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NUCLEOPHILICITY AND IONIZING POWER IN BINARY SOLVENT MIXTURES

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Grunwald and Winstein proposed eq 1 for correlation of solvolysis rates of S_N1 reactions,[1,2] where k and k_o are the solvolysis rate constants in a solvent and in 80% EtOH respectively, Y is the solvent ionizing power derived from Me_3CCl solvolysis, and m (denoted here m_{GW}) is the sensitivity of k to Y. It was recognized that eq 1 is a specific case of eq 2,[2a,c] where N is the solvent nucleophilicity and ℓ is the sensitivity to N, but eq 2 was not tested explicitly until recently.[3]

$$\log (k/k_o) = m\,Y \quad (= m_{GW}\,Y) \qquad (1)$$

$$\log (k/k_o) = m\,Y + \ell\,N \qquad (2)$$

The success of eq 1 in correlating solvolysis rates of several primary and secondary substrates was ascribed either to (a)insensitivity of the reaction to N, i.e., ℓ=0,[2c] or (b)the use of solvent systems, e.g., EtOH-H_2O, where N is nearly constant,[2c] or (c)that the solvents compared differ in polarity and nucleophilicity to an equal extent.[4] Schleyer et al. recently proposed a scale of N values based on MeOTs, tested eq 2, and demonstrated convincingly its superiority over eq 1 in analyzing solvent effects in solvolysis.[3]

We demonstrate now that case (c) which was not hitherto evaluated is widespread in binary solvent mixtures. In all these mixtures for which N values are available, except one, N and Y are nearly linearly correlated (eq 3,[5] Figure). Eq 4 is obtained from eqs 2 and 3 and the relationship between m_{GW} and m of eq 2 which measures the sensitivity to the ionizing power when contributions due to solvent nucleophilicity are excluded, is given by eq 5. The Table gives the important parameters of eq 3, and the sources of the Y and N values,[2b,3b,6-11] are given below the Figure.

$$N = a\,Y + b \qquad (3)$$

$$\log (k/k_o) = (m + a\,\ell)\,Y + b\,\ell \qquad (4)$$

$$m = m_{GW} - a\,\ell \qquad (5)$$

The six binary solvent mixtures belong to four classes. (i)In the aqueous-aprotic solvent mixtures dioxane-H_2O and acetone-H_2O the a values are small, positive and similar,i.e.,both N and

Table. Linear correlation between N and Y

Binary Solvent	Composition [a]	n [b]	a [c]	s [d]	r [e]
MeOH - H_2O	100 - 0	7	-0.064 ± 0.006	0.0236	0.976
EtOH - H_2O	100 - 0	7	-0.071 ± 0.008	0.0349	0.970
Acetone - H_2O	80 - 0 [f]	5	0.062 ± 0.009	0.0275	0.971
Dioxane - H_2O	80 - 0 [f]	5	0.047 ± 0.005	0.0150	0.986
TFE - H_2O	100 - 40	11	1.21 ± 0.24 [g]	0.3570	0.862
	100 - 70	8	2.56 ± 0.27 [g]	0.1680	0.967
	70 - 40	4	0.23 ± 0.005 [g]	0.0360	0.953
	100 - 50	5	6.46 ± 0.91 [h]	0.2492	0.963
	100 - 70	4	9.02 ± 0.35 [h]	0.0552	0.998
TFE - EtOH	100 - 0	10	-0.87 ± 0.09	0.271	0.959
	90 - 20	8	-0.83 ± 0.05	0.114	0.987

[a] V/v of the first to the second solvent, except for TFE-H_2O when it is wt/wt. [b] Number of solvent compositions used for the correlation. [c] Slope of eq 3. [d] Standard deviation. [e] Correlation coefficient. [f] The point for the 90% aqueous solvent deviates and was not included. [g] Based on Y(t-BuCl). [h] Based on Y(2-Adamantyl tosylate).

Y increase on addition of the more nucleophilic and better ionizing water. Solvolysis rates could be correlated with Y for the two mixtures together. (ii)In EtOH-H_2O and MeOH-H_2O the a's are small, negative and similar since the alcohols are slightly more nucleophilic than water and N and Y change in opposite directions. For classes (i) and (ii) m would differ only slightly from m_{GW}. (iii)In TFE-EtOH mixtures "a fair linear correlation between Y and N" was mentioned,[7] but the Figure shows that for the entire solvent range a curved concave downwards relationship fits the data better than a linear one. However, a fair relationship (Table) with high negative a value is obtained by excluding the two pure solvents.[12] These mixtures are ideal for studying appreciable changes in N and Y, since TFE has high Y and low N and EtOH has low Y and high N. Since $\ell \geq 0$, m will be significantly larger than m_{GW} for systems reacting with moderate solvent assistance, while for compounds such as 4,4'-dichlorobenzhydryl chloride ($m_{GW} = 1.30$)[8] and 1-anisyl-2-methylpropen-1-yl tosylate ($m_{GW} = 0.89$)[6] which reacts via the k_c route[3] the m and m_{GW} values will be very close. The solvolysis of benzyl halides in 0-100% TFE-EtOH gives curved log k vs. Y plots,[7] but when the nearly linear portions of the plots at 20-80% TFE-EtOH were used we calculated m_{GW} values of 0.47, 0.04 and -0.3 for 4-methylbenzyl chloride, benzyl chloride and 3-fluorobenzyl bromide, respectively. Use of $\ell = 0.75$, the value found for $PhCH_2OTs$ from eq 2 [3b] gives $m = 1.09$, 0.66 and 0.32 for these substrates, respectively. The m value for benzyl chloride is thus comparable to $m = 0.64$ for benzyl

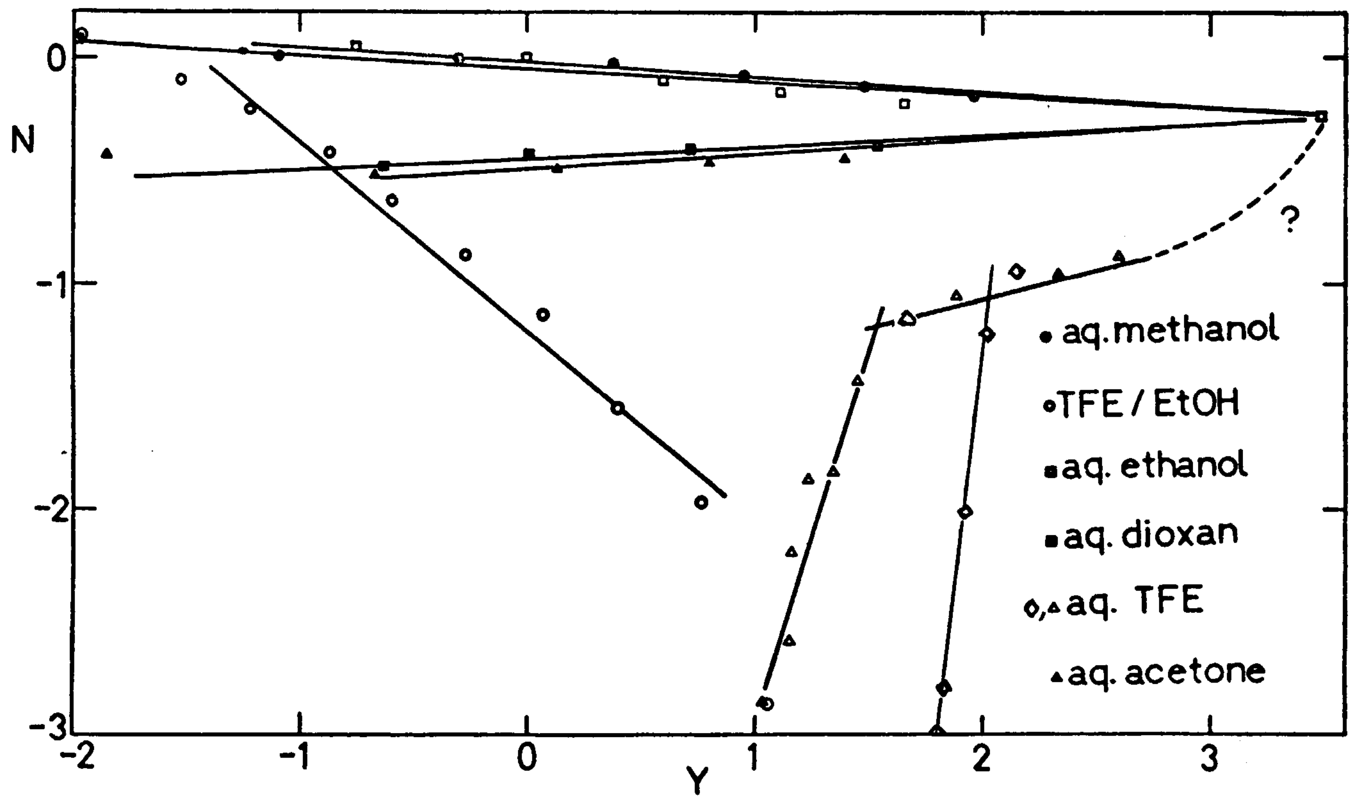

Figure. N vs. Y plots for binary solvent mixtures. Y values for MeOH-H_2O, EtOH-H_2O, Dioxane-H_2O and Acetone-H_2O are fron ref. 2b and based on t-BuCl. The N values are from ref. 3b. N and Y(t-BuCl) values for TFE-EtOH from ref. 7 are supplemented by new N values from ref. 6 and new Y values which are based on the solvolysis of 4,4'-dichlorobenzhydryl chloride or on E_T values from ref. 8. The N values for TFE-H_2O are from ref. 3 and 9, and they were plotted against the Y values based on t-BuCl (ref. 3b,10,11) (△) giving a curved plot which was approximated by two linear relationships. The dotted line connects the line for 70-40% TFE-H_2O with the point for pure water. The same N values were also plotted against the Y values which are based on 2-adamantyl tosylate (ref. 3b) (◆).

tosylate from eq 2,[3b] and the other m values are in the direction expected by the nature of the substituents.[3b] (iv)In TFE-H_2O different models give enormously different sets of Y values.[3b,10] The N-Y relationship based on t-BuCl[11] is curved but it can be treated as two regression lines with positive but much different a values, and a deviating point for pure water. Higher N and Y values for water compared with TFE account qualitatively for the trend, but in view of these and other complications,[10,11] mechanistic conclusions are unwarranted. Less Y values are available for 2-adamantyl tosylate as a model[3b], and although deviation from linearity at high Y values is possible it is noteworthy that the linearity observed at the 100-70% TFE-H_2O region (Figure) can explain the apparent anomalies of very low m_{GW} values for typical k_c substrates[10,13] and the relatively high m_{GW} values for several secondary vinylic substrates.[14] Here a=9.02 and since $\ell = (1-m)/0.7$ for tosylates,[3b] eq 5 gives $m = 1.08 - 0.08m_{GW}$, i.e., both apparently high and low m_{GW} values lead to $m \sim 1$, the value expected for k_c substrates.

While eq 2 should be always used when possible, these considerations will be useful for estimating m values from m_{GW} values where only limited data in these mixtures are available.

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