and are of the same order of magnitude as the hyperconjugative delocalization of the odd electron to the C_β–M σ bond. Hyperconjugative and p–d homoconjugative interactions also both increase with increasing atomic number of the metal. Interestingly, the p–d homoconjugation between the radical center and the metal is not significantly attenuated in $R_3MCH_2\dot{C}H_2$ compared to p–d conjugation in $R_3M\dot{C}H_2$.[10] It should be borne in mind that the contributions of hyperconjugative and homoconjugative interactions do not necessarily reflect their relative importance directly in the stabilization of the radicals in the same order.

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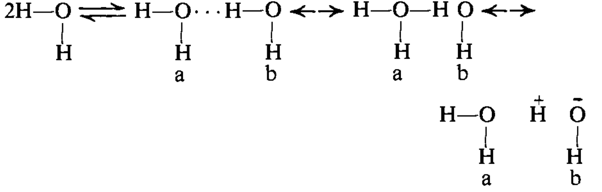
Dependence of the Acidity and Basicity of Water on the Extent of Its Hydrogen-Bonded Structure

Sir:

A pivotal idea in the flickering cluster model of liquid water is "cooperative" H bonding. Frank and Wen (FW) hypothesized that reaction 1 enhances both the



$$2\mathrm{H{-}\underset{H}{O}} \rightleftharpoons \mathrm{H{-}\underset{\underset{a}{H}}{O}\cdots H{-}\underset{\underset{b}{H}}{O}} \leftrightarrow \mathrm{H{-}\underset{\underset{a}{H}}{\overset{+}{O}}{-}H\ \underset{\underset{b}{H}}{\overset{-}{O}}} \leftrightarrow \mathrm{H{-}\underset{\underset{a}{H}}{O}\quad \overset{+}{H}\quad \underset{\underset{b}{H}}{\overset{-}{O}}} \qquad (1)$$

acidity of H in molecule a and the basicity of O in b.[1] This increases the equilibrium constants for formation of higher complexes by H bonding of the types $H_a\cdots OH_2$ and $O_b\cdots H\text{-}OH$.[2] Such cooperativity does not actually require both changes; diminished H_a acidity might be more than offset by sufficient increase in O_b basicity.

The predicted cooperativity is supported by *ab initio* MO-SCF calculations on linear water trimer.[3] Two calculations[3,4] estimate the altered charge distribution responsible for the dimer's enhanced H-bonding capability (Figure 1). Both show an increase (1.6–5.8%) in net negative charge on each open acceptor site (—▷), implying increased H-bonding basicity. Both show increased (2.5–5.2%) positive charge on the two unbonded H's of the proton acceptor, while the proton donor's single unbonded H becomes less positive (3.0–3.3%); in one case[3] the increase is quantitatively larger, in the other[4] case smaller. Hence the implication of increased H-bonding acidity in the dimer is less clean cut.

We now apply new and existing data to experimental tests of this corollary to the FW proposition: nonacidic, nonbasic solutes which promote water structure should alter the acidity and basicity of the medium.

We employed the ^{1}H chemical shift, δ_{CHCl_3}, of chloroform as a probe to study the H-bonding basicity of water as a function of structure-promoting additives. δ_{DMSO} was also measured in the same solutions as a potential solvent acidity probe, recognizing that the distance of these protons from the acceptor site makes DMSO an insensitive probe. Table I shows how δ varies with R in aqueous R_4NBr solutions of identical composition. The response of many water properties in such solutions to the change R = $CH_3 \rightarrow C_4H_9$ has been identified with strongly increasing water structure.[1,5–7] The δ_{CHCl_3} probe senses increasing $Cl_3CH\cdots OH_2$ H-bond strength in this series as judged from the increasing downfield shifts. This is consistent with enhanced H-bonding basicity with increasing water structure.[8] DMSO experiences very small high-field shifts not distinguishable from general medium effects.[8]

Table I. $CHCl_3$ and DMSO Chemical Shifts in Aqueous R_4NBr Solutions

R_4NBr[a]	δ_{CHCl_3}[b]	$\Delta\delta_{CHCl_3}$	δ_{DMSO}[b]	$\Delta\delta_{DMSO}$
$(CH_3)_4NBr$	−347.6	0	−37.2	0
$(C_2H_5)_4NBr$	−352.1	−4.5	−35.5	1.7
$(n\text{-}C_3H_7)_4NBr$	−364.2	−16.6	−34.6	2.6
$(n\text{-}C_4H_9)_4NBr$	−374.4	−26.8	−35.3	1.9

[a] 4.990 ± 0.001 *m*. All solutions 0.124 *M* in $CHCl_3$, 0.028 *M* in DMSO, and 0.095 *M* in CH_3CN. [b] δ in Hz at 60 MHz relative to internal CH_3CN; precision ±0.05 Hz; temperature, 39°. Downfield shifts are negative.

Figure 2 shows how the probe resonances respond to increasing X_{ROH} in the system water–*tert*-butyl alcohol. The downfield movement of δ_{CHCl_3} is monotonic but bulges in the region (3–9 mol % ROH) where extrema are observed in various properties and attributed to maximum water structuring.[9–11] To separate the mass-law contributions to the shifts we combined eq 2 and 3 to yield eq 4 in which $x = X_{t\text{-}BuOH}/X_{H_2O}$.[12]

$$t\text{-BuOH} + Cl_3CH\cdots OH_2 \overset{K}{\rightleftharpoons} Cl_3CH\cdots O(H)\text{-}t\text{-Bu} + H_2O \qquad (2)$$

$$\delta^{obsd}_{CCl_3H} = \delta_{CCl_3H\cdots OH_2}N_{CCl_3H\cdots OH_2} + \delta_{CCl_3H\cdots O(H)\text{-}t\text{-}Bu}N_{CCl_3H\cdots O(H)\text{-}t\text{-}Bu} \qquad (3)$$

$$(\delta^{obsd}_{CCl_3H} - \delta_{CCl_3H\cdots OH_2})/x = K(\delta_{CCl_3H\cdots O(H)\text{-}t\text{-}Bu} - \delta^{obsd}_{CCl_3H}) \qquad (4)$$

According to eq 4 a plot like Figure 3 should be linear with slope = K. Figure 3 shows no linear portion

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(1) H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

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(8) The general medium effect on δ_{CHCl_3} of the increasing volume fraction of hydrocarbon moieties in the solvent would be an increasing *high*-field shift.

(9) F. Franks and D. J. G. Ives, *Quart. Rev., Chem. Soc.*, 20, 1 (1966).

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(11) E. M. Arnett in "Physico-Chemical Processes in Mixed Aqueous Solvents," F. Franks, Ed., American Elsevier, New York, N. Y., 1967, p 105.

(12) If the formation constants for the two complexes in eq 2 are similar to those known for $Cl_3CH\cdots O(C_2H_5)_2$ and $Cl_3CH\cdots O{=}C(CH_3)_2$ (K_f = 3.75 and 2 M^{-1}),[13] the fraction of unbonded $CHCl_3$ is less than 0.01 (0.05) in solution in pure water (*t*-BuOH).

(13) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 231 (1967).

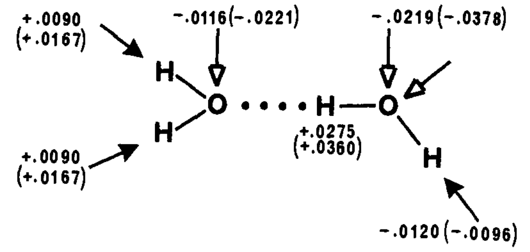

Figure 1. Changes in net atomic charges produced by dimerization.[3,4]

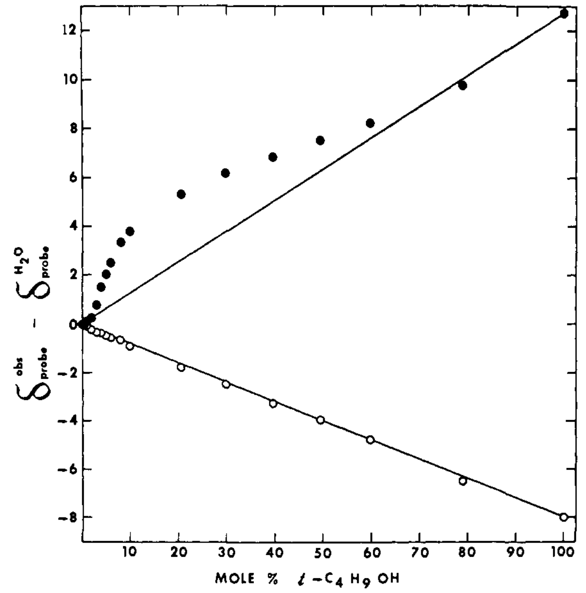

Figure 2. ¹H chemical shifts of $CHCl_3$ (●) and DMSO (○) *vs.* mole per cent *tert*-butyl alcohol in the system H_2O-*t*-BuOH at 37°. δ^{H_2O} is the shift at $X_{t\text{-BuOH}} = 0$. δ in hertz (at 60 MHz) downfield from external cyclohexane and corrected for bulk susceptibility differences. Precision: ±0.03 Hz. Original data tabulated in microfilm edition.[14]

but rather a maximum near 6 mol % *t*-BuOH, in the region of maximum water structuring. This is consistent with accompanying maximization of water's basicity.

δ_{DMSO} decreases linearly with X_{ROH} (Figure 2). The plot according to eq 4 is nearly linear and the data are consistent with $K \simeq 1.1$, at least down to *ca.* 5 mol % *t*-BuOH where the variable plotted loses precision rapidly. Thus eq 1 accounts for the observed shifts without considering water acidity changes. Whether this is due to low probe sensitivity or because the structural effect on water acidity is small must be investigated *via* better probes, probably using other nuclei.

The aqueous *t*-BuOH *OH* proton shifts[10,15] show an extra low-field shift in the 0–20 mol % *t*-BuOH region quite similar in direction and magnitude to δ_{CHCl_3} in Figure 2; but with the overall trend at higher *t*-BuOH concentration now upfield, the bulge of Figure 2 becomes a maximum at 6 mol % *t*-BuOH. If one hypothesizes that the dependence of H-bond stability on H-donor acidity is no less than that on acceptor basicity,[16] then the parallelism of δ_{OH} and δ_{CHCl_3} implies that the structure dependence of water acidity is small.

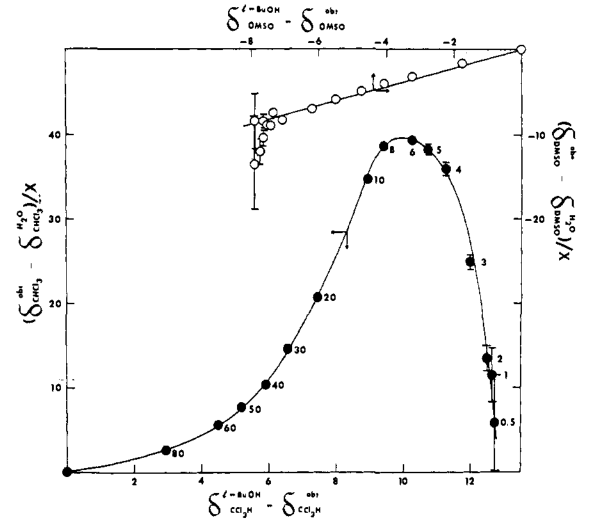

Figure 3. Chemical shift data for chloroform (●) and DMSO (○) plotted according to eq 4. Numbers near points are mole per cent *tert*-butyl alcohol.

Bergen and Long[17] (BL) showed that neutral salts of large organic ions (relative to KCl) provoke an exalted salting in of acidic (relative to neutral) nonelectrolytes. This is consistent with enhancement of water basicity by the structure-making ions, and BL in fact hinted at this explanation. Basic nonelectrolytes show *diminished* salting in by the R_4NX but not by the $ArSO_3Na$.

The weight of available evidence thus points strongly to enhanced water basicity as a consequence of enhanced water structure, but the effect (if any) on water acidity is ambiguous. These phenomena doubtless affect many common systems. Changing alkyl substitution or hydrocarbon-like cosolutes should alter the solvation of acidic and basic species and hence activity coefficients, and rate and equilibrium constants. In most cases, however, such effects are difficult to separate from other influences.

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(14) Original data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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Light-Induced Bond Switching in Oxygen and Nitrogen Analogs of Thiathiophthenes[1]

Sir:

An extended Hückel[2] calculation carried out on unsubstituted thiathiophthene (I), varying the angle α,

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(1) The electronic structure of thiathiophthenes. IV. Part III: R. Gleiter, D. Schmidt, and H. Behringer, *Chem. Comm.*, 525 (1971).

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