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relatively lower cmc's of FC surfactants. It can be noted in this context that the incremental free energy per CH_2 group for transfer from an aqueous to a FC environment is −690 cal/mol, while it is −1210 cal/mol for the transfer of a CF_2 group to a HC environment.[17] These trends in free energy differences are in line with the findings in the present paper.

For experimental reasons, all measurements have been made in D_2O instead of normal water. It could be argued that solubilization and aggregation behavior in micellar systems might differ significantly between these two solvents and that our results might not be comparable to those found in other studies made in normal water. We have investigated this problem in a rather complete study, which clearly indicates that such effects are insignificant.[19] Also, it is well established that cmc's, which are directly aggregation-related quantities, differ insignificantly between normal and heavy water.[13,20]

Conclusions

It is demonstrated that NMR self-diffusion measurements provide a tool for the elucidation of the actual compositions of micelles in mixed micellar solutions. In principle, the measurement approach could be extended to system of more than two surfactants.

Results from measurements in aqueous solutions in HC and FC surfactants are consistent with an assumption of two coexisting micelle types, one rich in HC surfactant and the other rich in FC surfactant. The origin of the effects leading to separate micelle types is the nonideal mixing process between hydrocarbons and fluorocarbons.

Registry No. SD, 1002-62-6; SPFO, 335-95-5; SPFN, 21049-39-8.

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Linear Solvation Energy Relationships. 21. Gas-Phase Data as Tools for the Study of Medium Effects

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We have examined functions relating the π^* scale of solvent dipolarity/polarizability to refractive indexes and dielectric constants for the gas phase and a wide range of solvents. It has been found that the Ooshika–Bayliss–McRae formalism provides an excellent fitting of the data for nonprotonic nonpolychlorinated aliphatic solvents ("select solvents") and for the gas phase, as well as a reasonable fitting for the perfluoroalkanes. This simple equation also correlates medium effects on other properties. Polychlorinated aliphatic and, particularly, aromatic solvents are not adequately described by this method. We believe that the latter behavior is not a consequence of the inexactitudes of the model but rather reflects more complex solvent/solute interactions at the molecular level. Finally, a clear link has been established between the $d\delta$ term in the solvatochromic equations and "cross terms" in equations by Carr and Brady and Taft, Abboud, and Kamlet.

I. The Present Status of the Relationship between the π^* Scale and Structural Properties of the Solvents

In recent years the use of empirical solvent property scales[4] has become increasingly generalized and their scope and usefulness seem now to be reasonably well established.[5] In this respect, we have been particularly involved in the application of the π^* scale of dipolarity/polarizability[6] to solvent effects on physical and chemical properties of dipolar reactants and indicators. We have

shown[5,6] that, in cases wherein hydrogen bonding effects are excluded, medium effects of a series of solvents of varying dipolarity on a property, XYZ, of a dipolar solute follow eq 1.

$$XYZ = XYZ_0 + s(\pi^* + d\delta) \qquad (1)$$

XYZ_0 is the regression value of the property in cyclohexane (the reference solvent), π^* is the solvent dipolarity/polarizability parameter, and δ is a "polarizability correction factor" equal to 0.0 for a select solvent set (SSS) of nonprotic nonhalogenated aliphatic solvents with a single dominant bond dipole, 0.5 for polyhalogenated aliphatic solvents, and 1.0 for aromatic solvents. The XYZ's that have been successfully correlated by eq 1 include positions of maximal absorption in UV/visible absorption[6a,7a] and fluorescence spectra,[5b,7b] NMR shifts and coupling constants,[5b,7d] IR spectra,[7c] logarithms of rate constants,[5b,7e] and free energies of transfer of polar solutes between solvents.[6b,c] For the SSS, eq 1 takes the extremely simple form of eq 2.

$$XYZ = XYZ_0 + s\pi^* \qquad (2)$$

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A great deal of attention is being paid to the problem of the relationships between the π^* scale and more fundamental properties of the solvents. We now know that for the SSS, π^* varies approximately linearly with the solvent molecular dipole moment, μ_s, according to eq 3.[8]

$$\pi^* = 0.023 + 0.233\mu_s \tag{3}$$

Thus, the π^* value for any solvent might (incorrectly) appear to be a measure of "dipolarity" alone.

That π^* might depend only on solvent dipolarity seems also to be strongly supported by reaction field models, among which the simplest is that developed by Onsager[9] and Kirkwood.[10] There, the solute molecule is assumed to be a sphere of radius a with a point dipole μ located at the center (note: μ_s is solvent dipole, μ is solute dipole). The solute dipole interacts with the solvent molecules, creating an electric field, the reaction field, E_R. In the case of a nonpolarizable solute embedded in an isotropic solvent, this theory leads to eq 4, wherein ϵ is the bulk dielectric constant of the solvent.

$$E_R = 2(\epsilon - 1)/(2\epsilon + 1)\mu/a^3 \tag{4}$$

The concept of reaction field is extremely valuable; E_R can be related to a number of solvent effects including UV/visible,[11] fluorescence,[12] IR,[13] and NMR[14] frequency shifts and free energies of transfer between solvents.[14] Thus, it has rationalized the proportionality between these seemingly unrelated phenomena. This model also predicts a correlation between medium effects and the dielelctric function, $\phi(\epsilon)$, eq 4'.

$$\phi(\epsilon) = (\epsilon - 1)/(2\epsilon + 1) \tag{4'}$$

If the solute polarizability is taken into account, the functional relationship between μ and E_R becomes more complex. It is worth pointing out that, in the cases where the solute refractive index is close to $\sqrt{2}$, the dielectric function in the Onsager–Kirkwood model is given by eq 5.[15b]

$$\psi(\epsilon) = (\epsilon - 1)/(\epsilon + 1) \tag{5}$$

On the conceptual basis of the reaction field, correlations have been sought[5b] between medium effects and these and other dielectric functions. In fact, not only do such correlations exist,[5b,c] but they appear often to be statistically excellent. For example, we find that for all select solvents for which data are available (covering the range *n*-heptane to Me$_2$SO), eq 6 applies at the 95% confidence level, with n (the number of data points) = 36, r (the correlation coefficient) = 0.969, σ (the standard deviation) = 0.07, and F (statistic) = 519.

$$\pi^* = -0.66(\pm 0.12) + 3.11(\pm 0.28)\phi(\epsilon) \tag{6}$$

The existence of equations such as eq 3 and 6, and the fact that many solvent-sensitive properties approximately follow equations of this form seems to imply that, for the SSS, medium effects are essentially determined by dipolar forces.

The above notwithstanding, it is known that dipole/dipole and dipole/induced dipole interactions are usually only a small fraction
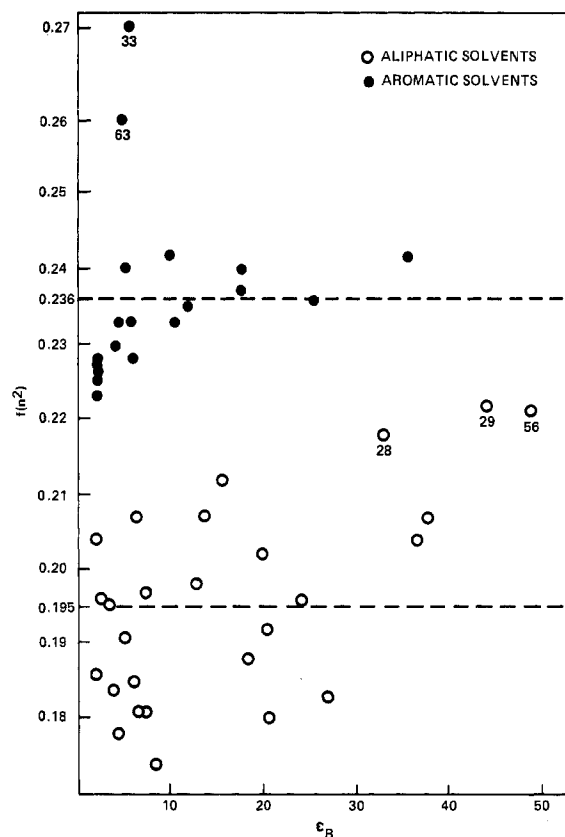
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(15) (a) This value is a reasonable approximation for most solvents. (b) See ref 25.

Figure 1. $\phi(n^2)$ plotted against solvent bulk dielectric constant. Solvent numbering as in Table I.

of the total solute/solvent interaction energies,[16] the leading term more frequently being London's dispersion forces.[17] The extension of reaction field theory to London's interactions predicts an approximate relationship between dispersion-originated solvent effects and the function $\phi(n^2)$, defined by eq 7, where n is the refractive index of the solvent.[18]

$$\phi(n^2) = (n^2 - 1)/(2n^2 + 1) \tag{7}$$

That the "tip of the iceberg" (i.e., the seeming dependence of solvent effects only on solvent dipolarity) should give such good descriptions of the overall phenomenology seems to indicate almost constant dispersion interactions through the SSS. We have shown earlier,[5b] and show again in Figure 1, that for most members of the SSS, $\phi(n^2)$ varies within quite narrow limits. A similar relationship, statistically distinct from that for the aliphatic solvents, appears to apply for the aromatic solvents (except bromo- and iodobenzene).

The simplest possible general expression for *total* medium effects on a property XYZ is given by eq 8, where A_1 is a measure

$$XYZ = XYZ_g + a_1A_1 + a_2A_2 \tag{8}$$

of the "dipolarity" of the solvent, A_2 is a measure of dipole–induced dipole and dispersion interactions, and XYZ_g stands for the value of the property in the gas phase (note the difference from eq 1 and 2, where XYZ_0 is the value of the property in cyclohexane).

In order to rigorously determine the coefficients a_1 and a_2 in eq 8, as well as to assess the validity of such an equation, one needs the *experimental* value of XYZ_g, together with values for XYZ

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obtained in a series of solvents spanning the widest possible range of A_1 and A_2 values. It is at this point that the following major difficulties appear. (i) Few properties or reactivity data are known *both in solution and in the gas phase.* If the gas phase value is not available, equations such as eq 8 cannot be strictly tested. In most cases, therefore, XYZ_g *becomes an adjustable parameter.* (ii) Given the very narrow range of variation of $\phi(n^2)$, reliable a_2 values generally cannot be obtained from a study of the SSS alone. A broader range of $\phi(n^2)$ can only be obtained by extending the study of such nonselect solvents as the polychlorinated aliphatics and the aromatics in the one direction, and to polyfluorinated compounds in the other. A number of π^* values for the latter type compounds have been determined by Carr and Brady[19] and by Bekárek and Jurina.[20]

II. Earlier Reported Correlations between the π^* Scale and Dipolarity/Polarizability Descriptors

Some of the reported correlations of the π^* scale with functions of μ, ϵ, and n are as follows. *For the select solvents only*: (a) eq 3,[8] with $n = 28$, $r = 0.972$; (b) eq 9, with $n = 28$, $r = 0.964$;[21]

$$\pi^* = 2.52\theta(\epsilon) - 0.23 \qquad (9)$$

$$\theta(\epsilon) = \frac{3\,\epsilon \ln \epsilon}{\epsilon \ln \epsilon - \epsilon - 1} - \frac{6}{\ln \epsilon} - 2 \qquad (9')$$

the θ term in eq 9 is Block and Walker's dielectric function, defined by eq 9';[22] this formalism is intended to account for the existence of dielectric saturation effects in the case of very dipolar solvents and solutes; (c) eq 10, reported by Bekarek,[23] with $n = 38$, $r =$

$$\pi^* = -0.573 + 14.65\phi(\epsilon)\ \phi(n^2) \qquad (10)$$

0.909. The $\phi(\epsilon)$ and $\phi(n^2)$ terms in eq 10 are those defined by eq 4 and 7.

For all non-hydrogen bond donor solvents: (a) eq 11,[7a] with

$$\pi^* = 0.012 + 0.229\mu_s + 10.71P \qquad (11)$$

$$P = [\phi(n^2) - 0.19][1 - 0.23\mu_s] \qquad (11')$$

$n = 30$, and $r = 0.966$; the P term in eq 11 is a "reducing function of n^2", defined by eq 11'; (b) eq 12, reported by Brady and Carr,

$$\pi^* = -2.16 + 5.88\theta(\epsilon_p) + 11.43\phi(n^2) - 23.16\theta(\epsilon_p)\phi(n^2) \qquad (12)$$

$$\epsilon_p = \epsilon - n^2 + 1 \qquad (12')$$

with $n = 76$ and $r = 0.965$;[24] ϵ_p in eq 12 is defined by eq 12', and $\theta(\epsilon_p)$ is defined by eq 9' where ϵ_p replaces ϵ. This expression applies to four perfluorinated solvents, aromatic and polychloroaliphatic solvents, and the SSS. According to Brady and Carr, $\theta(\epsilon_p)$ is a "dipolarity" descriptor that takes into account the dielectric saturation of the orientational component of the polarization of the dielectric. In other words, this approach involves the separation of the dipole/dipole interactions from the polarizability contributions (dipole/induced dipole and London interactions). (c) Finally, corresponding to eq 10 for the aliphatic solvents, Bekarek[23] has reported eq 13, $r =$ only 0.841, for the aliphatic and aromatic

$$\pi^* = -0.570 + 15.24\phi(\epsilon)\phi(n^2) \qquad (13)$$

solvents together, and eq 14, $r = 0.963$, for the aromatic solvents

$$\pi^* = 0.058 + 6.09\phi(\epsilon)\phi(n^2) \qquad (14)$$

alone. Particularly to be noted are the differences in slopes and intercepts between eq 10, applicable to aliphatic solvents alone, and eq 14, applicable to aromatic solvents alone.

From these results we draw the following conclusions. (1) The equations described above lead to widely different values of π^*_g, that is, π^* for a medium where in $\mu_s = 0$ and $\epsilon = n^2 = 1$. Thus eq 3 predicts $\pi^*_g = 0.023$, eq 6 predicts −0.48, eq 10 predicts −0.57,

eq 11 predicts −2.06, eq 13 predicts −0.57, and eq 14 predicts −0.06. Based on $\theta(\epsilon)$ and $\theta(\epsilon_p) = 0$, from a Taylor expansion analysis, eq 9 and 12 predict −0.23 and −2.16. *This is a key point.* It implies that, while all of the above expressions give good descriptions of medium effects through the usual range of solvents, as evidenced by quite respectable correlation coefficients, some (or all) may not properly account for some relevant physical factor. The gas-phase datum thus provides a unique opportunity for testing the validity of these expressions.

(2) As indicated earlier, the correlations involving the SSS (or the nonchlorinated aliphatic solvents alone) essentially involve dipolarity descriptors; this is clearly the case for eq 3, 6, and 9. Also, given that the values of $\phi(n^2)$ are near 0.19 for most of the SSS, the P term in eq 11 is quite small for these compounds. (In this connection, it is worth noting the similarities in the coefficients of μ_s in eq 3, which was obtained from a multiple parameter least-squares correlation involving aliphatic and aromatic solvents together.[7a] This suggests that if eq 11 is to be modified in an attempt to match the gas phase value of π^*, it is the definition of P, rather than the term in μ_s, that needs modification.) Further, within the SSS, the *differential* contributions of $\phi(n^2)$ to Bekarak's[20,23] and Carr's[19,24] equations are also small.

(3) Equations applying to "all solvents" contain, without exception, "cross terms", such as P in eq 11. Thus, they are not of the form of eq 8. Since, for the SSS, π^* appears as being a function of dipolarity descriptors alone, it follows that the "cross terms" are esstentially needed to accomodate the π^* values of the nonselect solvents. On very general grounds, Ehrenson[25] has shown that these factors should appear as second-order terms, the first order being given by an expression such as eq 8. It is a fact, however, that such terms have needed to be included in order to calculationally approximate the experimental values.

III. A Complementary Approach

The many attempts to relate the π^* scale to more fundamental properties of the solvents have now reached the point where we feel that new concepts and experimental information are needed. We therefore propose the following methodological guidelines.

Let there be a solvent sensitive property, XYZ, and a set of physical properties represented by the descriptors A_1, A_2, ..., A_i, ... We assume that the value taken by XYZ in the mth solvent, XYZ_m, can be expressed as a linear combination of the A_i's, and that

$$XYZ_m = XYZ_g + \sum_i a_i A_i(m) \qquad (15)$$

embodies all the main physical factors involved and applies for a large number of media.

Now, if the number of experimental points is sufficient, and if the physical factors are adequately described by the analytical form of the A_i's, then the experimental and calculated (through eq 15) values for XYZ_g must agree within the combined limits of experimental error and statistical reliability of the correlation. Whenever the amount of experimental data does not allow a reliable calculation of XYZ_g, the correlations involving experimentally determined XYZ_g values should be of the same statistical quality as those wherein the gas phase value is treated as an adjustable parameter. *It is then of the greatest importance to ensure that a satisfactory fitting with the experimental XYZ_g is not significantly detrimental to the quality of the fitting for the other media.* The relevance of the gas phase data in obvious: they provide stringent tests of the correlation equations, and more than double the range of the experimental $\phi(n^2)$ values.

With these concepts in mind, Abboud and co-workers[26] have recently determined the experimental π^*_g value to be −1.06 ± 0.10. We now attempt to correlate the experimental values of π^* for the SSS and the gas-phase result (but not the results for the aromatics, wherein we feel that a completely different effect obtrudes, and which we will consider in greater detail in a future

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TABLE I. Experimental Data Used in the Correlations

no.[a]	solvent	A_1[b]	A_2[b]	π^*[c]	G[d]	ΔG^*[e]	log $(k_{MEK}/k_{C_3H_8})$[f]	log $(k_{tol}/k_{C_4H_{10}})$[f]	log $(k_{diox}/k_{C_3H_8})$[f]
	gas phase	0.0	0.0	−1.06	0.0	43.5	0.0	0.0	0.0
1.	n-heptane	0.0	0.18624	−0.08		39.4	1.234	1.680	1.371
2.	cyclohexane	0.0	0.20403	0.0	49.0	37.8	1.224	1.649	1.73
3.	triethylamine	0.07991	0.19443	0.14	62.0	36.4	1.614	1.815	2.011
4.	diisopropyl ether	0.26465	0.18377	0.27			1.627	1.786	1.969
5.	di-n-butyl ether	0.16745	0.19844	0.24			1.567	1.819	1.995
7.	diethyl ether	0.31031	0.17797	0.27	64.0	35.8	1.601	1.843	2.018
11.	ethyl acetate	0.39844	0.18533	0.55				2.134	2.662
13.	tetrahydrofuran	0.4408	0.19761	0.58			1.946	2.084	2.404
16.	2-butanone	0.62275	0.18764	0.67				2.038	2.502
18.	acetone	0.64790	0.18032	0.71		32.6	2.436	2.107	2.702
23.	N,N-dimethylacetamide	0.66333	0.20469	0.88			2.589	2.423	2.952
25.	dimethylformamide	0.66514	0.20469	0.88		30.5	2.661	2.433	3.020
26.	hexamethylphosphoramide	0.6339	0.21405	0.87					2.714
27.	butyrolactone	0.666	0.20688	0.87			2.679	2.397	3.106
28.	N-methylpyrrolidone	0.63378	0.21752	0.92			2.577	2.463	2.994
29.	dimethyl sulfoxide	0.65566	0.2204	1.00	108.0	29.3	2.842	2.518	3.326
32.	nitromethane	0.68934	0.18794	0.85	99.0	30.2			
34.	acetic anhydride	0.60358	0.19177	0.76					
38.	n-butyl acetate	0.33894	0.18904	0.46					
40.	tetrahydropyran	0.35298	0.20179	0.51					
41.	cyclohexanone	0.59296	0.21214	0.76			2.086	2.062	3.023
42.	tri-n-butyl phosphate	0.44435	0.21282	0.65					
48.	tri-n-butylamine	0.0447	0.20500	0.16					
50.	acetonitrile	0.71353	0.17391	0.75	93.0	30.7			
51.	cyclopentanone	0.54467	0.20747	0.76					
52.	methyl acetate	0.43291	0.18131	0.60					
55.	methyl formate	0.50283	0.17455	0.62					
56.	sulfolane	0.64869	0.22184	0.98					
61.	1,2-dimethoxyethane	0.4425	0.18793	0.53					
75.	tetramethylurea	0.61210	0.21159	0.83					
86.	di-n-propyl ether	0.21162	0.18818	0.27					
89.	butyronitrile	0.63275	0.18879	0.71					
94.	diethyl malonate	0.44636	0.19980	0.64					
98.	3-heptanone	0.55319	0.19709	0.59					
137.	propylene carbonate	0.70405	0.20236				2.757	2.370	3.217
243.	perfluoro-n-octane	0.06295	0.14546	−0.41	36.0	39.8			
244.	perfluoro-n-heptane	0.05094	0.13995	−0.39					
247.	perfluoro-n-hexane	0.05094	0.13395	−0.40					
250.	propionitrile	0.67338	0.18293	0.71					

[a] Solvent numbering is the same in all papers of this series. [b] Defined in the text. [c] Reference 6a. [d] Reference 34. [e] In kcal/mol; ref 35. [f] Reference 40.

paper; see below) with functions of ϵ and n. Among the simplest ones having the form of eq 15, we have chosen

$$\pi^* = \pi^*_g + a_1 A_1 + a_2 A_2 \qquad (16)$$

where

$$A_1 = (\epsilon-1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2) \qquad (16')$$

and

$$A_2 = \phi(n^2) \qquad (16'')$$

These descriptors represent, respectively, the dipole/dipole forces and the polarizability contribution (including dispersion and dipole/induced dipole interactions). Their use for the analysis of solvatochromic effects was suggested nearly three decades ago by Ooshika, Bayliss, and McRae[11] and, quite recently, Kolling[27] has carried out correlations of this kind with π^* values of select and nonselect solvents.

When applying eq 16 to 36 members of the SSS (Table I), ranging from n-heptane ($\pi^* = -0.08$) to dimethyl sulfoxide ($\pi^* = 1.00$), we obtain

$$\pi^* = -0.95(\pm0.28) + 1.19(\pm0.09)A_1 + 5.05(\pm1.43)A_2 \qquad (17)$$

$$n = 36; \ r = 0.983; \ SD = 0.05; \ F = 472$$

(27) Kolling, O. W. *Trans. Kansas Acad. Sci.* **1981**, *84*, 32. This author took an approach much like our own. However, his attempt to include select and nonselect solvents in the same equation led to an expression which gives very unrealistic π^* values for the gas phase and fluorocarbons.

This equation correctly predicts the value of π^*_g. If we now repeat the correlation, including the π^*_g experimental datum, we obtain

$$\pi^* = -1.05(\pm0.10) + 1.18(\pm0.09)A_1 + 5.54(\pm0.56)A_2 \qquad (18)$$

$$n = 37; \ r = 0.991; \ SD = 0.05; \ F = 962$$

This clearly shows that the inclusion of the gas phase datum has not "forced" the correlations.

Equation 18 yields values of π^* for n-C$_6$F$_{14}$ (−0.22), n-C$_7$F$_{16}$ (−0.21) and n-C$_8$F$_{18}$ (−0.20) which differ by ca. 0.20 unit from the experimental values, so that, strictly speaking, eq 18 does not perform satisfactorily with the fluorocarbons. It is useful, however, to carry out a correlation involving these three media, the gas phase result, and the SSS.

$$\pi^* = -1.15(\pm0.12) + 1.26(\pm0.11)A_1 + 5.84(\pm0.74)A_2 \qquad (19)$$

$$n = 40; \ r = 0.988; \ SD = 0.07; \ F = 769$$

Although of somewhat poorer statistical quality than eq 18, eq 19 predicts values for the three perfluoroalkanes of −0.27, −0.27, and −0.22, i.e., differing by an average of 0.14 from the experimental results. These differences are well within the range by which the calculated π^*'s (through eq 18) for for some bona fide select solvents differ from the experimental values.

We therefore conclude that: (i) eq 19 describes the behavior of media ranging from the gas phase to Me$_2$SO; (ii) the inclusion of the perfluoroalkanes puts great stress on eq 18 because their $\phi(n^2)$ values of ca. 0.14 lie between the gas phase value of 0.00 and the ca 0.19 value for the majority of the select solvents;[28a]

(iii) The differences between the corresponding error; and (iv) the statistical quality of eq 19 is at least as high as the best of the earlier reported correlation equations.

The inclusion of the A_2 term, i.e., $\phi(n^2)$, rationalizes a number of relative π^* results, such as the significantly smaller value for n-hexane compared with cyclohexane. Also, acetonitrile and dimethyl sulfoxide have practically the same molecular dipole moment, which is lower than that of propylene carbonate; the latter compound also has the largest dielectric constant. Experimentally, however, the ranking of π^* values is $Me_2SO > PC > MeCN$. This is nicely accounted for by the polarizability contributions, $\phi(n^2)$ being 0.220 for Me_2SO, 0.207 for PC, and 0.174 for MeCN.

It is somewhat surprising that such a crude treatment should lead to an acceptable description of the many experimental results, and it is fair to ask whether this is fortuitous. An important paper by Carr and Brady[24] provides useful information in this regard. Among several alternative "all solvent" correlations by these authors was eq 20.

$$\pi^* = -1.43 + 2.15\theta(\epsilon_p) + 7.70\phi(n^2) - 1.23[\theta(\epsilon_p)]^2 \quad (20)$$

$$n = 76; \; r = 0.945; \; SD = 0.11$$

Carr and Brady pointed out that the statistical weight of the last term is very small. It is interesting, therefore that the second term is conceptually equivalent to A_1 and the third is exactly A_2. Moreover, their calculated π^*_g (-1.43) is reasonable if allowance is made for the combined uncertainties and the fact that Carr and Brady included in their correlations the aromatic solvents in which an additional effect may obtrude (see below). Although the statistical quality of the fit provide by eq 20 *appears to be* lower than that for eq 12, above, also proposed by Carr and Brady, ($sd = 0.11$ vs. 0.09), eq 20 contains one less parameter and predicts a more realistic π^*_g value.[28b]

IV. Analysis of Additional Solvent Effects

We have attempted to use the descriptors A_1 and A_2 to analyze other solvent effects, our choice of which was severely limited by the scarcity of gas phase data. The following comprise a representative sample.

The Ultraviolet Absorption Spectrum of Pyridine N-Oxide (PyO). The near-UV spectrum of PyO contains a strong absorption band near 280 nm, generally assigned to a $\pi \rightarrow \pi^*$ electronic transition.[29] Theoretical calculations[29] suggest that this transition involves a substantial amount of intramolecular charge transfer from the oxygen atom to the ring. Values of ν_{max} for this band have been determined in the gas phase and in a number of select solvents ranging from n-heptane to Me_2SO. In 1962, Kubota and Yamakowa[29] reported a successful correlation between a set of ν_{max} results and the Bayliss–MacRae equation, eq 16. Here we have extended this analysis to include their data with those of Kosower.[30] The result is given by eq 21. Experimentally[29,31] $(\nu_{max})_g = 35.96$ kK.

$$\nu_{max} = 35.96(\pm0.02) + 1.17(\pm0.02)A_1 - 2.98(\pm1.00)A_2 \text{ kK}$$
$$(21)$$

$$n = 13; \; r = 0.97; \; SD = 0.09 \text{ kK}; \; F = 80$$

Here, as in the examples to follow, we have established that the correlation is not significantly biased by the inclusion of $(\nu_{max})_g$. For example, if the same analysis is carried out without this datum, we obtain eq 21a.[32]

$$\nu_{max} = 36.01(\pm0.09) + 1.17(\pm0.22)A_1 - 3.25(\pm4.44)A_2 \text{ kK}$$
$$(21a)$$

$$n = 12; \; r = 0.97; \; SD = 0.09 \text{ kK}; \; F = 69$$

It is interesting that a_1 and a_2 in eq 21 should have opposite signs. This means, in accordance with the theoretical calculations, that the observed solvatochromism is a combination of a general bathochromic shift produced by dispersion interactions,[33] and a hypsochromic effect, which is a consequence of the reduction of the molecular dipole moment of PyO following the electronic excitation.

For historical reasons, the Bayliss–McRae formalism has been applied to electronic spectroscopy, while equations such as eq 4′ and 5 have been used to correlate IR, NMR, and reactivity data. In fact, however, eq 16 can be considered as deriving from reaction field theory, and we see no reason why it should not serve as a tool for the analysis of other physicochemical properties and reactivity parameters, such as the following.

Allerhand and Schleyer's G Scale.[34a] This scale of solvent dipolarity is based on medium-induced IR shifts of several vibrators; its relationship to the π^* scale has been dealt with in an earlier paper of this series.[34b] Values of G are available for the gas phase, n-C_8F_{18}, and a number of select solvents, including Me_2SO (data in Table I). The correlation equation involving all of these media is given by

$$G = -1.3(\pm9.6) + 72.2(\pm12.8)A_1 + 264.0(\pm53.7)A_1 \quad (22)$$

$$n = 8; \; r = 0.995; \; SD = 4.4; \; F = 236$$

The experimental $G_g = 0$, and the highest value is that for Me_2SO, 108.

The Dehydrohalogenation of tert-Butyl Chloride at 393 K.[35] Data for this reaction are available in media ranging from n-C_8F_{18} to Me_2SO (Table I); they span an interval of activation free energies, $\Delta G^{\ddagger}_{393}$, of 10.5 kcal/mol. The multiple linear regression equation for all the SSS is given by eq 23.[36]

$$\Delta G^{\ddagger}_{393} = 42.2(\pm5.9) - 11.6(\pm2.5)A_1 - 19.5(\pm31.3)A_2 \text{ kcal/mol} \quad (23)$$

$$n = 10; \; r = 0.977; \; SD = 0.98 \text{ kcal/mol}; \; F = 73$$

On the basis of Maccoll's experimental data,[37] Abraham and Abraham report a value of 43.5 kcal/mol for $(\Delta G^{\ddagger}_{393})_g$, in good agreement with the above calculation.[35] If the gas phase experimental datum is included, we obtain

$$\Delta G^{\ddagger}_{393} = 43.3(\pm2.0) - 11.4(\pm2.3)A_1 - 25.5(\pm11.5)A_2 \text{ kcal/mol} \quad (24)$$

$$n = 11; \; r = 0.984; \; SD = 0.93 \text{ kcal/mol}; \; F = 126$$

(28) (a) A referee has expressed concern about this result. This prompts us to report that since this paper was submitted, the experimental π_g^* value has been revised. We have carried out a complete deconvolution analysis of the UV-visible spectral absorption of the solvatochromic indicators in a number of solvents. This study, which should be submitted for publication very shortly, reveals that: (i) The "true" value of π_g^* is slightly more negative than -1.06: between -1.15 and -1.20. This is a consequence of a better assessment of the vibrational structure of the bands. This correction does not introduce any significant changes in any of the equations. It has, however, a very important consequence: the agreement between the experimental and calculated π^* values for the perfluorinated solvents is greatly improved. This follows from the great "leverage" exerted by the single gas-phase datum. We are indebted to this referee for his valuable suggestions. (b) In this case, the calculated numbers for the perfluoroalkanes become much closer to the experimental values, differences ranging from 0.07 to 0.13.

(29) Kubota, T.; Yamakawa, M. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 556.

(30) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253.

(31) Ito, M.; Hata, N. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 260.

(32) Here, as in the other cases, we notice that the inclusion of the gas-phase datum improves the quality of the correlation, while the coefficients a_1 and a_2 undergo relatively minor variations.

(33) See, for example, Longuet-Higgins, H. C.; Pople, J. A. *J. Chem. Phys.* **1957**, *27*, 192.

(34) (a) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 374. (b) Reference 7c. (c) Owing to the scarcity of experimental data, MeCN has been included in the correlation.

(35) These data have been taken from the careful critical compilation by Abraham and Abraham: Abraham, M. H.; Abraham, R. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 47.

(36) The dielectric constants used in the calculations were those given in ref 35. The refractive indexes were determined by extrapolation of values obtained in the 293–323 K range. In all cases, the calculated 393° values were about 4% lower than the 293° values.

(37) Maccoll, A. *Chem. Rev.* **1969**, *69*, 33.

This example is of interest because: (i) it is one of the rare cases where chemical reactivity has been studied both in the gas phase and in solution; (ii) cavity effects (see below) involving the reactant and the transition state are likely to cancel out to a large extent; and (iii) it favors the notion that an heterolytic mechanism[37] is operative both in the gas phase and in solution. This last point is in excellent agreement with recent results of gas-phase experiments by Chuchani and co-workers.[38]

The relatively small values of a_2 in eq 23 and 24, and their large uncertainties, even when the gas phase datum is included, may not be entirely due to the paucity and uncertainties of the experimental data. We can take them as implying that the transition stae is only slightly more polarizable than t-BuCl. Consequently, the medium effects are essentially governed by dipolar interactions.

Gas/Liquid Partition Coefficients. Free energies of transfer of dipolar solutes from the gas phase to various solvents seem prime candidates for testing these correlations. Abraham and co-workers[39] have shown, however, that the experimental ΔG_t values contain large contributions from cavity effects, and reaction field models can only account for the solute/solvent interactions. An approximate method of circumventing this difficulty has been proposed by Abraham;[39] it involves the correlation of the *differences* between the free energies of transfer of the dipolar solute and a nondipolar reference solute of the same molecular size. When we used this method in part 9 of this series,[40] good linear relationships were obtained between log (k_d/k_{nd}) and π^*, k_d, and k_{nd}, respectively, being the gas/liquid partition coefficients for the dipolar solute and the nondipolar reference solute.

If the cavity effects are, indeed, adequately eliminated, we can expect the log ratio, log (k_d/k_{nd}), to decrease with the dipolarity/polarizability of the solvent, and eventually become *nil* in the gas phase.[41] Using the values of log (k_d/k_{nd}), which are assembled in Table I (obtained from experimental data of Rohrschneider[42]), we have examined the following couples.

2-Butanone/Propane. For the SSS we obtain

$$\log (k_{MEK}/k_{C_3H_8}) =$$
$$-0.06(\pm 1.40) + 1.93(\pm 0.38)A_1 + 6.60(\pm 7.85)A_2 \quad (25)$$

$$n = 15; \, r = 0.967; \, SD = 0.16; \, F = 86$$

If the gas phase value of 0.00 is included, the correlation equation is given by

$$\log (k_{MEK}/k_{C_3H_8}) =$$
$$-0.02(\pm 0.34) + 1.93(\pm 0.33)A_1 + 6.34(\pm 1.37)A_2 \quad (26)$$

$$n = 16; \, r = 0.982; \, SD = 0.15; \, F = 179$$

Toluene/Butane. For the SSS, we obtain

$$\log (k_{tol}/k_{C_4H_{10}}) =$$
$$0.03(\pm 0.69) + 0.89(\pm 0.18)A_1 + 8.67(\pm 3.69)A_2 \quad (27)$$

$$n = 16; \, r = 0.970; \, SD = 0.08; \, F = 103$$

If the gas phase value is included, we obtain

$$\log (k_{tol}/k_{C_4H_{10}}) =$$
$$0.00(\pm 0.16) + 0.89(\pm 0.16)A_1 + 8.69(\pm 0.93)A_2 \quad (28)$$

$$n = 17; \, r = 0.993; \, SD = 0.08; \, F = 460$$

Dioxane/Propane. For the SSS, we obtain

$$\log (k_{diox}/k_{C_3H_8}) =$$
$$0.13(\pm 0.63) + 1.72(\pm 0.45)A_1 + 8.16(\pm 8.61)A_2 \quad (29)$$

$$n = 18; \, r = 0.934; \, SD = 0.20; \, F = 52$$

If the gas phase value is included, we obtain

$$\log (k_{diox}/k_{C_3H_8}) =$$
$$0.08(\pm 0.39) + 1.71(\pm 0.41)A_1 + 8.78(\pm 2.30A_2) \quad (30)$$

$$n = 19; \, r = 0.972; \, SD = 0.19; \, F = 136$$

In the three cases, the extrapolated $[\log (k_d/k_{nd})]_g$ is essentially nil within the limits of error. Also, the a_1 values qualitatively follow the order of the bond moments of the solutes. It is also noteworthy that for the weakly dipolar, highly polarizable toluene, the a_2/a_1 ratio is ca. *10*, whereas for 2-butanone it is only ca. 3. Further, if the molar volume of the nondipolar reference solute is substantially different from that of the dipolar solute, the calculated $[\log(k_d/k_{nd})]_g$ value is no longer nil, which seems to support the self-consistency of the approach.

A final comment: in terms of energy, the a_2A_2 terms seem too small compared with the a_1A_1. The reason is that, without exception, we have been examining the *differences* between solvent effects, viz., the couples: excited state/ground state, transition state/reactants, dipolar solute/nondipolar reference solute. This has the distinct advantage of eliminating cavity effects, but it also cancels out most of the dispersion interactions.

V. The Case of the Nonselect Solvents

Looking back to eq 1 and 2, it appears that the difference between the correlations involving the SSS and those extending to polychlorinated and aliphatic solvents lies in the $d\delta$ term. Through d values which usually range from -0.4 to 0.0 and δ values from 0.0 to 1.0, this "polarizability correction term" appears to be strongly solvent sensitive, and accommodates both aliphatic and aromatic solvents to the same correlation equations. On the other hand, equations like eq 3 and 18 give satisfactory results for the SSS but fail to reproduce the π^* values (as well as other solvent effects) for the nonselect solvents. *It follows that a fundamental link must exist between the $d\delta$ term in eq 1 and the cross term P in eq 11 or the $\theta\phi$ term in eq 12*, since the latter equations also appear to accommodate the results for the nonchlorinated aliphatic, polychlorinated aliphatic, and aromatic solvents together. We shall explore this point further in a forthcoming paper.[43]

There are several possible explanations for the failure of the Ooshika–Bayliss–McRae equation and other simple expressions to account for the behavior of the nonselect solvents. The simplest is to assume that these equations are not suitable for solvents with high refractive indexes. Such a rationale, however, is at odds with the following observations: Me_2SO and sulfolane (solvents 29 and 56 in Figure 1, n^{20}_D 1.48) are "well behaved" select solvents, and nitrobenzene (n^{20}_D 1.55) is an aromatic solvent whose π^* is quite close to the value calculated by means of eq 18 and 19. Benzene (n^{20}_D 1.50), the paramount case of "aromatic behavior", has a π^* value of 0.59, while for p-xylene, a cognate molecule (n^{20}_D 1.49), $\pi^* = 0.43$. All of these solvents have fairly similar refractive indexes, which differ significantly from the refractive indexes of the usual SSS (Figure 1).

Another possible rationale involves the high anisotropy of the nonselect solvents. All the correlations reviewed here carry with them the implicit assumption of the isotropic polarizability of the solvents. This is certainly not a good approximation for the aromatics or for compounds with C–X bonds (X = heavy halogen).[16,44] Finally, it may be that through their π systems, aromatic solvents can lead to more "specific" solvent–solute interactions.[45]

These issues—however difficult to settle—are not merely matters of opinion; they are amenable to theoretical and ex-

(38) Chuchani, G.; Martin, I. *J. Phys. Chem.* **1980**, *84*, 3188, and references cited therein.

(39) Abraham, M. H.; Nasehzadeh, A.; Moura Ramos, J. J.; Reisse, J. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 854, and references cited therein.

(40) Kamlet, M. J.; Taft, R. W.; Carr, P. W.; Abraham, M. H. *J. Chem. Soc., Faraday Trans. 1* **1982**, 1689.

(41) Our reasoning on this subject has been strongly influenced by Rosseinsky's studies on gas/liquid equilibria of polar molecules. Rosseinsky, B. *Nature* (London) **1970**, *227*, 944.

(42) Rohrschneider, L. *Anal. Chem.* **1973**, *45*, 1241.

(43) Abboud, J.-L. M.; Guiheneuf, G.; Lassaba, E.; Jaafar, A.; Kamlet, M. J.; Taft, R. W., to be submitted.

(44) Schroer, W.; Domke, W. D.; Naumann, K. H.; Lippert, E. in "Organic Liquids. Structure, Dynamics, and Chemical Properties", Buckingham, A. D.; Lippert, E.; Bratos, S., Eds.; Wiley: New York, 1978; Chapter 15.

(45) See, for example; (a) Person, W. B.; Mulliken, R. "Molecular Complexes. A Lecture and Reprint Volume", Wiley: New York, 1969. (b) Foster, R. "Charge-Transfer Complexes"; Academic Press: London, 1969.

perimental treatment. For example, and anticipating results to be published shortly,[43] Abboud and co-workers have found that π^* *values* for aromatics contain substantial contributions from *weak donor/acceptor interactions between the solvents and the solvatochromic indicators.* It is our opinion that an "analytical" approach based on the microscopic analysis of these factors can be a valuable complement to the "synthetic" goal of linking the dipolarity/polarizability scales to structural properties of the solvents through a "master" equation.

More Detailed Considerations. Most of the dipolar select solvents comprise a dipolar functionality, usually containing heteroatoms, and a number of methylene and/or methyl groups. Dipolar interactions tend to "sort out" the dipolar terminus from the remainder of the chain, but the average distance between the solute dipole and the solvent dipole or polarizable center is likely to depend on steric factors. Consonant with such an effect, the reaction field in eq 4 depends on the radius, a, of the solute cavity.

The seldom stated fundamental condition for expressions such as eq 18 and 19 to apply is the constant value for a. Strictly speaking, we cannot expect such an approximation to be valid (although, in the absence of an operational criterion we have assumed that we could). Under these circumstances (i.e., without including steric terms in A_1 and A_2), it would be difficult to justify on physical grounds the use of a fourth term in eq 19, even if this were to significantly improve the statistical quality of the correlations.

The above seems to indicate that great care should be exercised when using reaction field models at this level of sophistication. It is also of great importance that the empirical solvent dipolarity/polarizability measures like π^* and δ seem to accommodate most of these extraneous contributions (as is evidenced by the generally better statistical quality of correlations with ($\pi^* + d\delta$)

compared with corresponding correlations with A_1 and A_2). This fact alone justifies the continued use of the empirical solvent property scales rather than the more fundamentally based scales like A_1 and A_2.

Conclusions

We have sought simple functions of fundamental molecular properties, capable of accounting for the π^* parameters for the "select solvents" and the gas phase. We have found that the classical Ooshika–Bayliss–McRae formalism[11] provides a rather good fitting of data for these media (as suggested also by Kolling)[27] and for the perfluoroalkanes. This simple equation is also able to correlate medium effects on other properties. While there is room for a quantitative improvement of the correlations, possibly along the lines of Carr and Brady's[19,24] or Ehrenson's[25] more elaborate treatments, we consider the present approach to be heuristically satisfactory.

Polychlorinated aliphatic and, particularly, aromatic solvents are not adequately described by this method. At variance with other treatments, we have assumed that this is not a consequence of the crudeness of the model, but rather reflects more complex solvent/solute interactions at the molecular level. That this has been experimentally confirmed in the case of the aromatic solvents will be reported in a future paper. Finally, a clear link has been established between the $d\delta$ term in the solvatochromic equations and the cross terms in equations proposed by Brady and Carr[19,24] and by Taft, Abboud, and Kamlet.[7a]

Determination of Osmotic and Activity Coefficients in Mixed Electrolyte Systems. Systems Containing Clathrate-Forming Salts

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There is a paucity of thermodynamic data on mixed electrolyte systems containing clathrate-forming compounds covering the entire ionic strength fraction range. Using an isopiestic vapor pressure apparatus, we have determined osmotic coefficients for aqueous solutions containing sodium chloride and the clathrate-forming salt tetra-*n*-butylammonium chloride over a wide range of total ionic strength and ionic strength fraction at 25 °C. We have used the Scatchard–Rush equations to fit the osmotic coefficient data for solutions of each pure component and the mixtures. From these equations we calculated the excess free energy of mixing and the activity coefficients of each solute component as a function of ionic strength fraction and total ionic strength. Friedman's interaction parameters, g_0 and g_1, are calculated and the results discussed.

Introduction

While there have been several investigations[1-5] that have determined the acitivity and osmotic coefficients as well as the excess

free energy of mixing for aqueous mixed electrolyte solutions containing a tetraalkylammonium halide, there is a plaucity of thermodynamic data covering the entire ionic strength fraction range for mixed electrolyte systems containing clathrate-forming compounds such as tetra-*n*-butylammonium chloride. Roy and co-workers[2-4,6] have used electromotive force measurements to measure the thermodynamic properties of HBr in the presence of aqueous NH_4Br, $(C_2H_5)_4NBr$, $(n\text{-}C_3H_7)_4NBr$, and $(n\text{-}C_4H_9)_4NBr$ at 25 °C. By applying the Pitzer equations[7-9] they were able to determine the thermodynamics of the tetraalkyl-

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