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A PERTURBATION MOLECULAR ORBITAL APPROACH TO IONIC SOLVATION. A NEW MULTIPARAMETER SOLVENT CORRELATION BASED ON SOLVENT IONIZATION POTENTIALS AND ELECTRON AFFINITIES.[1]

Ralph C. Dougherty

Department of Chemistry, Florida State University

Tallahassee, Florida 32306

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The recent appearance of several multiple parameter solvent correlations[2-4] prompted us to examine the potential of perturbation molecular orbital (PMO) theory as a guide to the properties of organic solvents. Solvent ion interactions must involve only second order and higher perturbations, otherwise a solvent-ion reaction would occur. In principle the expression for the second order energy of interaction between the ions and the solvent, (1)[5], on a time-average basis could provide a qualitative guide to solvation effects. There are several problems with equation (1). First it is not linear and it is therefore difficult to produce an intuitive

$$\delta E_{solv} = \sum C_i \; 2 \left(\sum_{m}^{occ} \sum_{n}^{all} - \sum_{m}^{all} \sum_{n}^{occ} \frac{a_{mr}^2 \, b_{ns}^2 \, \beta_{rs}^2}{E_m - F_n} \right) \qquad (1)$$

model that can be directly related to it. Second the equation depends on the atomic orbital coefficients (a_{mr} and b_{ns}), the resonance integrals (β_{rs}), and the orbital energies (E_m and F_n) for the solvent and each of the ions. These parameters are not easily found, and even if they were, the algebra involved in solution of equations like (1) is best left to a computer. It is, however, possible that equation (1) could serve as a model for a simplified empirical approach to solvation.

The leading terms in equation (1) will involve the interactions between the highest occupied orbitals (HOMO) of the solvent and ions and the corresponding lowest unoccupied orbitals (LUMO) of the ions and the solvent, or the virtual LUMO of a protonic solvent. The virtual LUMO of a hydrogen bonding solvent is the MO that would become a doubly occupied NBMO on proton transfer. The energies of these orbitals can be approximated from ionization potential and electron affinity data. For hydrogen bonding solvents the energy of the virtual LUMO is the

electron affinity of the radical obtained by loss of the hydrogen bonding hydrogen. The resonance integrals may be approximated by the same data using the Mulliken approximation, $\beta_{AB} = CS_{AB}(IP_A+EA_B)$.[5] Equation (1) then reduces to a series of terms of the form

$$\delta E_{solv} = \sum C_i' \frac{(IP_A+EA_B)^2}{IP_A-EA_B} \qquad (2)$$

Where A and B refer to the solvent and cation or the anion and solvent respectively. The equation can be expanded as

$$\delta E_{solv} = \sum C_i'(IP_A+EA_B)\left[1 + 2EA_B\left(\frac{1}{IP_A-EA_B}\right)\right] \qquad (3)$$

Dewar suggests that it may be reasonable to neglect the dependence on $\frac{1}{IP_A-EA_B}$ in the last part of equation (3).[6] In which case collection of the solvent dependent terms and rearrangement gives a power series in IP_{solv} and EA_{solv} of the form

$$\delta E_{solv} = C_i(IP_{solv}+EA_{solv}) + C_2(IP_{solv}) + C_3(EA_{solv})^2 + C_4 \qquad (4)$$

The C's will depend on the IP's and EA's of the reagents as well as the interaction constants mentioned above. We have arranged the terms in equation (4) in the order shown because the sum $(IP_{solv} + EA_{solv})$ can be though of as the solvent ionizing power. The IP_{solv} term should reflect the solvent nucleophilicity, and the $(EA_{solv})^2$ term should represent the electrophilicity of the solvent. The same expression can be obtained by a Taylor series expansion of equation (2) if we neglect the $\frac{C'}{IP_{solv}}$ term while retaining the $(EA_{solv})^2$ term. The $\frac{C'}{IP_{solv}}$ term adds very little to the correlation while the $(EA_{solv})^2$ term significantly improves the correlation in three of four cases which follow. A two term equation ($\delta E_{solv} \approx C_1 (IP_{solv} + EA_{solv}) + C_2$) produces a reasonable correlation (with exclusion of the acetic acid data) for the solvolysis reactions in Table 1, both of which strongly depend on the solvent ionizing power.

Table 1 lists the correlations of four different solvent properties with equation (4). The fit, and observed values of these properties as well as the solvent ionization potentials and electron affinities[8-11] are listed in Table 2 to illustrate closeness of fit.

In spite of the extremely limited data set, the values of the constants in Table 1 indicate several interesting things about the processes involved. The correlation for the Winstein

TABLE 1

Correlation of Solvent Properties with Equation (4)

Solvent Property	Least Squares Coefficients in Equation (4) C_1[a]	C_2[a]	C_3[a]	C_4[a]	F value[b]	F for significance[b] at 1%
$\log_{10} k_{50°}$ methylsotylate[12] solvolysis	2.74±.09	-2.11±0.09	-0.79±0.02	-14.17	$8x10^5$	$5x10^3$
Y, $\log_{10} k_s/k_o$ t-butyl-chloride[13,14]	2.6±.5	-0.12	-0.44±.11	-31.9	$4x10^4$	$5x10^3$
$\log_{10} k_{25°}$ ethyl iodine-pyridine Menschutkin Reaction[15]	-22.9±1.0	22.9±1.0	6.3±0.3	14.9	$5x10^4$	$5x10^3$
dielectric constant[14]	71.8±6.0	-47.3±6.0	-16.3±1.2	-306	$5x10^3$	30

a) Errors are standard deviations; units are consistent with ionization potentials and electron affinities in electron volts.

b) "F values" measure closeness of fit; the closeness of fit increases approximately logarithmicly with F (G.W. Snedecor, Statistical Methods, Iowa State College Press, Ames, 1946).

TABLE 2

Observed Values and Values Obtained From A Fit of Equation (4) For Four Solvent Properties

Solvent Property		Solvent H_2O	MeOH	EtOH	nPrOH	iPrOH	nBuOH	AcOH
Ionization Potential (ev)[7]		12.59	10.85	10.48	10.17	10.17	10.24	10.35
Electron Affinity (ev)		1.83[8]	1.49[a]	1.68[9]	1.87[9]	1.77[9]	1.90[9]	3.3[11]
$\log_{10} k_{50°}$ methylsotylate solvolysis	fit	-3.86	-4.97	-5.18		-5.38		-7.20
	obs.[12a]	-3.86	-4.97	-5.18		-5.38		-7.20
Y, $\log_{10} k_s/k_o$ t-butyl chloride solvolysis 25°	fit	3.491	-1.079	-2.043		-2.73		-1.639
	obs.[13,14]	3.493	-1.090	-2.033		-02.73		-1.639
$\log_{10} k_{25°}$ ethyliodide-pyridine Menschutkin Reaction	fit		-5.71	-5.96	-6.06	-6.09	-6.06	
	obs.[15]		-5.71	-5.97	-6.06	-6.08	-6.06	
dielectric constant, 25°	fit	78.5	32.5	24.8	19.8	18.6	17.0	6.20
	obs.[14]	78.5	32.6	24.3	20.1	18.3	17.1	6.19

a) Estimated by extrapolation from the values for ethanol and isopropanol, and comparison of the two divergent values in the literature.[8,9]

Gruenwald ionizing power, Y,[13] is primarily controlled by the (IP_{solv} + EA_{solv}) term. The difference between the Y correlation and the correlation for the logs of the rates of methyltosylate solvolysis is primarily controlled by the IP term. The linear difference between these two functions has been identified by Bentley, Schadt and Schleyer as the solvent nucleophilicity.[4] The correlation for the logs of the rates of a Menschutkin reaction is controlled by -(EA_{solv}) and $(EA_{solv})^2$ terms, that is the "electrophilicity" of the solvent appears to control the relative reactivity in this S_N2 reaction. The dielectric constant, on the other hand, is strongly correlated with all three terms.

In order for equation (4) or related equations to be useful in predictions of solvent properties, the number of accurately known electron affinities must be dramatically increased.

REFERENCES AND NOTES

(1) This work has been supported by a grant from the National Science Foundation.

(2) F.W. Fowler, A.R. Katritsky and R.J.D. Rutherford, J. Chem. Soc. (B), 1971, 460.

(3) P.E. Peterson and F.J. Waller, J. Amer. Chem. Soc., 94, 991 (1972).

(4) T.W. Bentley, F.L. Schadt and P.V.K. Schleyer, J. Amer. Chem. Soc., 94, 992 (1972).

(5) M.J.S. Dewar, The Orbital Theory of Organic Chemistry, McGraw-Hill, New York, 1969.

(6) M.J.S. Dewar, Tetrahedron Suppl. 8, 75 (1966).

(7) R.W. Kiser, Introduction to Mass Spectrometry and Its Applications, Prentice-Hall, Inglewood Cliffs, New Jersey, 1965.

(8) L.M. Branscomb, Phys. Rev., 148, 12 (1966).

(9) J.M. Williams and W.H. Hamill, J. Chem. Phys., 49, 4467 (1968).

(10) F.M. Page, U.S. Dept. of the Army Report DA-91-591-EVC-3206 (1965).

(11) S. Tsuda and W.H. Hamill, Advances in Mass Spectrom., 3, 249 (1966).

(12) a) R.E. Robertson, Cand. J. Chem., 31, 589 (1953);
b) R.E. Robertson, Cand. J. Chem., 33, 1536 (1955);
c) J.B. Hyne and R.E. Robertson, Cand. J. Chem., 34, 863 (1956).

(13) a) S. Winstein, E. Gruenwald and H.W. Jones, J. Amer. Chem. Soc., 73, 2700 (1951);
b) S. Winstein, A.H. Fainberg and E. Grunwald, J. Amer. Chem. Soc., 79, 4146 (1957).

(14) C. Reichardt, Angew. Chem. Internat. Ed., 4, 29 (1965).

(15) U.S. National Bureau of Standards Circular 410, "Homogenous Reaction Kinetics," Washington, 1951, Table 652.447.