Clearly the best fit is obtained for eight protons or four water molecules. Further confirmation is provided by the fact that a simulated spectrum for eight deuterons, where only the magnetogyric ratio was changed, matched the experimental spectrum in D_2O almost exactly.

Since proton hyperfine structure is observed, it is evident that some delocalization of the d electron onto the water ligands occurs. In other words the interaction of Ti^{3+} with H_2O molecules is *not purely ionic.* The question is whether the magnitude of the proton hyperfine coupling can give some insight as to the extent of covalency in this complex.

The d electron is undoubtedly stabilized in the d_{xy} orbital, and thus only π bonding with the water molecules in the equatorial plane is possible. The highest bonding molecular orbital in H_2O is a pure $2p_z$ oxygen orbital perpendicular to the plane of the H_2O molecule.[7] It can participate in π bonding with Ti(III) if the plane of the H_2O molecule is oriented perpendicular to the equatorial plane of the complex. This type of π bonding would allow some spin density in the $2p_z$ oxygen orbital on H_2O, but to zero order there would be no spin density in the hydrogen 1s orbitals, and thus no proton hyperfine splitting should be seen. However, it is well known that higher-order calculations will allow some hydrogen spin density through the mechanism of spin polarization.[8] These calculations show that for a fragment of the type XH where X has a π spin density $\rho_X{}^\pi$ one may write

$$a^H = Q_{XH}{}^H \rho_X{}^\pi$$

A number of radicals of the type ROH, where R is generally a conjugated system, have been studied. From these studies[9] it is concluded that $Q_{OH}{}^H \sim 33$ G. Although the bonding situation is not exactly analogous, $Q_{OH}{}^H$ should not be too different in H_2O. If we take the above value of $Q_{OH}{}^H$ with the observed $a^H = 1.80$ G, we obtain a *total* spin density of $\sim$0.22 on all four water molecules.

There is additional evidence that a significant degree of covalency with water ligands is present. The $^{47,49}Ti$ hyperfine coupling in our complex is 14.2×10^{-4} cm^{-1}, whereas the hyperfine coupling for Ti^{3+} in a tetragonal site in MgO is 15.7×10^{-4} cm^{-1}.[10] The bonding in the latter case would be expected to be closer to purely ionic. It has been found that the magnitude of the central-ion hyperfine coupling is closely related to the spin density on the central ion.[11] Thus from the two lines of argument presented above, one may conclude that between 10 and 20% of the spin density is delocalized onto the water ligands in our complex. The actual figure is probably closer to the upper limit, as even in MgO some covalency is probably present.[10]

We are not yet ready to say what the exact nature of the complex is except that it contains four water molecules and at least one *tert*-butyl alcohol molecule. Since all protons are observed to be equivalent, we propose that the *tert*-butyl alcohol molecule attaches in an axial position with the four water molecules in equatorial positions. The nature of the other axial ligand is not known.

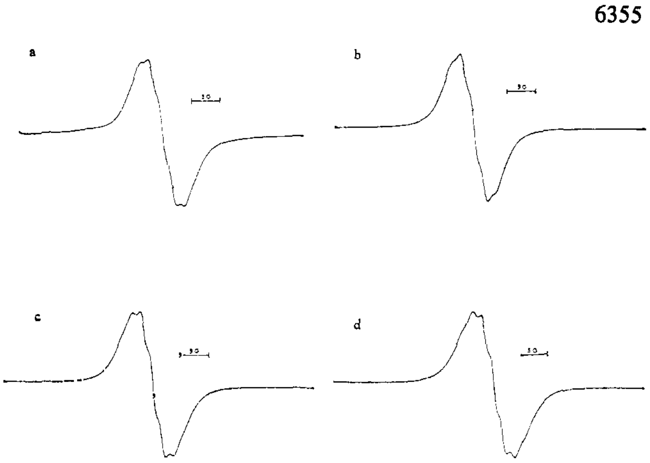

Figure 1. (a) First-derivative esr spectrum of 10^{-2} *M* $TiCl_3$ in a 20% (v/v) *tert*-butyl alcohol-water solution at pH 2.0. (b) Computer simulation based on *six* equivalent protons with a hyperfine splitting of 1.80 G and a Lorentzian line shape with a peak-to-peak width of 1.96 G. (c) Same as part b, except for *eight* equivalent protons. (d) Same as part b, except for *ten* equivalent protons. The ranges marked on the figure are 5 G.

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Energy–Volume Coefficients of Alcohol–Water Mixtures

Sir:

The energy–volume coefficient (or "internal pressure"), $(\partial U/\partial V)_T$, is one of the most fundamental thermodynamic properties of a liquid system and relates the susceptibility of the internal energy to isothermal volume change. Since both the internal energy and volume are sensitive to intermolecular interaction, it can be argued that this parameter will reflect changes in the "structure" and state of intercomponent interaction present in liquid mixtures. If this simple hypothesis is valid, the energy–volume coefficient should prove to be a valuable probe in the investigation of binary liquid systems. A few previous investigations of nonaqueous mixtures[1,2] support this claim. However, no studies of this type have been reported for aqueous–organic mixtures despite the fact that these systems often exhibit unusual properties[3] and have been used extensively in physicochemical investigations. We have investigated three aqueous alcohol systems which exhibit positive deviations from Raoult's law.[3] This behavior is determined by large negative excess entropies, suggesting considerable "structural" changes on mixing. Further, by comparing different

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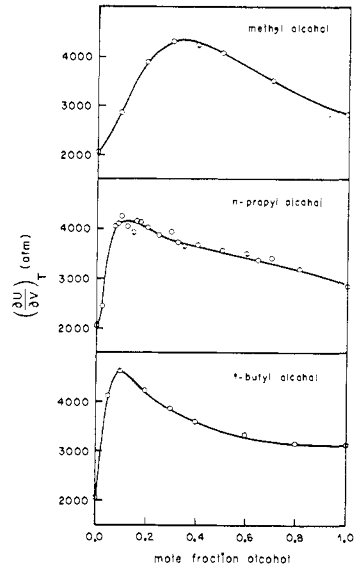

Figure 1. Energy–volume coefficients for alcohol–water mixtures at 30.0°.

aqueous alcohol mixtures it is possible systematically to study the effect of varying the "hydrophobic" character of the organic component in admixture with water. Accordingly, we report in this communication energy–volume coefficients for various mixtures of water with methyl alcohol, *n*-propyl alcohol, and *tert*-butyl alcohol.

The energy–volume coefficient is related to the thermal pressure coefficient, $(\partial P/\partial T)_V$, by the "thermodynamic equation of state"

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{1}$$

We have measured the experimentally accessible thermal pressure coefficients at a number of temperatures in the range 20–55° for the various alcohol–water mixtures using a constant-volume thermometer of the general type described by Lau, Malcolm, and Fenby.[4] Full details of the experimental procedure will be published at a later date. Energy–volume coefficients for various mixtures at atmospheric pressure and at 30° were calculated using eq 1 and are considered accurate to ±1%.

Plots of the energy–volume coefficient *vs.* solvent composition for the three alcohol–water systems examined are shown in Figure 1. The most important feature of these plots is the maximum in $(\partial U/\partial V)_T$ which occurs in the highly aqueous region of solvent composition for all systems. Such a maximum in $(\partial U/\partial V)_T$ indicates that the internal energy of the system is most sensitive to isothermal volume change at that composition. It is not unreasonable to assume that the energy of a highly structured liquid will be a sensitive function of volume. Hence the observed maximum in the so-called internal pressure is in keeping with the concept of optimization of structure by small additions of alcohol to the system.[3]

It is seen from Figure 1 that the maxima for mixtures of the two larger, or more hydrophobic, alcohols with water occur at lower alcohol mole fractions than in the case of the methyl alcohol–water system. The relative positions of the maxima are maintained if the data are plotted against volume fraction instead of mole fraction as shown in Figure 1. This relationship appears to be quite general for other properties of alcohol–water mixtures.[3] An additional feature of these data is the relative constancy in size of the maxima in all three systems. This observation is surprising, since other structure-sensitive properties of these mixtures tend to pass through much larger extrema in the case of the aqueous *tert*-butyl alcohol system than in the case of the aqueous methyl alcohol system.[3] Accordingly, it seems that the factors responsible for the size of the maxima in $(\partial U/\partial V)_T$ for the systems discussed here are not particularly sensitive to the hydrophobic nature of the alcohol.

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The Formation of Alkene Radical Cations in Solution and the Structure of the Cyclooctatetraene Radical Cation

Sir:

Alkene radical cations have been proposed as transient intermediates in various oxidation reactions of olefins,[1] and their absorption spectra reported in the solid state.[2] However, except for a few highly conjugated olefins,[3,4] no simple olefinic radical cations have been observed in solution.[5]

By a modification of our method for the generation of aromatic radical cations,[6] we have now been able to observe the esr spectra of simple olefinic radical cations in solution. The modification involved the addition of 10% $BF_3 \cdot CH_3COOH$ to the cobaltic acetate–trifluoroacetic acid solution so as to increase the oxidizing power of the cobaltic ion.[7] Using the previously described flow system, we were able to obtain esr spectra for the radical cations derived from a variety of tetrasubstituted olefins.

The esr spectrum of the tetramethylethylene radical cation, the central portion of which is shown in Figure 1, consisted of at least nine equally spaced lines separated by 16.6 G; the splitting was due to four identical methyl groups.

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