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A Study of Preferential Solvation utilizing Nuclear Magnetic Resonance

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If a solute is dissolved in a mixed solvent, the solvation shell of the solute need not maintain the composition of the bulk solvent, but may preferentially contain one component. Such preferential solvation has long been considered important, and has been tentatively explored by thermodynamic methods which no not isolate effects in the direct contact solvation shell of the solute.

We report two new methods for the study of preferential solvation utilizing: (1) the effect of solvents on the n.m.r. chemical shift of the solute and, (2) the effect of a paramagnetic solute on the n.m.r. transverse relaxation time (T_2) of nuclei in the solvent molecules. The interactions in both cases are short range[1,2] and should isolate contact solvation.

The chemical shift of the ^{59}Co nucleus in tris(acetylacetonato)cobalt(III), Co(acac)$_3$, is very sensitive to the solvent.[3] In mixed solvents such as chloroform–acetone, the chemical shift appears to be the average of the chemical shifts in the pure solvents weighted according to the mole fraction of each solvent in the contact solvation shell. A typical plot showing the ^{59}Co chemical shift of Co(acac)$_3$ in $CHCl_3$–CCl_4 mixtures is given in the Figure. (Note the curvature indicative of considerable preferential solvation.) A convenient measure of the degree of preferential solvation is the bulk solvent composition at which both solvents participate equally in the contact solvation shell. This is the composition at which the chemical shift lies halfway between the two pure solvent values. We have called this point the equisolvation point. Equisolvation points for a number of solvent pairs solvating Co(acac)$_3$ are given in the Table.

If a solute is paramagnetic [*e.g.*, Cr(acac)$_3$], solvent molecules may be exchanging rapidly between a diamagnetic environment (bulk solvent) and a paramagnetic environment (the solvation shell). Under these conditions, the transverse relaxation time of the solvent protons is given[4] by:

$$1/T_2 = p_A/T_{2A} + p_B/T_{2B}$$

where T_2 is the observed relaxation time (obtained from the line width at half height by $\pi\Delta\nu = 1/T_2$), p_A is the probability of finding a solvent molecule in the diamagnetic environment, T_{2A} is the relaxation time in the diamagnetic environment, and p_B and T_{2A} are the corresponding quantities for the paramagnetic environment. In solutions relatively dilute in paramagnetic solute, p_A is approximately unity and T_{2A} may be easily evaluated from line widths in the absence of paramagnetic solute. Thus the measured line width minus a small correction for T_{2A} is proportional to p_B/T_{2B}. One cannot readily determine T_{2B}, but it need not be known for the determination of equisolvation points. For a given component of a solvent mixture, the product

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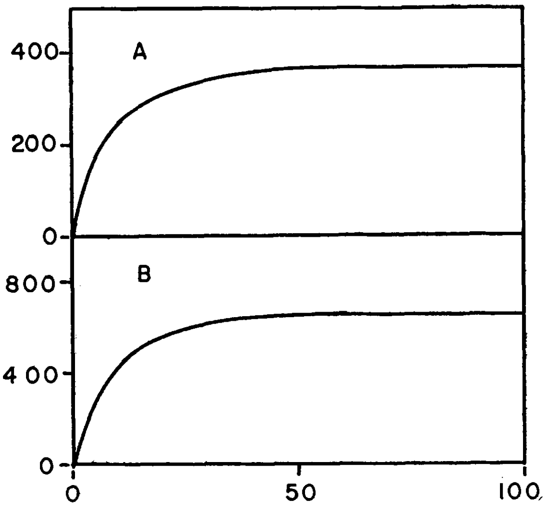
[1] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 1957, **53**, 601.

[2] N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, 1961, **34**, 842.

[3] R. Freeman, G. R. Murray, and R. E. Richards, *Proc. Roy. Soc.*, 1957, *A*, **242**, 455.

[4] H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 430.

of p_B/T_{2B} and the bulk concentration of that component is proportional to the number of molecules of that solvent component in the solvation shells. The appropriate plot for data on the proton of $CHCl_3$ in $CHCl_3$–CCl_4 mixtures with the solute $Cr(acac)_3$ is also shown in the Figure. The equisolvation point is reached when the above quantity reaches half of its magnitude in pure $CHCl_3$. Equisolvation points for a number of solvent pairs with the solute $Cr(acac)_3$ are also given in the Table.



(A) The function (line broadening in c./sec. × % $CHCl_3$) versus *% $CHCl_3$ in the solvent mixture $CHCl$–CCl_4 with the solute $Cr(acac)_3$. (B) Chemical shift in c./sec. of the ^{59}Co resonance of the solute $Co(acac)_3$* versus *% $CHCl_3$ in the solvent mixture $CHCl_3$–CCl_4.*

The assumptions involved in this analysis receive strong support from the results on the acetylacetone complexes. The expectation that solvation will be similar for such similar solutes is amply confirmed. The most "preferred" solvents in the list are $CHCl_3$ and methanol, the only ones capable of hydrogen bonding. Recent work has shown that these two solvents do indeed form weak hydrogen bonds with acetylacetone complexes.[5]

Preliminary temperature-dependence data confirm the expectation that solvation is less preferential at higher temperature. For example, the equisolvation points of the $CHCl_3$–CCl_4 systems are 5·5% $CHCl_3$ (by vol.) at 25° and 11·5% at 48°.

TABLE

Summary of Equisolvation Points[a]

Solvent System	*Co(acac)₃*[b]	*Cr(acac)₃*[c]
$CHCl_3$–CCl_4	5·5	5·4
$CHCl_3$–C_6H_6	16·2	(ref.d)
$CHCl_3$–dioxan	22·3	22·8
$CHCl_3$–acetone	26·8	24·3
$CHCl_3$–methanol	81·0	71·1

[a] The values reported are the percents by volume of $CHCl_3$ in the bulk solvent to produce equisolvation.

[b] Determined by the chemical shift of ^{59}Co.

[c] Determined by the line width of the $CHCl_3$ proton resonance.

[d] Could not be determined because of overlap of the $CHCl_3$ and C_6H_6 signals.

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[5] J. P. Fackler, Jr., and T. S. Davis, Paper No. 112M, 149th Meeting, American Chemical Society, Detroit, Mich., 1965.