If it is assumed that the primary reactive species produced on photolysis of O_3 is atomic oxygen[8]

$$O_3 + h\nu \longrightarrow O + O_2 \qquad (2)$$

then two different detailed mechanisms may be proposed to explain the HOX formation

$$\text{(A)} \qquad O + HX \longrightarrow HOX \qquad (3)$$

$$\text{(B)} \qquad O + HX \longrightarrow HO + X \qquad (4)$$

$$HO + X \longrightarrow HOX \qquad (5)$$

A second product, H_2O, is probably produced by the competing reaction

$$HO + HX \longrightarrow HOH + X \qquad (6)$$

It is interesting to note that no bands assignable to the OH (OD) radical were observed despite the probable formation of this species as an intermediate in the production of H_2O (D_2O). Those bands which Ogilvie[9] suggested might belong to matrix isolated OH and OD at 3574 and 2635 cm^{-1} were sought but not found.

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Nuclear Magnetic Resonance Solvent Effects and Molecular Interactions

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Abstract: Certain solvent shifts in nmr spectroscopy have previously been explained by reaction field theory, with somewhat poor results. The authors attempt a different approach in this paper by explaining the shift in terms of collision complexes. Calculations with this model match observed shifts to within experimental error. Derived values for K, ΔH, and ΔS of the collision complexes are reasonable, K's being of order 10^{-1} l./mole, $\Delta H \sim -1.5$ kcal/mole, and $\Delta S = -6$–12 eu/mole.

It is well known that the chemical shifts of the hydrogens in a solute molecule are dependent upon the solvent used.[1,2] This solvent shift, δ_{obsd}, can be defined as the change in chemical shift for a given proton resonance on passing from a reference phase to an infinitely dilute solution in a solvent.

$$\delta_{obsd} = \delta_{ref} - \delta_{soln} \qquad (1)$$

It is generally accepted that such a solvent shift has many components.[2,3]

$$\delta_{obsd} = \delta_b + \delta_w + \delta_a + \delta_E + \delta_s \qquad (2)$$

Each of these contributions has been the subject of several investigations. A brief summary is given below. δ_b arises if an external reference is used, and is due to the bulk susceptibility differences of the solution and reference samples. In principle the effect is precisely calculable.[4,5] It can be separated from the other contributions to the solvent shift by a simple experiment outlined by Frei and Bernstein,[5,6] or by use of an internal reference.

δ_w is a downfield shift thought to arise from dispersion interactions,[2] calculations based on this model leading to better than order-of-magnitude agreement.[7] The effect is measured by use of nonpolar, isotropic solutes (*e.g.*, methane) and an external reference. A susceptibility correction is required; the separation from magnetic anisotropic effects (see below) is not necessarily obvious. The measurement or calculation of δ_w for anisotropic or polar solutes is quite difficult.

The importance of magnetic anisotropy contributions (δ_a) has been recognized for some time, particularly for aromatic solvents. Several quantitative calculations of *inter*- and *intra*molecular effects have been made for aromatic hydrocarbons.[8-10] Other important magnetic anisotropy shifts have been found in molecules containing carbonyl, nitro, and nitrile substituents.[3,11] δ_a has been detected experimentally by major deviations from expected behavior of methane based on δ_b and δ_w.[3] Thus precise measurements are limited by the uncertainties in these two values, as well as by possible "polar effects" if the solute has a dipole moment.

The solvent shifts experienced by polar molecules include all the terms described so far and, in addition, a "polar solvent shift."[3] A widely accepted explanation

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(1) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 16.

(2) P. Laszlo in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. III, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, London, in press.

(3) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 32, 1227 (1960).

(4) W. C. Dickenson, *Phys. Rev.*, **81**, 717 (1951).

(5) D. J. Frost and G. E. Hall, *Mol. Phys.*, 10, 191 (1966).

(6) K. Frei and H. J. Bernstein, *J. Chem. Phys.*, 37, 1891(L) (1962).

(7) B. B. Howard, B. Linder, and M. T. Emerson, *ibid.*, **36**, 485 (1962).

(8) C. E. Johnson and F. A. Bovey, *ibid.*, 29, 1012 (1958).

(9) B. P. Dailey, *ibid.*, 41, 2304 (1964).

(10) E. D. Becker, R. B. Bradley, and C. J. Watson, *J. Am. Chem. Soc.*, 83, 3743 (1961).

(11) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Compounds," Pergamon Press, London, 1959.

is that the polar molecule induces a dipole in the surrounding solvent. The electric field thus created (the "reaction field") produces a small change in the solute chemical shift. The effect should thus depend on the dipole moment and polarizability of the solute and the dielectric constant of the solvent.[3,12] The simple Onsager model proposed by Buckingham has many well-recognized deficiencies.[13] More elaborate, expanded treatments are available.[14,15] For a detailed review see ref 2.

The "polar shift" has been frequently defined by a simple experimental procedure. An internal reference compound, typically an isotropic, nonpolar molecule (*e.g.*, tetramethylsilane, henceforth abbreviated TMS), is used. The polar shift is reported as the solvent-induced difference in the chemical shifts of the solute of interest and the reference compound. Because of the difficulties associated with gas-phase measurements, a dilute solution in solvents such as heptane or cyclohexane is used as the reference phase.

It should be clearly recognized that such an experimental definition is fraught with many problems of interpretation. It is by no means obvious that the dispersion and magnetic anisotropy contributions to the polar solute resonance are accurately compensated for by the behavior of the internal reference.

Solvent shifts which are *very* poorly described by the above considerations are ordinarily treated as specific solute–solvent interactions. The major cases are hydrogen bonding[16] and the interaction of polar solutes and aromatic solvents.[17] These systems are describable by well-defined equilibrium constants.[18,19] Theoretical calculations for the H-bonding systems are available.[20]

This paper reexamines the solvent effects shown by polar solutes. In view of the relatively poor performance of the reaction field theory and the lack of a clear boundary between specific interactions and "bulk" effects, we propose that most, if not all, of the "polar solvent effects" can be treated as arising from specific solute–solvent complexes. In this paper we summarize the evidence that leads to this interpretation and discuss the nature of these complexes.

Experimental Section

All samples were run on a Varian A-60A spectrometer equipped with a variable-temperature probe. Chemical shifts were measured by the side-band technique using 1–5% TMS as an internal reference. The smallest sweep-width setting (50 cps) was used, permitting direct reading to ±0.01 cps. The sweep was recalibrated on each use of the spectrometer and, if necessary, a correction factor (always less than ±0.01 cps per 1 cps on the chart paper) was used. The audiooscillator (HP 200 CD) was monitored by a frequency counter (HP Model 522B) operated in the period mode. Averages of several hundred periods were used in calculating the side-band frequency. After warm-up the oscillator drift and short-term instabilities were not greater than ±0.03 cps, and often better than one part in 10^5. Relatively rapid scan rates (100 to 250 sec) were used to minimize spectrometer drift which approached ±0.2 cps (absolute) but only ±0.05 cps on a differential basis. Precision on sealed samples was ±0.05 cps. Larger errors were sometimes introduced during sample preparation (see below), so that the accuracy of the measurements, over-all, was approximately ±0.2 cps.

Samples were prepared, in most cases, from spectrograde reagents (Matheson), stored under N_2 atmosphere, and used without further purification. Analytical grade reagents were used with or without distillation, depending on the quality of the available materials. Any other reagents were distilled and dried. Several checks showed that no effect of impurities in the analytical grade reagents was detectable in our measurements.

Solutions were prepared either volumetrically or gravimetrically, the latter technique being more satisfactory. In either case the volume or weight of the active solvent was measured directly, rather than being computed by difference. Volumetric accuracies were ±1%; gravimetric accuracies were probably limited by evaporation of volatile solvents but approached ±0.3%. We investigated the effects of O_2 by preparing approximately one-third of our samples under N_2 atmosphere and then applying a wax seal. Reproducible readings could be obtained for a week or two with such samples without difficulty. In most cases the effect of O_2 was not detectable.

Temperatures were measured using the Varian-supplied methanol or ethylene glycol samples. Peak separation was determined *via* the side-band technique. Probable accuracies were ±2° with stability at any one temperature being ±1°. The ambient probe temperature varied between 39 and 44° over a period of some months.

Results

There are several lines of evidence from nmr experiments which have led us to prefer a specific association description of the data to that of either the "reaction field" theory or of a generalized nonspecific "bulk" effect. We begin by showing that monomer–dimer, and more rarely, monomer–dimer–trimer, equilibria are *sufficient* to describe *quantitatively* the concentration dependence of the solvent effects.[21] Next we consider the temperature dependences of these solvent effects and show that the temperature effects are consistent with such a model. Last, the data are examined in light of the predictions of the reaction field theory.

Solvent shifts for a given solute are reported for either infinitely dilute solutions (δ_{obsd}) or for 1 vol % solutions (δ_{obsd}'). The shifts are calculated by use of eq 1 with dilute solutions of the solute in heptane or cyclohexane serving as the reference phase.

1. Concentration Studies. A straightforward method of distinguishing between bulk effects and specific interactions is to vary the concentrations of the active species. In these experiments we kept a constant volume per cent of the solute (1%) and varied the relative amounts of inert solvent (cyclohexane or heptane) and active solvent. As shown in Figure 1, the concentration dependence of solvent shifts for nitromethane ($MeNO_2$) in various concentrations of dioxane and carbon tetrachloride is clearly nonlinear. This finding, which is general for all our data, rules out any bulk effect in which the chemical shift varies linearly with the solvent concentration.

There are several ways to decide whether the concentration dependence is representative of simple equilibria. For now we note that for the monomer–dimer case (A + B = AB) the solvent shift and the equilibrium constant are given by

$$\delta_{\mathrm{obsd}} = \alpha\delta_{\mathrm{A}} + \beta\delta_{\mathrm{AB}} \qquad (3)$$

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(12) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(13) P. Laszlo and J. I. Musher, *J. Chem. Phys.*, **41**, 3906 (1964).

(14) P. Diehl and R. Freeman, *Mol. Phys.*, **4**, 39 (1961).

(15) W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, *J. Chem. Phys.*, **36**, 3481 (1962).

(16) Reference 1, Chapter 15.

(17) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(18) E. D. Becker, *J. Chem. Phys.*, **31**, 269 (1959).

(19) P. J. Berkeley, Jr., and M. W. Hanna, *J. Phys. Chem.*, **67**, 846 (1963).

(20) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).

(21) We will use the phrase "solvent effects" to include all the chemical shift differences observed under the "Internal Reference" experimental procedure.

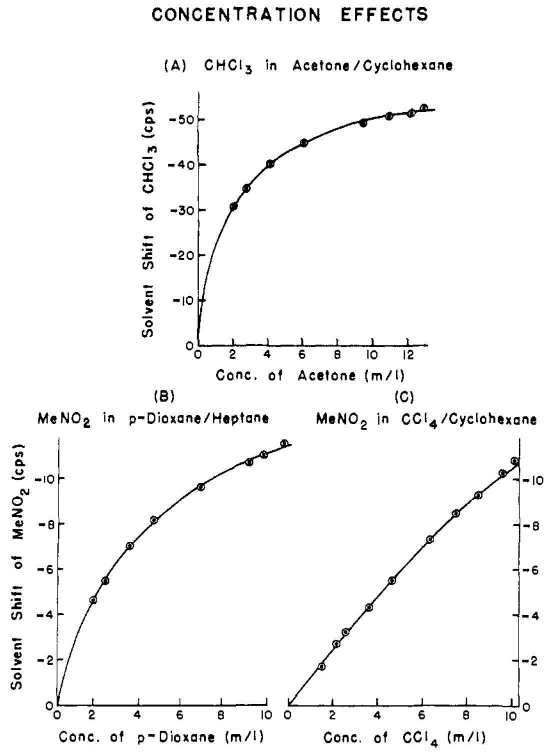

Figure 1. Concentration dependence of solvent shifts: (A) $CHCl_3$ (1%) in acetone–cyclohexane mixtures, 43° (curvature attributed to hydrogen-bond formation); (B) $MeNO_2$ (1%) in *p*-dioxane–heptane mixtures, 43°; (C) $MeNO_2$ (1%) in CCl_4–cyclohexane mixtures, 43°.

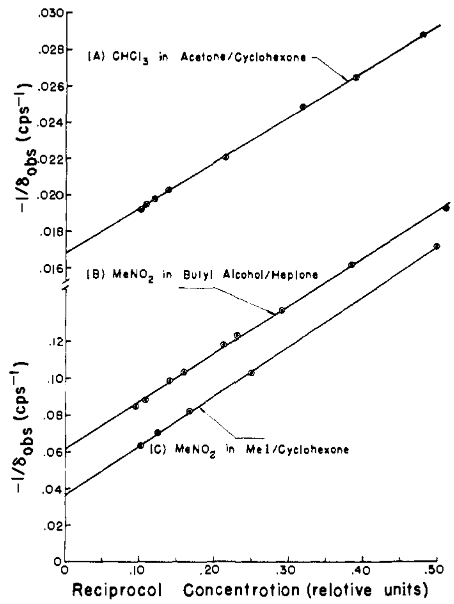

Figure 2. Double reciprocal plots of solvent shifts, 1/concn *vs.* $1/\delta_{obsd}$. Relative concentrations of "active" solvent are used; concentration of neat "active" solvent is 10.0. (A) $CHCl_3$ in acetone–cyclohexane; (B) $MeNO_2$ in *n*-butyl alcohol; (C) $MeNO_2$ in MeI. Note change of vertical scale for acetone data.

$$K_{AB} = \frac{\beta}{\alpha(B_0 - \beta A_0)} \tag{4}$$

where α is the mole fraction of the solute as monomer, β is the mole fraction of the solute as dimer, and δ_A and δ_{AB} are the solvent shifts associated with pure monomer and dimer, respectively. A_0 and B_0 are the initial concentrations of solute and active solvent, respectively. If we define $\Delta_{AB} = \delta_A - \delta_{AB}$ and arrange the concentrations such that $B_0 > A_0$, then[22]

$$\frac{1}{\delta_{obsd}} = \frac{1}{\Delta_{AB}} + \frac{1}{K_{AB}\Delta_{AB}B_0} \tag{5}$$

Thus a double reciprocal plot of $1/\delta_{obsd}$ *vs.* $1/B_0$ should yield a straight line over its *entire* range (as long as B_0 remains much greater than A_0).[23] Representative plots are shown in Figure 2. With good data the straight-line fit matches the data to ±0.2 cps (the uncertainty in our measurements). In all cases where this formulation is applicable the fit is considerably better than ±1 cps (Table I).

The power of this method of analysis is well illustrated by the solvent shifts found for nitromethane in the series of bromoalkanes. We find that a single equilibrium constant and a single Δ_{AB} accurately describe the solvent effects in all neat liquids from C_2 to C_{16} and all solutions of these liquids in aliphatic hydrocarbons (*cf.* Figure 3). Thus for these molecules of equivalent functional group, the molar concentration of the group is the only important variable, as would be expected in our treatment. We have begun experiments on multifunctional molecules. Of particular interest here are the results for multisubstituted chloro- and bromoalkanes given in Table II. Clearly, widely separated "active sites" (*e.g.*, 1,5-dibromopentane) act independently of each other giving a K_{AB} (per bromine) and a Δ_{AB} identical with an *equimolar* mixture of any monobromoalkane. As the active groups approach each other, this independence is lost. This interpretation is supported by the mathematical analysis given below.

Table I. Limiting Solvent Shifts and Thermodynamic Parameters for AB Dimers

Solute	Active solvent	Δ,[a] cps	K,[a] l./mole	ΔH,[a] kcal/mole	ΔS,[a] eu/mole	Av dev, cps
$MeNO_2$	CS_2	−25	0.03	−0.7	−9.1	±0.2
$MeNO_2$	*n*-BuCl	−17	0.09	−1.0	−8.0	±0.2
$MeNO_2$	CH_2Cl_2	−21	0.10			±0.2
$MeNO_2$	$CHCl_3$	−26	0.10			±0.2
$MeNO_2$	CCl_4	−48	0.03	−0.3	−8.1	±0.1
$MeNO_2$	$CH_3(CH_2)_xBr$[b]	−20	0.11	−0.9	−7.2	±0.1
$MeNO_2$	CH_2Br_2	−26	0.13	−0.7	−6.3	±0.1
$MeNO_2$	$CHBr_3$	−35	0.11	−1.5	−9.3	±0.1
$MeNO_2$	CH_3I	−28	0.09	−0.1	−5.4	±0.1
$MeNO_2$	*p*-Dioxane	−16	0.22	−0.9	−5.8	±0.1
$MeNO_2$	*n*-BuOH	−16	0.25	−1.1	−6.4	±0.2
$MeNO_2$	Benzene	+95	0.17	−1.5	−8.5	±0.2
$MeNO_2$	Toluene	+94	0.19			±0.2
MeI	$CHCl_3$	−37	0.02			±0.1
CH_2Cl_2	$CHCl_3$	−48	0.02			±0.1
$CHCl_3$	*p*-Dioxane	−40	0.48			±0.2
$CHCl_3$	Acetone	−59	0.52	−3.4	−12.2	±0.2
$CHCl_3$	CCl_4	−30	0.04			±0.2

[a] For uncertainties see text. [b] See text, x = 1–15.

Consider the set of "isomeric" dimers, AB, AB′, AB″, . . . , each of the same composition but each with its own equilibrium constant, K_i, and dimer shift, Δ_i.

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[22] C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Chem. Phys.*, 23, 1244 (1955).

[23] See Appendix I for further discussion.

Table II. Limiting Solvent Shifts and K_{AB} for $MeNO_2$ in Multifunctional Alkanes

Active solvent	Δ, cps	K, l./mole	K per mole of halogen
$CH_3(CH_2)_xBr$	−20.1	0.11	0.11
1,5-$Br_2C_5H_{10}$	−21.2	0.24	0.12
1,3-Br_2Pr	−21.1	0.20	0.10
1,2-Br_2Et	−21.7	0.13	0.065
CH_2Br	−26	0.13	0.065
$CHBr_3$	−35	0.11	0.04
n-BuCl	−17.2	0.09	0.09
1,4-Cl_2Bu	−17.6	0.21	0.105
CH_2Cl_2	−21	0.10	0.05
$CHCl_3$	−26	0.10	0.03
CCl_4	−48	0.03	0.01

These parameters can apply to either different active sites or different geometries on one active site. Setting up the equilibria and solving for δ_{obsd} yields

$$\delta_{obsd} = \frac{B_0 \sum K_i \Delta_i}{1 + B_0 \Sigma K_i} \tag{6}$$

Notice that eq 6 reduces to the equation for a single AB dimer ($i = 1$) as we now prove. We let $n_i = \Delta_i/\Delta_{AB}$, $e_i = K_i/K_{AB}$; then

$$\delta_{obsd} = \frac{K_{AB}B_0\Delta_{AB}\sum n_i e_i}{1 + K_{AB}B_0 \sum e_i} \tag{7}$$

Now if we define new variables Δ' and K' so that $K' = K_{AB}\Sigma e_i$ and $\Delta' = (\Delta_{AB}\Sigma n_i e_i)/(\Sigma e_i)$, then

$$\delta_{obsd} = \frac{K' B_0 \Delta'}{1 + K' B_0} \tag{8}$$

which is the same form as the equation for a single AB dimer (see eq 5). Thus such an arbitrary set of dimers of identical composition could not be distinguished by a *dilution* experiment from a single dimer whose equilibrium constant and dimer shift were K' and Δ'.

Thus K' and Δ' are apparent parameters for the multifunctional systems. They are related to the K_i's and Δ_i's of each site by the definitions above so that

$$K' = \sum_i K_i \tag{9}$$

and

$$\Delta' = (\sum_i \Delta_i K_i)/\sum K_i$$

The special case of long-chain dibromoalkanes has, by assumption, $K_1 = K_2 = K_{AB}$ for monobromoalkanes, which gives K' (per molecule) $= 2K_{AB}$ and $\Delta' = 2K_{AB}(\Delta_{AB})/2K_{AB} = \Delta_{AB}$, as observed. Those systems where intramolecular interactions occur in the solvent require more information for useful analysis (*e.g.*, 1,2-dibromoethane).

In several cases involving highly polar solutes and solvents, it was impossible to fit a straight line to the double reciprocal plots. In all such cases the data can be described by postulating a trimer with the formula AB_2 (again, A being very dilute). If we assume the concentration of B_2 to be negligible compared to B_0, the appropriate equilibria are

$$A + B \rightleftharpoons AB$$

$$AB + B \rightleftharpoons AB_2$$

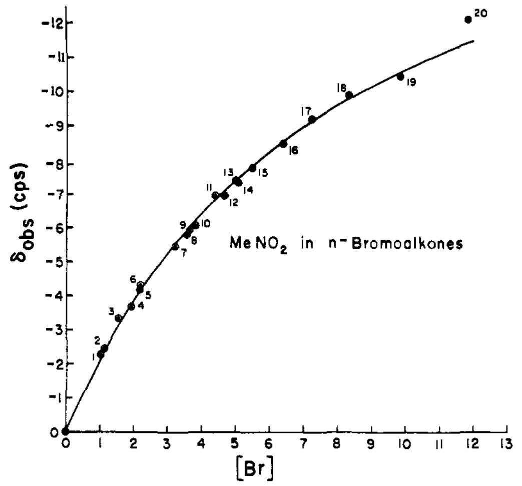

Figure 3. Solvent shifts for $MeNO_2$ in *n*-bromoalkanes. ● denotes concentrated solutions ($\geq$90%) of *n*-bromoalkanes in cyclohexane or *n*-heptane. ⊙ denotes more dilute solutions. $MeNO_2$ infinitely dilute in all cases; solid curve calculated from eq 5 with K_{AB} = 0.1286 and Δ_{AB} = 18.93. Compounds and approximate compositions are as follows: (1) 20% *n*-$C_9H_{19}Br$, (2) 30% *n*-$C_{14}H_{29}Br$, (3) 30% *n*-$C_9H_{19}Br$, (4) 30% *n*-$C_7H_{15}Br$, (5) 30% *n*-$C_6H_{13}Br$, (6) 20% *n*-C_3H_7Br, (7) 50% *n*-$C_5H_{11}Br$, (8) 50% *n*-$C_6H_{13}Br$, (9) 90% *n*-$C_{12}H_{25}Br$, (10) 60% *n*-$C_7H_{15}Br$, (11) 40% *n*-C_3H_7Br, (12) 90% *n*-$C_9H_{19}Br$, (13) 60% *n*-$C_6H_{13}Br$, (14) 90% *n*-$C_8H_{17}Br$, (15) 90% *n*-$C_7H_{15}Br$, (16) 90% *n*-$C_6H_{13}Br$, (17) 90% *n*-$C_5H_{11}Br$, (18) 90% *n*-C_4H_9Br, (19) 90% *n*-C_3H_7Br, (20) 90% C_2H_5Br.

and defining Δ_{AB} as before and $\Delta_T \equiv \delta_A - \delta_T$ where δ_T is the chemical shift of pure trimer, the equation for the solvent shift is

$$\delta_{obsd} = \frac{K_{AB}B_0\Delta_{AB} + K_{AB}K_TB_0^2\Delta_T}{1 + K_{AB}B_0 + K_{AB}K_TB_0^2} \tag{10}$$

We can use the double-reciprocal plot of $1/\delta_{obsd}$ *vs.* $1/B_0$ for analysis. As $B_0 \rightarrow 0$, the concentration of trimers can be neglected and

$$\frac{1}{\delta_{obsd}} \longrightarrow \frac{1}{K_{AB}B_0\Delta_{AB}} + \frac{1}{\Delta_{AB}} \tag{11}$$

as found for the simple monomer–dimer case. An extrapolation of the limiting line for dilute B_0 will yield as intercept $1/\Delta_{AB}$, and the slope of the line will be $1/(K_{AB}\Delta_{AB})$.

As $B_0 \rightarrow \infty$, the dimers can be neglected and then

$$\frac{1}{\delta_{obsd}} \longrightarrow \frac{1}{\Delta_T} \tag{12}$$

$$\frac{d(1/\delta_{obsd})}{d(1/B_0)} \longrightarrow \frac{(\Delta_T - \Delta_{AB})}{\Delta_T}\left(\frac{1}{K_T\Delta_T}\right) \tag{13}$$

Thus $1/\delta_{obsd}$ approaches a second linear region for higher concentrations of B_0. The limiting values (eq 12 and 13) will yield the trimer parameters if Δ_{AB} has already been found from the dependence of δ_{obsd} on low concentrations of B_0. Notice that the sign of the limiting slope at high concentrations depends on the relative magnitudes of Δ_{AB} and Δ_T. We have so far only observed positive deviations, indicating that the solvent shift of the trimer is greater than that of the dimer (downfield).

In practice there are several limitations to this graphical method of analysis, and the derived parameters should be viewed as approximate. Generally, the di-

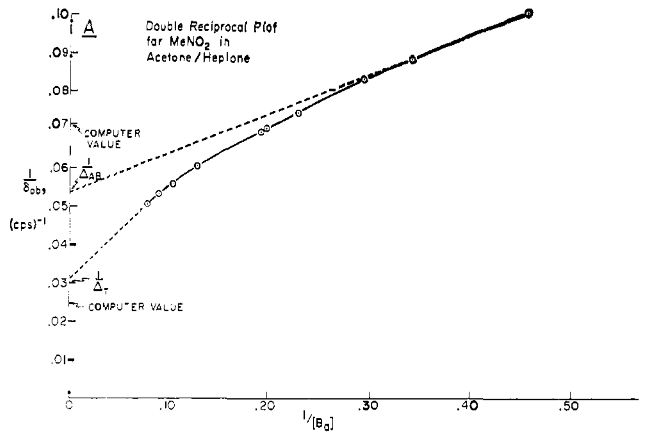

Figure 4. Double reciprocal plot of $MeNO_2$ in acetone–heptane (concentration of acetone in moles/l.). The straight dotted lines indicate extrapolations to $1/\Delta_i$; see text.

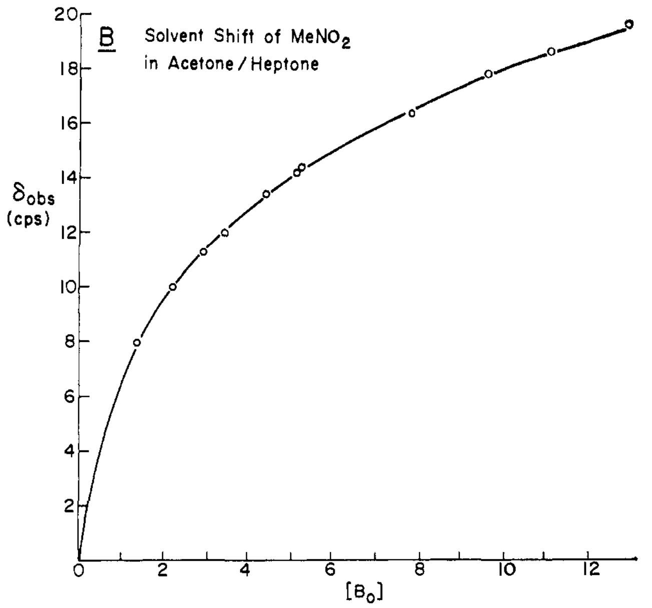

Figure 5. Solvent shifts for $MeNO_2$ in acetone–heptane. Points are experimental, 43°. Solid curve is calculated from eq 10 using K_{AB} = 0.76 l./mole, K_T = 0.029 (l./mole)^2, Δ_{AB} = 14.0 cps, Δ_T = 40.0 cps. These values were derived by computer analysis.

mer parameters and Δ_T are more reliable than K_T. Typical results for AB_2 systems are shown in Figures 4 and 5 and Table III.

Table III. Approximate Equilibrium Constants and Limiting Solvent Shifts for AB and AB_2 Systems[a]

		Dimers		Trimers	
Solute	Active solvent	Δ_{AB}, cps	K_{AB}, l. mole	Δ_T, cps	K_T, (l. mole)^2
$MeNO_2$	Acetone	−14	0.76	−40	0.03
$MeNO_2$	Benzonitrile	−10	0.4	−60	0.04
$MeNO_2$	2-Nitropropane	−15	0.6	−30	0.05
CH_2Cl_2	Acetone	−30	0.3	−60	0.06
MeI	Acetone	−16	0.1	−30	0.04

[a] These values are quite approximate (±50%). $MeNO_2$–acetone results are better (±10%) by virtue of more data points and computer analysis.

We have also studied a few systems in which only one active component was present. The postulated inter-

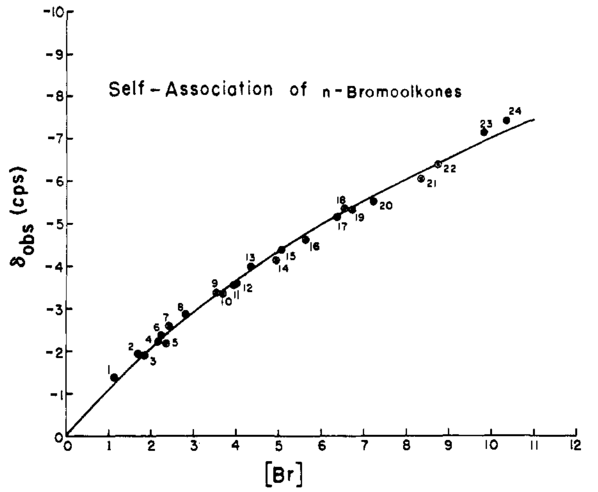

Figure 6. Self-association of *n*-bromoalkanes. ● denotes concentrated solutions (90%) of *n*-bromoalkanes in cyclohexane or *n*-heptane. All δ_{obsd}'s are measured relative to the chemical shift obtained from extrapolation to infinite dilution; solid curve calculated from eq 15 with K_{A2} = 0.0265 and Δ_{A2} = 25.0. Compounds and approximate compositions are as follows: (1) 20% *n*-$C_8H_{17}Br$, (2) 30% *n*-$C_8H_{17}Br$, (3) 20% *n*-C_4H_9Br, (4) 20% *n*-C_3H_7Br, (5) 30% *n*-$C_7H_{15}Br$, (6) 40% *n*-$C_8H_{17}Br$, (7) 30% *n*-$C_5H_{11}Br$, (8) 50% *n*-$C_8H_{17}Br$, (9) 50% *n*-$C_7H_{15}Br$, (10) 40% *n*-C_4H_9Br, (11) 70% *n*-$C_8H_{17}Br$, (12) 50% *n*-$C_5H_{11}Br$, (13) 40% *n*-C_4H_9Br, (14) 70% *n*-$C_7H_{25}Br$, (15) 90% *n*-$C_8H_{17}Br$, (16) 70% *n*-$C_5H_{11}Br$, (17) 90% *n*-$C_7H_{15}Br$, (18) 59% *n*-C_3H_7Br, (19) 60% *n*-C_3H_7Br, (20) 90% *n*-$C_5H_{11}Br$, (21) 90% *n*-C_4H_9Br, (22) 80% *n*-C_3H_7Br, (23) 90% *n*-C_3H_7Br, (24) 95% *n*-C_3H_7Br.

action is

$$A + A \rightleftharpoons A_2$$

with the equilibrium constant

$$K_2 = \frac{A_2}{(A_0 - 2A_2)^2} \qquad (14)$$

Equation 14 can be solved for A_2; the result is substituted into an equation analogous to eq 3, yielding

$$\delta_{obsd} = \frac{[1 + 4K_2A_0 - (1 + 8K_2A_0)^{1/2}]\Delta_{A_2}}{4K_2A_0} \qquad (15)$$

It will be recognized that these systems are formally identical with the self-association in H-bonding systems. There have been many suggestions for analyzing eq 15, primarily by iterative means. These we shall not discuss since they are well described in the literature.[24,25]

A much simpler alternative involves a graphical method. We can rewrite eq 15 in the form

$$\rho = \delta/\Delta_{A_2} = \frac{1 + 4\beta - \sqrt{1 + 8\beta}}{4\beta} \qquad (16)$$

where $\beta = K_{A_2}A_0$. A graph of log ρ *vs.* log β can be prepared and values of Δ and K can be read off the superimposed graph of log δ_{obsd} and log A_0. Figure 6 shows this analysis for bromoalkane solutions in hydrocarbons compared with the theoretical curve whose parameters were obtained from a log–log graph. Such a mathematical model gives a good fit to these data.

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(24) (a) S. H. Marcus and S. I. Miller, *J. Am. Chem. Soc.*, **88**, 3791 (1966); (b) M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958).

(25) (a) E. D. Becker, U. Liddel, and J. N. Shoolery, *J. Mol. Spectry.*, 2, 1 (1958); (b) C. F. Jumper, M. T. Emerson, and B. B. Howard, *J. Chem. Phys.*, **35**, 1911 (1961).

Table IV. Temperature Effects δ_{obsd}' (cps) as a Function of Temperature

Solute	Solvent (neat)	Temperature, °C 67°	40°	7°	1°	−44°	k,[a] cps/deg
$MeNO_2$	Heptane	+0.1	0		−0.1	−0.2	0.003
$MeNO_2$	Acetone		−19.7		−22.3	−24.9	0.07
$MeNO_2$	MeOH		−11.9			−13.4	0.02
$MeNO_2$	C_6H_6	56.2	62.2	70.3			0.23
$MeNO_2$	CCl_4		−10.8	−12.0			0.03
$MeNO_2$	MeI		−15.7	−16.6			0.03
$MeNO_2$	CH_2Br_2		−16.7	−17.6			0.03
$MeNO_2$	Benzonitrile	−12.6	−14.3	−15.6			0.05
$MeNO_2$	CS_2		−8.3	−9.3			0.03
$MeNO_2$	$CHBr_3$	−17.5	−19.3				0.07

[a] This coefficient has little quantitative relation to the strength of a solute–solvent interaction but serves as a qualitative indication of complex formation: J. V. Hatton and W. G. Schneider, *Can. J. Chem.*, **40**, 1285 (1962).

The critical region of this treatment occurs when $\beta \approx 0.2$ to 2.0. Thus the difficult measurements of the limiting slope as $A_0 \rightarrow 0$ are avoided. One still needs an accurate estimate of the monomer chemical shift, which in turn requires measurements on dilute solutions and extrapolation to $A_0 = 0$. There are interpretative difficulties with all of these methods, largely due to the possibility of higher polymers (A_2, A_4, ... A_n) at high concentration. A similar method can be used for AB dimers and a generalized version for A, A_n polymers is given in Appendix II.

Thus it would appear that an accurate description of the solvent shift for a wide variety of substances, as a function of concentration, is found in the monomer–dimer, monomer–dimer–trimer, and self-association cases discussed above.

2. Chemical Shifts as Functions of Temperature. If the solvent shifts are indicative of specific complexes, a prediction of their temperature dependence is straightforward. One expects that the equilibrium constants for each complex would be, in general, temperature sensitive. Since a negative entropy of association is very likely, the equilibrium constants should increase with decreasing temperature, leading to larger solvent shifts at a given solvent concentration.[26]

These expectations are fulfilled in the cases we have studied. Typical temperature effects are given in Table IV. The enthalpies of association were obtained from the van't Hoff equation. The entropy changes in turn were obtained from ΔH and K. The results fall in the range of −0.5 to −3 kcal/mole for ΔH and −5 to −10 eu/mole for ΔS (Table I). The plausibility of these numbers for weak associations tends to support this treatment of the data.[27]

A sensitive check of the internal consistency of this treatment of the temperature and concentration dependences of the polar solvent effects is available if one compares the solvent effects of a single solution at any two temperatures. The following equation holds for AB dimers,[28] where, at temperature T_i, K_{Ti} is the equilibrium constant, δ_{Ti} is the observed solvent shift at a given concentration, and Δ_{Ti} is the limiting solvent shift.

$$\frac{K_{T1}}{K_{T2}} = \frac{\delta_{T1}(\Delta_{T2} - \delta_{T2})}{\delta_{T2}(\Delta_{T1} - \delta_{T1})} \tag{17}$$

Analogous equations for A, AB_n, and A, A_n systems are given below.

$$\frac{KB_0{}^n}{K'(B_0{}')^n} = \frac{\delta_{obsd}}{\delta_{obsd}{}'}\frac{(\Delta_{AB_n}{}' - \delta_{obsd}{}')}{(\Delta_{AB_n} - \delta_{obsd})} \tag{18}$$

$$\frac{K_{A_n}(A_0{}')^{n-1}}{K_{A_n}{}'(A_0)^{n-1}} = \frac{\delta_{obsd}}{\delta_{obsd}{}'}\frac{(\Delta_{AB_n}{}' - \delta_{obsd}{}')}{(\Delta_{A_n} - \delta_{obsd})} \tag{19}$$

In these equations, the Δ_{Ti}'s are shown as temperature sensitive, although they could be constant over some temperature range. If our treatment is correct, the K's cannot be concentration dependent. Hence, if we compute the right-hand side of eq 17 for a single solvent concentration with solvent shifts measured at two temperatures, we could obtain a constant which is the ratio of the equilibrium constants. The result of these calculations for $MeNO_2$ in n-butyl alcohol (n-BuOH) and $CHBr_3$ are given in Table V. We cite this agreement as further evidence that a specific complex model affords an accurate description of the nmr shifts. If the integrated form of the van't Hoff equation is applicable, eq 17 provides the basis for a very precise estimate of ΔH.

Table V. Test of Eq 17[a] for $MeNO_2$ in BuOH and $CHBr_3$

BuOH[b] Concn, M (40°)	K_L/K_H[d]	$CHBr_3$[c] Concn, M (40°)	K_L/K_H[d]
1.22	2.11	2.24	1.25
1.57	2.17	3.36	1.25
1.95	2.11	4.47	1.24
2.60	2.10	7.78	1.23
3.44	2.11	10.90	1.23
4.32	2.06		
10.5	2.19		

[a] Δ is assumed to be temperature independent. [b] T_L = −44°, T_H = 40°. [c] T_L = 43°, T_H = 66°. [d] Not corrected for density change, which introduces a small factor approximately independent of concentration.

In passing we note a simple method for an approximate determination of ΔH. For any system described by a single equilibrium, if the conditions $\Delta \cong \Delta'$ and $\Delta \gg \delta_{obsd}$, $\delta_{obsd}{}'$ hold, then eq 17–19 simplify to

$$\frac{K}{K'}d \cong \frac{\delta_{obsd}}{\delta_{obsd}{}'} \tag{20}$$

where d is a density correction term equal to $(B_0/B_0{}')^n$ or $(A_0{}'/A_0)^{n-1}$ for the cases discussed. These conditions

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(26) An additional increment is expected if solutions of constant weight or volume fraction are used since the density and hence molarity of the solvents increases with decreasing temperature for all systems of interest here.

(27) I. Prigogine and R. Defay, "Chemical Thermodynamics," Longmans, Green and Co., London, 1965, Chapters 24–26.

(28) P. Laszlo and D. H. Williams, *J. Am. Chem. Soc.*, **88**, 2799 (1966).

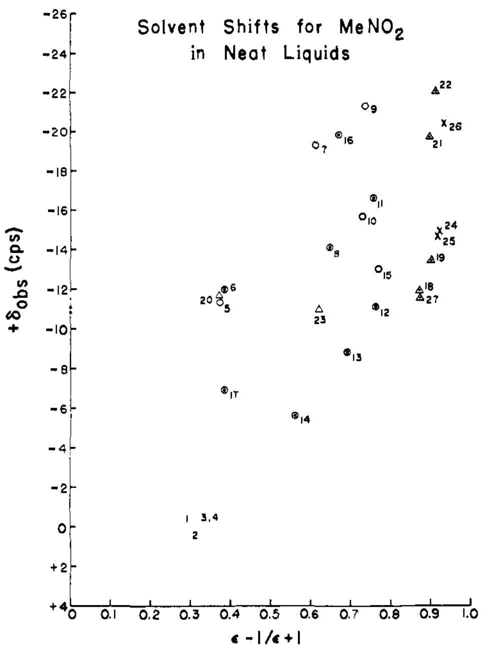

Figure 7. Solvent shifts for $MeNO_2$ in various neat liquids plotted against reaction field parameter. All points from neat liquids at room temperature (41–43°) unless otherwise indicated: (1) hexane, (2) octane, (3) dodecane, (4) cyclohexane, (5) CCl_4, (6) CCl_4, 7°, (7) $CHBr_3$, (8) $CHCl_3$, (9) CH_2Br_2, (10) CH_3I, (11) CH_3I, 7°, (12) C_3H_7Br, (13) $C_6H_{13}Br$, (14) $C_{16}H_{31}Br$, (15) CH_2Cl_2, (16) CH_2I_2, (17) $CCl_2{=}CCl_2$, (18) 1-butanol, (19) 1-butanol, −44°, (20) 1,4-dioxane, (21) acetone, (22) acetone, 2°, (23) diethyl ether, (24) 2-nitropropane, (25) benzonitrile, (26) nitrobenzene, (27) benzaldehyde.

are most likely to be met if the temperature range is narrow and if the active components are very dilute. The great simplicity of this method of determining ΔH makes precise measurements of dilute solutions attractive. The integrated form of the van't Hoff equation predicts a change in δ_{obsd} of approximately 5%/kcal of interaction enthalpy per 10° change in temperature. Density changes are typically 1–2% for a 10° change in temperature.

Error Analysis. The uncertainties in the experimental measurements have been discussed. The uncertainties in the derived quantities are more complex since they are functions of K and Δ. For moderate K's (>0.10) and Δ's, uncertainties are ±10%. For small K's (~0.01) uncertainties are much larger (~100%); in these cases the Δ's are good to ±25%. Values of ΔH obtained from eq 17 depend on the measurements directly rather than on derived values for K. Uncertainties are better than 20% for all but the smallest K's. ΔS values depend directly on the absolute value of K; errors range from 50 to 10% as K increases.

Table VI. Dielectric Constants and Observed Solvent Shifts for $MeNO_2$ in Several Solvents

Solvent	$\epsilon_{40°}$	$-\delta_0$, cps
Cyclohexane	1.99	0.0
CCl_4	2.20	11.3
$CHCl_3$	4.72	14.1
CH_2Cl_2	7.8	13.0
CH_2Cl_2	7.8	13.0
CH_2Br_2	6.68	21.3
CH_2I_2	(5.1)	19.8
p-Dioxane	2.18	11.7
Et_2O	4.30	11.0
1-Butanol	14.9	11.9

3. **Reaction Field Theory.** The specific complex approach appears to offer a quantitative treatment of solvent shifts in organic systems. It is worthwhile to make a brief comparison with the reaction field theory which is the presently accepted treatment of "polar solvent shifts."[2] We show in Figure 7 that the simple version of the reaction field theory is not quantitatively applicable to the solvent shifts for $MeNO_2$ in neat liquids. In some ways the correlation is even worse than Figure 7 indicates. If we select solvents with similar functional groups but different dielectric constants (Table VI), observed solvent shifts are approximately *independent* of ϵ.

Table VII. Predicted Solvent Shifts for BuOH–Heptane Mixtures

BuOH, M	Calcn solvent effects $-\delta_0 = a\frac{\epsilon - 1}{\epsilon + 1} + b^a$	$-\delta_0$ from assocn model (eq 5)	Exptl $-\delta_{obsd}$, cps
1.22	1.4	3.6	(3.21)
1.57	2.1	4.4	4.47
1.95	2.6	5.1	5.19
2.60	4.2	6.2	6.16
3.44	6.1	7.3	7.29
4.32	7.6	8.2	8.11
4.68	8.2	8.5	8.48
6.24	9.7	9.6	9.66
7.06	10.5	10.1	10.06
9.15	11.2	10.9	10.90
10.5	(11.9)	11.4	11.87

[a] f (ϵ) evaluated following Abraham[29] and Buckingham, Schaefer, and Schneider.[3] b is set equal to zero for resonance of $MeNO_2$ in heptane. a is not predictable from theory and was chosen to yield the observed solvent shift in 10.5 M 1-butanol.

The concentration dependence of solvent effects in mixtures of 1-butanol and heptane is shown in Table VII. Solvent effects were calculated from the Buckingham model[3,29] from the measured dielectric constants of the mixtures.[30] Although the calculated value in neat butanol was adjusted to match the experimental result (a generous assumption considering the scatter in Figure 7), the general fit is not good and is systematically low at low concentrations of alcohol. Solvent shifts calculated on the association model are given for comparison. Note that butanol provides one of the more favorable cases for the reaction field theory.[31] Using the "best slope" from Figure 7, the predicted values for $MeNO_2$ in dioxane are off by a factor of 2 (up to 6 cps). It is, of course, quite possible that there are mixtures in which the variation of dielectric constant with composition does correlate with solvent shifts. Our point is that such correlation is not a general phenomenon and perhaps only reflects the fact that the dielectric constant is related in a direct but nonlinear way to the microscopic properties of the liquids involved.

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(29) R. J. Abraham, *Mol. Phys.*, 4, 369 (1961).

(30) J. Timmermans, "The Physico-chemical Constants of Binary Systems in Concentrated Solutions," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1959.

(31) The small amount of $BuOH \cdots MeNO_2$ hydrogen bonding would not be expected to influence the methyl protons of $MeNO_2$.

Temperature dependences of dielectric constants give the correct sign but equally incorrect magnitudes for solvent effects at various temperatures. The slope of the curve relating δ_{obsd} to $(\epsilon - 1)/(\epsilon + 1)$ at different temperatures varies from 35 to 72 cps. The limits of the corresponding slope in Figure 7 are approximately 16–30 cps. Finally, the reaction field treatment could not lead to the observed agreement with eq 17 (Table IV).

Discussion

This treatment of solvent effects in terms of specific complexes is an obvious extension of the *formalism* used with hydrogen-bonded interactions or the benzene, polar solute complexes. For hydrogen-bonded systems large amounts of supporting evidence for complexation is available from many experimental techniques.[32] Evidence for specific complexes in polar liquids or in aromatic solvents is more tenuous.[22,33-35] For the present we will focus on the evidence presented here. Three major arguments are offered to support this model.

1. The precision of the mathematical description of the solvent effects is quite good, essentially within experimental error.
2. The same mathematical description readily accommodates the nmr solvent shifts found for weak hydrogen bonds, polar solutes in aromatic solvents, and polar solutes in the solvents discussed here. We do not, of course, imply that the mechanism of interaction is the same in these three cases. We only point out that the same formalism can apply to all these interactions. To the extent that specific complexation for weak hydrogen bonds is well established, the similarity with the behavior of polar liquids supports the model of specific complexes in the latter case.
3. The derived thermodynamic parameters are quite reasonable for weakly interacting systems. Both the enthalpy (-0 to -3 kcal) and entropy changes (-6 to -12 eu) on association follow an extrapolation of the hydrogen-bonding values found for $CHCl_3$ and CH_2Cl_2. The enthalpy and entropy of association also provide a quantitative description of the temperature dependencies of the solvent shifts (see further discussion below).

These arguments provide a certain amount of circumstantial evidence for the specific association model. A much wider range of experiments, including non-nmr results are clearly required before a firm conclusion can be reached.

Several aspects of the specific interaction model need further discussion. First, the thermodynamic measurements have an unusual reference state. It will be remembered that an "inert" (*e.g.*, hydrocarbon) reference state has been employed. Two observations support the assumption of the inertness of the hydrocarbon solvents. First, weak interactions would produce curvature of the double-reciprocal plot (see Appendix I) which is not observed. Second, a temperature dependence of solute resonance would be expected for an active solvent. However, the chemical shift of $MeNO_2$ in heptane or cyclohexane moved less than 0.3 cps in 70°. For comparison, carbon tetrachloride would produce approximately a 1.4-cps shift for this temperature change (Table IV).

A much more important reservation surrounds the use of an internal reference compound. All of the results must be interpreted as the difference between the interaction of polar solute and solvent and the interaction of nonpolar reference (TMS) and solvent. This situation is quite analogous to that employed in hydrogen-bonding experiments. But it is clear that many of the interactions in solution are excluded from measurement if they affect solute and reference equally. These excluded interactions are certainly not small compared to the ones that are measured.

For a typical organic liquid the total interactions can be roughly estimated by the changes in the thermodynamic functions on condensation of a gas to a liquid ($\Delta H_{\text{vap}} \simeq 8$ kcal/mole; $\Delta S_{\text{vap}} \simeq 20$ eu/mole). Only a small fraction of the total interactions are actually being observed ($\Delta H_{\text{dimer}} \sim 1$ kcal/mole, $\Delta S_{\text{dimer}} \sim -8$ eu/mole). We speculate that the nmr experiments are primarily measuring the "polar" contributions (*i.e.*, dipole, dipole-induced dipole, and higher multipole terms), because most nonpolar interactions, being roughly a function of the total number of electrons in the molecules, can be expected to be approximately the same if the reference compound and the solute are of similar size, as here.

Our picture of these interactions should be clarified. First, the very weak nature of these interactions is not consistent with a two-state system (*i.e.*, "monomer" and "dimer") on a molecular level. Rather, we are surely measuring a weighted average of a wide range of "pair-wise" interactions. A similar averaging must occur with respect to orientation. The discussion of "isomeric" dimers (eq 6–9) shows that an infinite number of instantaneous geometries will yield only a single average K and Δ. We thus assume the complexes to be very short-lived with lifetimes of the order of the collision times in liquids (10^{-11} sec). The "ordering" of the liquid associated with the interactions is likely to be both short term and short range (nearest neighbor).

The general problem of functional group contributions to the thermodynamic properties of molecules has been discussed in detail by Leffler and Grunwald.[36] Their analysis offers the possibility of deriving a useful physical model for complex interactions in solution when sufficient experimental data are available.

A major shortcoming of the present state of our model is the lack of predictability of the limiting solvent shifts. We feel we can still eliminate from consideration those simple modifications of the reaction field effect which assume a continuous dielectric. The limiting solvent shifts are not well represented by any monotonic function of the dielectric constant of the solvent (Table I), Preliminary measurements of a narrow range of halogen-containing compounds (Table I) indicate that the limiting shifts are roughly correlated with the expected first-order anisotropy effects (I > Br > Cl). The magnetic anisotropy of aromatic solvents is the accepted source

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(32) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(33) (a) M. Horak and J. Pliva, *Spectrochim. Acta*, 21, 911, 919 (1964); (b) R. Ulbrich, *Z. Naturforsch.*, **19b**, 978 (1964).

(34) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1715 (1963).

(35) R. C. Fort, Jr., Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966, Paper S23.

(36) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, New York, N. Y., 1963, particularly Chapter 6. We thank one of our referees for this useful reference

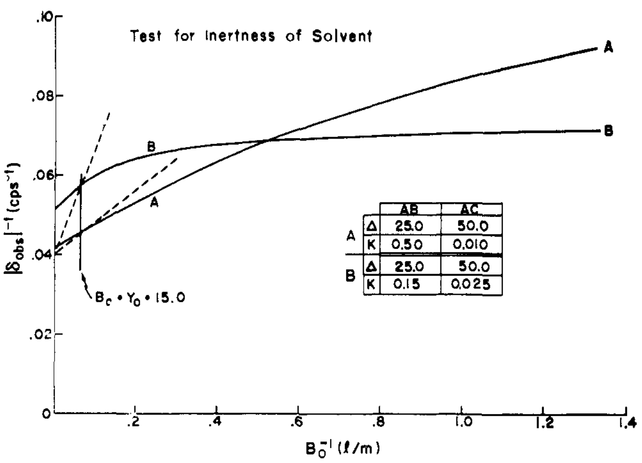

Figure 8. Test for inertness of solvent (two solutions of eq I-2 for $Y_0 = 15.0$). δ_{obsd} is the chemical shift of solute A and B_0 is the concentration of solvent B_0 (note: $B_0 + C_0 = Y_0$). The dotted lines represent the results which would have been obtained had the solvent C been inert. The solid vertical line represents the maximum concentration of B experimentally possible; the solid curves to the left of this line are extrapolations. Note how much more severe the error is for case B than it is for case A.

of solvent shifts in these compounds. Thus it is possible that some combination of reaction field and anisotropic components explains the limiting solvent shifts. Further studies are in progress on this point.

The advantages of this approach over the reaction field treatments are the more precise quantitation for both concentration and temperature dependences and the separation of the nmr (limiting solvent shifts) and thermodynamic (ΔF, ΔH, ΔS) problems. Furthermore, there is no need to postulate anomalous solvents. The disadvantage of this model, with respect to reaction field theory, is that a more complex description of interactions in solutions is required.

Conclusions

We proposed a specific complex model to explain the polar solvent shifts. Such a model delineates two separate problems: (1) the limiting solvent shifts and (2) the thermodynamic quantities (K's, ΔH's, ΔS's). Evidence to support this picture comes primarily from the precise mathematical description of concentration and temperature effects. Additional evidence comes from the reasonable magnitude of the thermodynamic parameters and the close similarity of weak hydrogen-bonded systems.

Acknowledgment. The authors wish to thank Messrs. Mark D. Jewett and Frank Puleo for their assistance in the preparation and running of some of the samples. We gratefully acknowledge the financial assistance of an Eastman Kodak research grant.

Appendix I. Limitations of Double-Reciprocal Plot

Consider the set of dimers AB, AC, AD, ..., using similar definitions and conditions (*i.e.*, B_0, C_0, D_0, ..., $\gg A_0$) where B_0, C_0, D_0, ... are molar concentrations of different solvents all present in the same solutions. In this case the appropriate equation is

$$\delta_{obsd} = \frac{K_{AB}B_0\Delta_{AB} + K_{AC}C_0\Delta_{AC} + K_{AD}D_0\Delta_{AD} + \ldots}{1 + K_{AB}B_0 + K_{AC}C_0 + K_{AD}D_0 + \ldots} \quad \text{(I-1)}$$

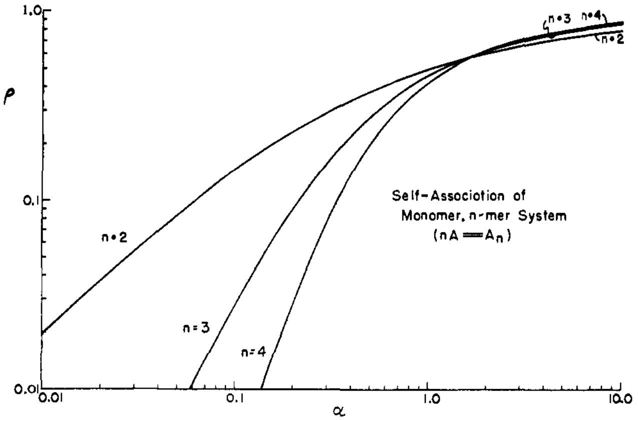

Figure 9. Self-association of monomer–n-mer system for the reaction $nA = A_n$ for $n = 2, 3, 4$. ρ and α are reduced variables (see eq II-3 and II-4 and 26). These curves can be used to determine n, K, and Δ. Note that the limiting slope for each curve as $\alpha \rightarrow 0$ is $n - 1$.

A very interesting situation arises if the solvent concentrations are not independent. This situation might occur if a poor choice of "inert solvent" is made and complexes of measurable strength are formed. Assume for convenience that the "active" solvent, B, and the "inert" solvent, C, have the same molar volume so that $B_0 + C_0 = Y_0$, the total molar concentration. We again assume B_0, $C_0 \gg A_0$ and

$$\frac{1}{\delta_{obsd}} = \frac{1 + B_0(K_{AB} - K_{AC}) + K_{AC}Y_0}{B_0(K_{AB}\Delta_{AB} - K_{AC}\Delta_{AC}) + K_{AC}Y_0\Delta_{AC}} \quad \text{(I-2)}$$

where K_{AB} and Δ_{AB} refer to the dimer AB and K_{AC} and Δ_{AC} refer to the dimer AC. If K_{AC} and Δ_{AC} are not negligible compared to K_{AB} and Δ_{AB}, the double reciprocal plot will not yield a straight line. As Figure 8 indicates, even reasonably small interactions for the AC dimer will give quite pronounced negative curvature. This should be distinguished from the positive curvature which arises if the assumption $B_0 \gg A_0$ breaks down. Thus linearity on a double-reciprocal plot provides a rather sensitive test for the "inertness" of the inert solvent. Some confusion might arise if the possiblity of trimers (AB_2) exists because double-reciprocal plots could yield curves of similar shape over some concentration ranges (see text). However, this problem is not usually serious because trimers become important only at high concentrations in strongly interacting solvents, whereas the situation of competition between two solvents for the solute is severe only when the interaction under study is not much stronger than possible interactions with the "inert" solvent. Aliphatic hydrocarbons as inert solvents are strongly recommended because even very weakly interacting solvents such as CCl_4 and CS_2 yield linear double-reciprocal plots when heptane or cyclohexane are used as diluents (with $MeNO_2$ the dilute solute).

Appendix II. Polymeric Self-Association

Consider a system composed completely of monomer and *single* n-mer species; then

$$nA \rightleftharpoons A_n$$

and, letting $X = [A_n]$

$$K = \frac{X}{(A_0 - nX)^n} \qquad \text{(II-1)}$$

and

$$\delta_{\text{obsd}} = \frac{nX\Delta_{A_n}}{A_0} \qquad \text{(II-2)}$$

There are several studies in the literature, primarily of strongly associated species such as alcohols, in which the assumptions and approximations needed to determine n are discussed.[22,37,38] A general and precise graphical method for determining the value of n for such equilibria is discussed below.

We shall use an indirect method to generate a log–log plot of reduced variables. Substituting $\rho = \delta_{\text{obsd}}/\Delta_{A_n}$ into eq II-2, solving for X, and substituting this expression into eq II-1 and rearranging, we have

$$K_{A_n}A_0^{n-1} = \frac{\rho}{n(1 - \rho)^n} \qquad \text{(II-3)}$$

then

$$\alpha = \left[\frac{\rho}{n(1 - \rho)^n}\right]^{1/(n-1)}$$

where

$$\alpha = \varphi A_0, \text{ and } \varphi = K_{A_n}^{(1/n-1)}$$

Rather than solving for ρ in terms of α, it is only necessary to select convenient values of ρ and calculate the unique values of α associated with them (for each n). Figure 9 presents log–log plots of ρ *vs.* α for $n = 2$, 3, and 4. To determine whether a single monomer–n-mer equilibrium describes the observed chemical shifts, one compares a plot of log δ *vs.* log A_0 to the plots for various n's. Δ_{A_n} can then be found as before. K_{A_n} is calculated from

$$K_{A_n} = \varphi^{n-1} \qquad \text{(II-4)}$$

From eq II-3 we see that the limiting slope of a plot of log ρ *vs.* log α as $\rho \rightarrow 0$ is $n - 1$. Thus log–log plots yield n, Δ, and K for the monomer–n-mer equilibria.

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(37) L. A. LaPlanche, H. B. Thompson, and M. T. Rogers, *J. Phys. Chem.*, **69**, 1482 (1965).

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Dynamic Enhancement of Fluorine Nuclear Magnetic Resonance Signals. Some Effects of Chemical Environment

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Abstract: Dynamic polarization of fluorine nuclei in free-radical solutions (diphenylpicrylhydrazyl and galvinoxyl) has been studied for a selection of fluorocarbons of different chemical nature. The observed nmr enhancements and the amount of scalar coupling, due to electron density at the F nucleus, are shown to vary considerably upon change of radical or fluorocarbon. Aromatic fluorocarbons always show higher scalar rates than do saturated compounds. The halo-substituted fluorobenzenes show regular trends indicative in part of complicated π-system interactions. Exchange polarization, after the manner of coupling on free radicals, and complex formation appear to be the dominant mechanisms producing the observed effects.

In contrast to hydrogen,[1] the dynamic polarization of fluorine nuclei is extremely sensitive to the detailed chemical environment of the resonating nucleus. Observed ^{19}F nmr enhancements are governed by the type of free radical and fluorocarbon present.[2] Moreover, the presence of an additional nonfluorine-containing compound in the system can strongly influence the signal strength.[3] Because the interactions between these species become exceedingly complex when all three are varied independently, we have limited ourselves here primarily to the presentation of detailed experimental results for systems designed to isolate variations in polarization arising from different fluorocarbons interacting with a given radical, diphenylpicrylhydrazyl (DPPH). The fluorocarbons used not only demonstrate the range of nmr enhancements to be expected for F in different chemical environments, but also lead to generalizations which relate observed enhancements to the aromatic character of the fluorocarbon, to the position of the ^{19}F nucleus in aromatic isomers, and to the number of F atoms in a given compound. In addition, the effects of NO_2, I, Br, and Cl as substituents are investigated.

Theoretical interpretation of the results is not straightforward. We present data for a selection of fluorobenzenes in DPPH and galvinoxyl (GALV) which demonstrate that relative enhancements within a series of fluorocarbons can change drastically upon change of radical. This, when coupled with our previous results[2] for hexafluorobenzene with various radicals, shows that any comprehensive theory must not be restricted to interpretations arising solely from the ground-state properties of the radical or the fluorocarbon: interactions between the two must be con-

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