogen bonding to the vanadyl oxygen. When carbon tetrachloride is added ethanol readily gives up the sixth position to it, although since the difference between α and β is small the interactions for both these solvents must be rather weak. Displacement of the second ethanol molecule from the vanadyl oxygen then follows significantly less readily.

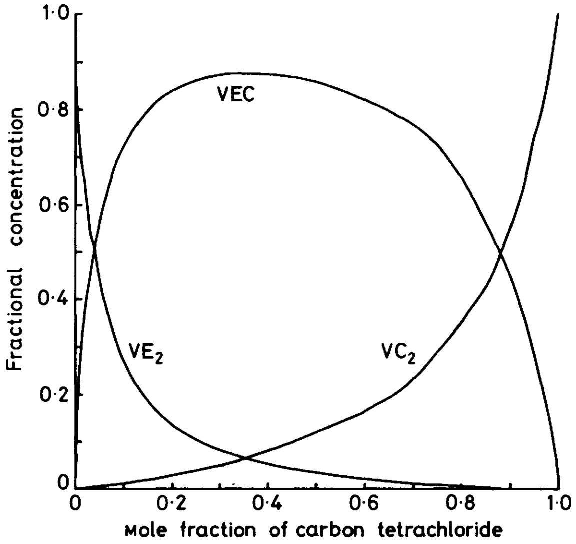

Figure 2. Equilibrium fractional concentrations of variously solvated complexes, calculated from the analysis of equation (6)

Acknowledgements

We thank the S.E.R.C. for equipment grants, the Gulbenkian Foundation for financial support for M. C. B. S., Mrs. J. Stevenson for technical assistance, and Dr. A. O. S. Maczek for advice on the least-squares fitting procedure.

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Received 21*st April* 1982; *Paper* 2/656