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Classification of solvents on the basis of topology of the molecule

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Attempt has been made to classify the solvents on the basis of the topology of the molecule. The principal components of nine topological parameters for all the solvents have been determined. From the first principal component (PC_1) the solvents have been classified into positive and negative principal component class, where most of the nonpolar solvents have negative PC_1 values and most of the polar solvents have positive PC_1 values.

Solvents influence the chemical or physical processes by solvating the substrate either through Van der Waals force, hydrogen bonding or by providing solvent pockets or cages for encapsulating the substrate. To provide these characteristics the functional groups present in the solvent molecule, their orientation, and structure of the molecule as a whole play important roles. According to the characteristics of the solvent various modes of classification have been proposed by different workers. Parker[1] has classified the organic solvents, considering polarity into account, to three major groups; viz protic, dipolar aprotic and apolar aprotic. With increasing complexity in nature of study in chemical processes the solvents are classified into a number of classes. Richardt[2] and Griffith[3] have reviewed and discussed several classifications of solvents. By considering dielectric constant and dipole moment Dack[4] has grouped the solvent into four different classes. Similarly by considering functional groups, acidity, basicity, proticity, H-bonding characteristics, polarity, polarizability, nucleophilicity and electrophilicity, solvents have been classified into three to fourteen different groups[1,5-12]. In most cases the number of classes and the number of classification parameters are arbitrarily chosen.

The topological parameters find a unique place in correlation chemistry because they represent the molecule as a whole. Various physicochemical properties have been well-correlated with different topological parameters[13-18]. In this paper we have made an attempt to consider the topological parameters as the basis set for classification of solvents.

Data base and Analytical method

The solvent parameters, Kirkwood function (K), molecular refraction (MR), molecular dipole moment (μ), Hilderbrand parameter (δ), index of refraction (n), boiling point (bp), and HOMO and LUMO energies (ε_H, ε_L) values have been taken from ref. (19). Log P values of the solvents have been obtained from the collection of Leo *et al.*[20].

Calculation of topological parameters

Three different, yet related, type groups of parameters have been selected to represent solvents numerically.

1. *Wiener numbers* (W & $\bar{W}$) *and information indices* (I_D^W & $\bar{I}_D^W$)—Wiener number (W) is the first topological index and represents the sum of all possible topological distances of a hydrogen suppressed molecular graph[21]. W is calculated from the distance matrix of the molecular graph. It is a square $n \times n$ matrix, where n is the number of vertices in the hydrogen depleted molecular graph. The entries of the matrix being $d_{ij} = d_{ji}$ representing the number of bonds between vertices i and j by the shortest path. To differentiate heteroatom the d_{ii} and d_{ij} entries are modified as assigned by Randic *et al.*[22]

$$d_{ii} = 1 - Z_c / Z_i \qquad \ldots (1)$$

where $Z_c = 6$, and Z_i atomic number of atom i.

$$d_{ij} = \Sigma k_r \qquad \ldots (2)$$

$$k_r = 1/W_r (Z_c^2 / Z_i \times Z_j)$$

where W_r is the bond weight with value 1, 1.5, 2 and 3 for a single, aromatic, double and triple

bond respectively, Z_j being the atomic number of atom 'j'.

From the distance matrix, W is computed as:

$$W=\sum_{ij} d_{ij}\ /2 \qquad \ldots (3)$$

The mean wiener number is thus determined as

$$\bar{W}=2W/n(n-1) \qquad \ldots (4)$$

The information indices are obtained by the statistical treatment of the topological distances of the chemical graph through the formalism of information theory. The information index (I_D^W) is defined as:

$$I_D^W=W \log_2 W-\Sigma(k_d)(d \log_2 d) \qquad \ldots (5)$$

where the distance d appears k_d times in the partition. The mean infomation index ($\bar{I}_D^W$) is calculated as:

$$\bar{I}_D^W=I_D^W/W \qquad \ldots (6)$$

2. *Molecular connectivity and valence molecular connectivity* ^1x *and* $^1x^v$—In the hydrogen suppressed molecular graph, a δ value is assigned to each vertex (atom) corresponding to the number of non-hydrogen atoms bonded to it. A connectivity value for a bond C_k (connecting atom i and j) is computed as follows.

$$C_k=(\delta_i \delta_j)^{1/2} \qquad \ldots (7)$$

Finally ^1x is calculated as the sum of all connectivity terms.

$$^1x=\Sigma C_k \qquad \ldots (8)$$

$^1x^v$ is calculated from the hydrogen depleted molecular graph, by assigning δ_v value to each vertex as follows[23,24]

$$\delta_v=Z_i^v-h_i \qquad \ldots (9)$$

where Z_i^v represents the number of valence electrons and h_i denotes the number of hydrogen atoms attached to the particular atom. Thereafter, $^1x^v$ is calculated as in the case of ^1x by substituting δ_v for δ, for δ in Eq. 7.

3. *Information content (IC), structural information content (SIC) and complementary information content (CIC)*—A total molecular graph (where hydrogen is not suppressed) is constructed for the molecule. For each vertex (atom), partition coordinates are assigned according to the bonding of the connected atoms with its immediate neighbourhood. The coordinates bear the information of types of bonds between the concerned atom and the adjacent atom. The coordinates are, then, classified according to their partition coordinates. From the probability of the class and the number of atoms in the molecular graph IC has been calculated using Shanon's formula[25]

$$IC=-\sum_{i=1}^{k} P_i \times \log_2 P_i \qquad \ldots (10)$$

where $P_i=n_i/n$ is the probability that a randomly selected element will lie in the ith partitioning class, and n is the number of atoms in the molecular graph. Structural information content defined by Basak *et al.*[26] is as follows:

$$SIC=IC/\log_2 n \qquad \ldots (11)$$

Another information-theoretical topological index i.e. complementary information content (CIC), defined by Ray Chaudhury *et al.*[27] is

$$CIC=1/n \sum_{i=1}^{k} n_i \times \log_2 n_i \qquad \ldots (12)$$

where k is the number of partitioning class. The values obtained by these methods are given in Tables 1 and 2.

Analysis

The topological parameters have wide applications in explaining homologous series. However, very few topological parameters have yet been reported to explain the functional groups. The change in topological parameters due to change in functional groups can be well established by giving weight to the vertex due to the heteroatoms. Connectivity parameters $^1x^v$ can differentiate the molecular graph due to heteroatom[22]. As an example cyclohexane, benzene, pyridine, dioxane and piperidine have same ^1x values (3.00) whereas the $^1x^v$ values of all the solvents are different. All the parameters derived from W are also degenerate.

The interrelationship of the topological parameters have been given in Table 3. There is no high correlation between the parameters except W and I_D^W ($r=0.992$).

In principal component analysis (PCA) a matrix is first constructed consisting of the correlations (covariances) among the variables of interest. The eigenvalues and eigenvectors of this matrix are then determined. The eigenvectors so obtained are orthogonal, and the sum of their eigenvalues equals the original number of variables. Each eigenvector is a linear combination of the original

Table 1—First principal component (PC_1) of TIs, selected topological parameters (W, $\bar{W}$, I_D^W and $\hat{I}_D^W$) for a set of 83 solvents

Solvent	PC_1	W	$\bar{W}$	I_D^W	$\hat{I}_D^W$
Hexane	−2.972	35.00	2.333	129.6	3.704
Cyclohexane	−1.635	27.00	1.800	102.1	3.782
Triethylamine	−2.284	43.85	2.088	186.7	4.256
Carbondisulphide	3.993	1.998	0.666	4.278	2.141
Sulpholane	0.180	21.07	1.003	89.80	4.263
Dimethyl sulphoxide	2.622	3.548	0.591	10.16	2.864
Dimethylformamide	1.389	13.89	1.389	45.93	3.306
Dimethylacetamide	0.189	23.55	1.570	90.43	3.839
Hexamethylphosphotriamide	−4.134	79.01	1.437	441.6	5.589
N-methylpyrrolidone	−0.482	33.78	1.609	146.0	4.322
Nitromethane	3.275	5.140	0.857	14.64	2.848
Acetonitrile	4.060	2.715	0.905	4.363	1.607
Butyronitrile	0.938	17.29	1.729	54.41	3.147
Propionitrile	2.493	8.001	1.333	19.73	2.466
Acetone	2.153	7.375	1.229	19.03	2.580
Butanone	0.926	15.75	1.575	50.69	3.218
3-Pentanone	−0.493	27.87	1.858	103.7	3.718
Cyclohexanone	−1.623	38.50	1.833	164.4	4.271
Diethyl ether	−0.052	17.25	1.725	62.21	3.606
Dibutyl ether	−5.588	110.2	3.063	543.4	4.929
Diisopropyl ether	−1.935	42.25	2.012	180.3	4.266
Tetrahydrofuran	0.667	13.75	1.375	45.41	3.303
Dioxane	−0.325	23.00	1.533	88.79	3.848
Dimethoxy-1,2-ethane	−0.364	28.00	1.867	102.5	3.660
Acetic anhydride	0.036	35.25	1.679	151.3	4.291
Methyl acetate	1.848	13.50	1.350	44.73	3.313
Ethyl acetate	0.371	25.12	1.675	95.47	3.800
Diethyl carbonate	−1.902	57.87	2.067	268.8	4.645
Propanediol 1,2-carbonate	0.315	32.00	1.524	138.9	4.341
Benzene	−0.164	18.09	1.206	68.42	3.782
Toluene	−0.742	30.12	1.434	127.8	4.244
o-Xylene	−1.756	44.82	1.601	209.0	4.662
p-Xylene	−1.945	46.16	1.649	214.0	4.637
Mesitylene	−2.954	64.20	1.783	321.9	5.014
Styrene	−1.617	45.65	1.630	211.4	4.630
Fluorobenzene	−0.846	28.44	1.354	122.2	4.297
Chlorobenzene	−0.990	26.88	1-280	115.9	4.311
Bromobenzene	−1.113	25.97	1.237	111.7	4.302
Iodobenzene	−1.418	25.68	1.223	110.3	4.295
o-Dichlorobenzene	−1.819	37.05	1.323	176.0	4.751
m-Dichlorobenzene	−1.839	37.73	1.347	179.1	4.746
Pyridine	0.893	17.37	1.158	66.36	3.817
Nitrobenzene	−1.626	57.38	1.594	288.8	5.032
Benzonitrile	−0.959	44.29	1.582	205.8	4.646
Acetophenone	−2.310	64.42	1.817	325.9	4.981
Diphenyl ether	−8.400	183.8	2.357	111 5	6.064
Anisole	−1.420	44.65	1.595	208.1	4.661
Ethylbenzoate	−4.998	124.0	2.254	691.3	5.575
Carbontetrachloride	1.060	8.236	0.824	30.93	3.755
Chloroform	1.588	5.118	0.853	15.93	3.112
Dichloromethane	2.206	2.706	0.902	6.114	2.259
sym-Dichloromethane	0.912	7.412	1.235	20.80	2.806

(*Contd*)

Table 1—First principal component (PC_1) of TIs, selected topological parameters (W, $\bar{W}$, I_D^W and $\bar{I}_D^W$) for a set of 83 solvents

Solvent	PC_1	W	$\bar{W}$	I_D^W	$\bar{I}_D^W$
Trichloroethylene	1.094	9.177	0.918	32.95	3.590
Dichloro-1,1-ethane	1.195	6.412	1.069	18.24	2.844
Formamide	4.005	2.857	0.952	5.579	1.953
N-Methylformamide	3.070	7.517	1.253	19.77	2.629
Water	5.932	0.250	0.000	0.000	0.000
Methanol	4.594	1.000	1.000	0.811	0.811
Ethanol	3.191	3.750	1.250	6.549	1.746
Butanol	0.496	19.25	1.925	61.61	3.201
Tert-Butyl alcohol	0.883	15.25	1.525	50.52	3.313
Glycol	2.276	9.000	1.500	24.02	2.669
Isopropyl alcohol	1.931	8.500	1.417	22.23	2.615
s-Butyl alcohol	0.729	17.25	1.725	56.09	3.251
Diethylene glycol	−1.256	47.75	2.274	202.6	4.243
Benzyl alcohol	−1.294	47.65	1.702	221.5	4.648
1-Propanol	1.893	9.500	1.583	24.24	2.552
Isobutyl alcohol	0.803	17.00	1.700	54.36	3.197
Isoamyl alcohol	−0.482	31.00	2.066	117.2	3.779
2-Pentanol	−0.623	31.00	2.066	116.9	3.771
3-Pentanol	−0.600	30.00	2.000	113.7	3.788
1-Pentanol	−0.927	34.00	2.267	127.0	3.736
Tert-Pentyl alcohol	−0.239	27.00	1.800	103.7	3.842
1-Octanol	−5.853	118.2	3.285	582.5	4.926
Cyclohexanol	−1.744	40.75	1.940	174.5	4.282
Trifluoroethanol	1.359	23.00	1.534	91.63	3.983
2-Methoxyethanol	1.217	17.00	1.700	55.58	3.269
Acetic acid	3.530	6.875	1.146	18.73	2.724
Trifluoroacetic acid	1.573	32.66	1.555	144.4	4.419
Piperidine	−0.557	25.86	1.724	98.48	3.808
Aniline	−0.247	29.40	1.400	139.3	4.737
Propylamine	1.839	9.714	1.619	24.47	2.519
Diethylamine	0.698	18.43	1.843	58.75	3.188

Table 2—Selected topological parameters (IC, SIC, CIC, $^1\chi$ and $^1\chi^v$) for set of 83 solvents

Solvent	IC	SIC	CIC	$^1\chi$	$^1\chi^v$
Hexane	1.140	0.243	3.560	3.914	3.914
Cyclohexane	0.918	0.220	3.252	3.000	3.000
Triethylamine	1.363	0.306	3.096	3.346	3.070
Carbondisulphide	0.918	0.579	0.667	1.414	0.408
Sulpholane	1.907	0.488	2.000	3.207	2.411
Dimethyl sulphoxide	1.571	0.473	1.751	1.732	0.983
Dimethylformamide	1.781	0.497	1.804	2.270	1.388
Dimethylacetamide	1.688	0.432	2.219	2.643	1.822
Hexamethylphosphotriamide	1.571	0.323	3.287	4.830	3.466
N-Methylpyrrolidone	2.092	0.523	1.908	3.304	2.545
Nitromethane	1.842	0.656	0.965	1.732	0.812
Acetonitrile	1.792	0.693	0.793	1.414	0.724
Butyronitrile	1.781	0.497	1.804	2.414	1.784
Propionitrile	1.880	0.593	1.290	1.914	1.284
Acetone	1.571	0.473	1.751	1.732	1.204
Butanone	1.700	0.460	1.999	2.270	1.765

Contd.

Table 2—Selected topological parameters (IC,SIC,CIC, $^{1}\chi$ and $^{1}\chi^{v}$) for set of 83 solvents

Solvent	IC	SIC	CIC	$^{1}\chi$	$^{1}\chi^{v}$
3-Pentanone	1.674	0.418	2.326	2.808	2.525
Cyclohexane	1.450	0.355	2.637	3.394	2.911
Diethyl ether	1.426	0.365	2.481	2.414	1.991
Dibutyl ether	1.530	0.322	3.224	4.414	3.991
Diisopropyl ether	1.378	0.314	3.014	3.126	2.781
Tetrahydrofuran	1.547	0.418	2.154	2.500	2.077
Dioxane	1.379	0.362	2.429	3.000	2.155
Dimethoxy-1,2-ethane	1.549	0.387	2.451	2.914	1.894
Acetic anhydride	2.046	0.553	1.655	3.126	1.816
Methyl acetate	2.049	0.592	1.410	2.270	1.316
Ethyl acetate	1.950	0.512	1.857	2.770	1.904
Diethyl carbonate	1.991	0.478	2.179	3.808	2.604
Propandediol 1,2-carbonate	2.353	0.636	1.347	3.288	2.122
Benzene	1.000	0.279	2.585	3.000	2.000
Toluene	1.533	0.392	2.374	3.394	2.411
o-Xylene	1.658	0.398	2.512	3.804	2.827
p-Xylene	1.658	0.398	2.512	3.788	3.155
Mesitylene	1.664	0.379	2.728	4.181	3.232
Styrene	1.649	0.412	2.351	3.932	2.608
Fluorobenzene	1.000	0.279	2.585	3.394	2.022
Chlorobenzene	1.000	0.279	2.585	3.394	2.513
Bromobenzene	1.000	0.279	2.585	3.394	2.903
Iodobenzene	1.000	0.279	2.585	3.394	3.626
o-Dichlorobenzene	1.000	0.279	2.585	3.804	3.031
m-Dichlorobenzene	1.000	0.279	2.585	3.788	3.025
Pyridine	1.790	0.517	1.669	3.000	1.850
Nitrobenzene	2.006	0.527	1.801	4.304	2.499
Benzonitrile	1.914	0.517	1.786	3.932	2.384
Acetophenone	1.993	0.488	2.095	4.304	2.865
Diphenyl ether	1.548	0.342	2.976	6.449	4.230
Anisole	1.774	0.444	2.226	3.932	2.523
Ethylbenzoate	2.258	0.514	2.135	5.342	3.565
Carbontetrachloride	0.722	0.311	1.600	2.000	2.408
Chloroform	0.722	0.311	1.600	1.732	2.085
Dichloromethane	0.722	0.311	1.600	1.414	1.702
sym-Dichloromethane	0.811	0.270	2.189	1.194	2.202
Trichloroethylene	0.918	0.355	1.667	2.270	2.188
Dichloro-1,1-ethane	0.811	0.270	2.189	1.732	1.967
Fromamide	1.792	0.693	0.792	1.414	0.493
N-Methylformamide	2.281	0.720	0.888	1.914	1.024
Water	0.918	0.579	0.667	0.000	0.000
Methanol	1.792	0.693	0.792	1.000	0.447
Ethanol	1.880	0.593	1.290	1.414	1.023
Butanol	1.871	0.479	2.035	2.414	2.023
Tert-Butyl alcohol	1.688	0.432	2.219	2.00	1.724
Glycol	1.922	0.579	1.400	1.914	1.132
Isopropyl alcohol	1.781	0.497	1.804	1.732	1.413
s-Butyl alcohol	1.871	0.479	2.034	2.270	1.951
Diethylene glycol	1.970	0.482	2.188	3.414	2.210
Benzyl alcohol	2.046	0.512	1.954	3.932	2.580

(Contd)

Table 2—Selected topological parameters (IC, SIC, CIC, $^1\chi$ and $^1\chi^v$) for set of 83 solvents

Solvent	IC	SIC	CIC	$^1\chi$	$^1\chi^v$
1-Propanol	1.947	0.543	1.638	1.914	1.523
Isobutyl alcohol	1.871	0.479	2.035	2.270	1.879
Isoamyl alcohol	1.945	0.467	2.225	2.770	2.379
2-Pentanol	1.833	0.440	2.336	2.770	2.451
3-Pentanol	1.833	0.440	2.336	2.808	2.489
1-Pentanol	1.792	0.430	2.378	2.914	2.523
Tert-Pentyl alcohol	1.792	0.430	2.378	2.561	2.170
1-Octanol	1.607	0.338	3.148	4.414	4.023
Cyclohexanol	1.634	0.385	2.614	3.394	3.075
Trifluoroethanol	1.880	0.593	1.290	2.561	1.005
2-Methoxyethanol	2.035	0.550	1.665	2.414	1.513
Acetic acid	2.046	0.802	0.594	1.732	0.928
Trifluoroacetic acid	2.046	0.802	0.594	2.943	1.013
Piperidine	1.736	0.425	2.351	3.000	2.707
Aniline	2.006	0.527	1.801	3.394	2.199
Propylamine	2.035	0.550	1.665	1.914	1.615
Diethylamine	1.674	0.418	2.326	2.414	1.121

Table 3—Simple correlation matrix of topological parameters used to derive principal components

	W	$\bar{W}$	I_D^W	$\hat{I}_D^W$	IC	SCI	CIC	$^1\chi$	$^1\chi^v$
W	1.00								
$\bar{W}$	0.69	1.00							
I_D^W	0.99	0.61	1.00						
$\hat{I}_D^W$	0.76	0.58	0.72	1.00					
IC	0.15	0.33	0.13	0.10	1.00				
SIC	−0.27	−0.25	−0.24	−0.42	0.72	1.00			
CIC	0.55	0.63	0.49	0.65	−0.31	−0.85	1.00		
$^1\chi$	0.88	0.64	0.85	0.95	0.13	−0.39	0.67	1.00	
$^1\chi^v$	0.75	0.65	0.70	0.82	−0.17	−0.69	0.86	0.85	1.00

variables and represents a principal component. The process can be viewed as one in which the first principal component axis is constructed to account for a maximum amount of variance in the data; the second component axis accounts for a maximum amount of the remaining variance under the constraint that it be orthogonal to the first component, and so forth, until all component axes are constructed. The eigenvalues, per cent of variance and cumulative per cent of variance are given in Table 4. The first principal component (PC_1) is associated with 63.1% of total variance of all the topological parameters. The second and third PCs are associated with 22.4% and 7.2% of the variance respectively. The first three PCs can explain 92.7% of the total variance cumulatively. As the PCs are generated from the topological parameters the dominating components of each PC have been identified by simple correlation analysis. For the purpose PC_1 and PC_2 have been correlated with all the nine topological parameters individually and the correlation coefficients are given in Table 5. All the parameters except IC and SIC correlate well with PC_1 while these two parameters contribute more to PC_2. Since the first principal component (PC_1) is due to the maximum contribution of all topological parameters, it is planned to consider PC_1 as the basis of classification of the solvents.

Discussion

It is interesting to note that major nonpolar solvents have negative PC_1 values while most of the polar solvents have positive PC_1 values. To study the quantitative structure property relationship between PC_1 values and various physicochemical properties like Kirkwood function (K), molecular refraction (MR), molecular dipole moment (μ), Hilderbrand parameter (δ), refractive index (n), boiling point (bp) and the energy of HOMO (ε_H) and LUMO (ε_L), the data are subjected to multiple regression analysis. The statistical results are

Table 4—Eigenvalues, per cent variance and cumulative per cent of variances derived from PCA

PCs	Eigenvalues	Variance (%)	Cumulative variance (%)
1	5.679	63.1	63.1
2	2.015	22.4	85.5
3	0.646	7.2	92.7
4	0.414	4.6	97.3
5	0.105	1.2	98.4
6	0.089	1.0	99.4
7	0.033	0.4	99.8
8	0.017	0.2	100.0
9	0.002	0.0	100.0

Table 5—Correlation coefficients (r) of first principal component (PC_1) and second principal component (PC_2) with all the topological parameters

TIs	r	
	PC_1	PC_2
W	−0.89	0.30
$\bar{W}$	−0.75	0.29
I_D^W	−0.85	0.30
$\bar{I}_D^W$	−0.89	0.12
IC	0.03	0.93
SIC	0.59	0.79
CIC	−0.83	−0.42
$^1\chi$	−0.94	0.18
$^1\chi^v$	−0.94	−0.18

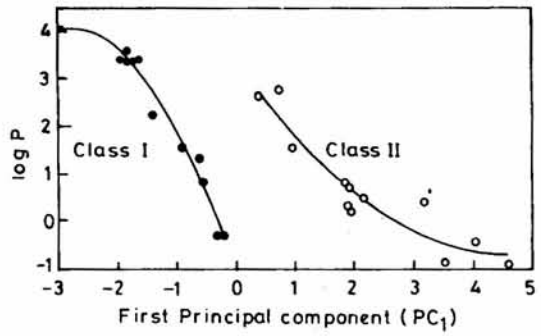

Fig. 1—Plot of First Principal Component versus log P

Table 6—Correlation coefficients (r) of first principal component (PC_1) and second principal component (PC_2) with Physicochemical properties: Kirkwood function (K), molecular refraction (MR), molecular dipole moment (μ), Hilderbrand parameter (δ), index of refraction (n), boiling point (bp), and HOMO and LUMO energies (ε_H, ε_L)

Properties	PC_1	PC_2	PC_1, PC_2
K	0.38	0.41	0.57
MR	0.93	0.08	0.94
μ	0.18	0.41	0.45
δ	0.48	0.30	0.57
μ	0.37	0.11	0.39
bp	0.43	0.34	0.55
ε_H	0.60	0.01	0.61
ε_L	0.01	0.04	0.03

Table 7—Correlation analysis of various empirical properties with First Principal Component (PC_1) of TIs

Chemical processes	r	n	Ref.
Fluorescence maxima of *p*-aminophenyl benzimidazole in various solvents	0.90	7	29
Fluorescence maxima (nm) of 3-amino-fluoroethane in different solvents	0.90	6	30
Kosower's values on the studies on thermochromic behaviour of 6-nitrospiropyran.	0.86	8	31
Absorption maxima values on the studies on thermochromic behaviour of 6-nitrospiropyran.	0.94	9	31
Activation parameter (E_a) values on the studies on thermochromic behaviour of 6-nitrospiropyran.	0.86	9	31
Entropy values (ΔS) on the studies on thermochromic behaviour of 6-nitrospiropyran.	0.82	9	31
Partial rate coefficients (k_1k_2/k_{-1}) on the reaction of 1-fluoro-2,4-dinitrobenzene (DNFB) with piperidine in aprotic solvents at 15°C.	0.84	7	32
Partial rate coefficients (k_1k_3/k_{-1}) on the reaction of 1-fluoro-2,4-dinitrobenzene (DNFB) with piperidine in aprotic solvents at 15°C.	0.89	7	32
Values of K_A^F/K_A^{Cl} for the reaction of DNFB and DNCB with piperidine in aprotic solvents at 15°C.	0.81	8	32
Second order reaction rate coefficients for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine in hydroxylic solvents at 15°C.	0.85	6	33
Second order reaction rate coefficients for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine in hydroxylic solvent at 25°C.	0.88	7	33
Second order reaction rate coefficients for the reaction of 1-chloro-2,4-dinitrobenzene with piperidine in hydroxylic solvent at 40°C.	0.89	6	33

given in Table 6. Except molecular refraction the other physicochemical properties do not have good correlation with PC_1. Addition of PC_2 to the regression equation does not have significant improvement in the correlation coefficient values.

Hansch *et al.*[28] have introduced log P, a parameter for hydrophobicity obtained by measuring the partition of organic substrates in octanol-water medium, to use in QSAR studies. The PC_1 values for octanol and water are found to be -5.853 and 5.932 respectively. Except the value for diphenyl ether (-8.4), these two values are the extreme two points of the rest. This observation prompted us to correlate the log P values with the PC_1 values. The plot of PC_1 versus log P is given in Fig. 1. From the plot it is clear that solvents can be classified into two major classes, one having positive PC_1 values and the other with negative PC_1 values.

Some solvents, e.g. halomethanes, carbondisulphide etc. having nonpolar characteristics have positive PC_1 values. Similarly some polar solvents have also negative PC_1 values. Thus it is observed that this classification does not depend solely on polarity. To investigate the applicability of PC_1 as a solvent parameter, the experimental data of some chemical processes[29-33] have been correlated with the PC_1 values. The statistical results are given in Table 7. In almost all cases the correlation coefficients are found to be significant (0.81-0.94).

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