

ON THE PROBLEM OF EMPIRICAL CHARACTERISTICS OF A MEDIUM AND THEIR MUTUAL RELATIONS

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New parameters of polarity, acidity, and basicity of a medium, which are more suitable to characterize nonspectral solvent effects, were derived by dividing the Taft-Kamlet solvent parameters π^* , α , and β by a function of the refractive index n , $f(n) = (n^2 - 1)/(2n^2 + 1)$. The new parameters were used in evaluating the effect of the medium on reaction rates, equilibria, solubilities, hyperfine splitting constants in EPR spectra, fluorescence life time, free energy of dissolution of ions and ion pairs, and on the Snyder solvent factors of the elution strength in chromatography.

Many investigators have attempted since long to create an universal method of characterizing the effect of the medium on chemical and physical processes. Intense studies in this field led to the establishment of more than 40 ensembles of different solvent characteristics, whose mutual relations are often only rough¹⁻³. Spectral data for suitably chosen indicators (UV-VIS, IR, NMR, EPR) served as standards for these solvent characteristics. Changes in the positions of spectral lines have been used to estimate or evaluate the influence of the medium on the studied nonspectral property.

The aim of the present work is to eliminate the inconsistency between the shift of the spectral lines and the changes in the equilibrium or kinetic data induced by the solvent.

In interpreting the solvent-induced changes in the position of spectral lines, we showed⁴⁻⁶ that for limited ensembles (*e.g.*, 29 select solvents recommended by Taft and Kamlet) the solvent shifts, $\Delta\bar{\nu}$ (with respect to vapor state), are proportional to the product of functions of the refractive index n and of the relative permittivity D :

$$\Delta\bar{\nu} = kf(n^2)f(D) = k[(n^2 - 1)/(2n^2 + 1)](D - 1)/(2D + 1). \quad (1)$$

On the basis of the model used⁴, $f(D)$ characterizes the equilibrium arrangement of a cybotactic sphere of totally polarized solvent molecules in the vicinity of a solute molecule, and $f(n^2)$ characterizes the additional, only deformation polarization of these cybotactic solvent molecules during excitation of the solute.

The function $f(n^2)$ is thus significant only for the evaluation of the influence of the medium on the excitation process (position of the spectral line) and not on the "chemical" or spectral properties which are not connected with the excitation process (hyperfine splitting constants in EPR spectra). Now, if we replace $\Delta\tilde{\nu}$ in Eq. (1) by an empirical dipolarity parameter derived from it, e.g., π^* , and the function $f(D)$ by an empirical characteristic of the arrangement of cybotactic solvent molecules, say, π_n^* , we obtain

$$\pi^* = kf(n^2)\pi_n^* \quad (2)$$

Cyclohexane is taken again as a standard solvent with $\pi_n^* = \pi^* = 0$. Similarly, we can write for the Taft-Kamlet parameters of acidity, α , and basicity, β , derived

TABLE I

Correlations of the solvent properties with the proposed solvent parameters and with the Taft-Kamlet parameters

System	Y_n	s_n	b_n	a_n	R_n^a	a_n^a	No^b	R_{KT}^c	s_{KT}^c
1	-4.35	0.980	—	—	0.992	0.17	38	0.972	0.31
2	-2.75	0.430	—	—	0.982	0.13	14	0.980	0.14
3	15.11	-1.440	—	—	0.992	0.50	12	0.971	0.93
4	37.67	-1.888	—	—	0.980	1.05	12	0.972	1.25
5	-4.00	0.731	—	—	0.975	0.23	15	0.929	0.38
6	-3.47	0.684	—	—	0.984	0.17	15	0.938	0.33
7	12.56	-1.675	—	—	0.947	0.71	9	0.806	1.30
8	4.94	-0.587	-4.76	—	0.917	0.28	5	0.880	0.33
9	-0.18	-0.273	—	—	0.962	0.16	6	0.955	0.17
10	1.32	-0.218	—	—	0.930	0.14	13	0.882	0.18
11	1.13	-0.226	—	—	0.936	0.14	13	0.889	0.18
12	3.86	-0.126	—	-0.146	0.980	0.08	12	0.967	0.10
13	15.04	0.155	—	0.151	0.965	0.12	26	0.891	0.21
14	13.96	0.151	—	0.143	0.977	0.09	26	0.962	0.12
15	15.16	0.138	—	0.125	0.982	0.07	26	0.903	0.16
16	0.03	0.104	0.077	—	0.966	0.05	22	0.948	0.07
17	13.42	-2.865	—	—	0.988	0.63	23	0.948	1.30
18	17.04	-2.972	—	—	0.978	0.53	14	0.842	1.38
19	42.21	-7.919	-4.14	—	0.975	1.53	14	0.833	3.83
20	-11.89	2.507	—	—	0.965	0.52	19	0.795	1.20
21	15.33	-3.05	—	—	0.954	0.72	18	0.798	1.45
22	3.55	-0.218	-1.01	—	0.945	0.10	9	0.890	0.15

^a Correlation with new parameters; ^b number of solvents used in the study; ^c correlation with Taft-Kamlet parameters.

from the spectral shifts,

$$\alpha = k' f(n^2) \alpha_n, \quad \beta = k' f(n^2) \beta_n. \quad (3)$$

Thus, we obtained from the Taft-Kamlet parameters π^* , α , and β new parameters of dipolarity, π_n^* , acidity, α_n , and basicity, β_n , which according to the starting model concept⁴ characterize only the equilibrium spatial and energetic relations in the cybotactic sphere.

To test this model, we correlated the solvent effects on chemical and physical properties of 22 ensembles with the original and modified Taft-Kamlet solvent parameters. We considered the systems studied by these authors using their parameters, and moreover systems involving a higher number of solvents. These were as follows (the numbers refer to Table I): 1. Logarithm of the rate constant ($\log k$) for the reaction of tri-*n*-propylamine with methyl iodide⁷. 2. $\log k$ for the decomposition of tert-butyl ester of formic acid⁸. 3. $\log k$ for the decomposition of tert-butyl chloride⁹ at 298 K. 4. $\log k$ for the decomposition of tert-butyl chloride⁹ at 373 K. 5. $\log k$ for the reaction of triethylamine with ethyl bromo acetate¹⁰. 6. $\log k$ for the reaction of triethylamine with ethyl iodoacetate¹⁰. 7. $\log k$ for the decomposition of α -chlorobenzyl methyl ether¹. 8. Logarithm of the equilibrium constant for dimerization of benzoic acid¹². 9. Logarithm of the keto-enol tautomeric equilibrium constant for ethyl acetoacetate¹³. 10. Free energy of the *cis-trans* equilibrium of 2-methoxy-5-isopropyl-1,3-dioxane^{14,16}. 11. Free energy of the *cis-trans* equilibrium of 2-ethoxy-5-isopropyl-1,3-dioxane^{14,16}. 12. Life time of the fluorescence of Rose Bengal dye¹⁷. 13. EPR hyperfine splitting constant for di-tert-butyl nitroxide¹⁸. 14. EPR hyperfine splitting constant for 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy¹⁸. 15. EPR hyperfine splitting constant for 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrroline-1-yloxy¹⁸. 16. Snyder's coefficients¹⁹ of the elution strength ϵ^0 . 17. Free energy of the transition of the ion pair $(\text{CH}_3)_4\text{N}^{(+)}\text{I}^{(-)}$ between methanol and another medium²⁰. 18. Free energy of dissolution for the ion pair $(\text{CH}_3)_4\text{N}^{(+)}\text{I}^{(-)}$ (ref.²⁰). 19. Free energy of dissolution for the free ions $(\text{C}_2\text{H}_5)_4\text{N}^+$ and I^- (ref.²⁰). 20. Solubility of $(\text{C}_2\text{H}_5)_4\text{NI}$ in aprotic solvents²⁰. 21. Free energy of dissolution for the ion pair²⁰ $(\text{C}_2\text{H}_5)_4\text{N}^{(+)}$. 22. Logarithm of molecular ellipticity for the 2-benzoylbenzoic acid amphetamine system²¹.

Regression coefficients Y_n , s_n , a_n , and b_n for the dependence of the studied property Y on the solvent parameters π_n^* , α_n , and β_n

$$Y = Y_n + s_n \pi_n^* + a_n \alpha_n + b_n \beta_n \quad (4)$$

are given in Table I together with the correlation coefficients and standard deviations for the correlations of the solvent effects with the new solvent parameters (R_n , a_n) and with the Taft-Kamlet parameters^{15,22} (R_{KT} , s_{KT}). It is seen that the new parameters are in all cases more suitable than the old ones.

To evaluate the influence of the medium on the position of spectral lines, it is, of course, necessary to use the products of the new parameters with the function $f(n^2)$.

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