SOLVENT EFFECT — CLASSIFICATION OF PARAMETERS DESCRIBING INFLUENCE OF SOLVENTS

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On the basis of factor analysis of data matrices containing 35 empirical and non-empirical parameters for 85 solvents (or a limited matrix of 20 parameters for 51 solvents), an orthogonal set of parameters with normed normal distribution has been suggested which characterizes influence of the solvents on chemical processes. A four-parameter equation has been suggested for description of the solvent effect in the form $A = A_0 + a \cdot AP + b \cdot BP + eEP + pPP$, where AP, BP, EP, PP are newly introduced parameters expressing individual types of interactions between solvent and solute. A comparison has been carried out of these parameters with those defined earlier. The new set of parameters was tested with 22 examples taken from literature. The correlations obtained show higher or comparable agreement as compared with those carried out earlier. Values of the regression coefficients make it possible to discuss the reaction mechanisms from the point of view of solvent effects.

Solvent effect on chemical processes is intensively studied but far from fully understood yet. At present there are two approaches to quantitative description of this effect. The theoretical approach describes solvent as an isotropic environment of the dissolved particles and characterizes it by a suitable macroscopic quantity (relative permittivity, refractive index, cohesive energy) which is used in deriving the relation for the so called reaction field[1]. Application of these relations to the activation complex theory gives a linear relation between logarithm of the rate constant and a function of this quantity[2-5], the values of the given function being used as parameters characterizing the solvent in correlations of solvent effect on chemical processes. This approach has the drawback in that it only involves contributions of non-specific solvation. The other approach has found more applications so far. Here the rate constant parameter is considered to be a linear function of a suitably chosen empirical parameter. The empirical parameters are defined with the use of various equilibrium, kinetic, and spectral models, and there exist more than 30 such parameters at present[6-8]. Mathematical formulation of this empirical approach was given by Taft and coworkers[8] and denoted as LSER (Linear Solvation Energy Relationships).

Success of this correlation depends mostly on the difference between the process in question and the model used for defining the chosen parameter. Therefore, approaches were suggested which describe the solvent effect by several parameters.

Katritzky and coworkers[9] tested various multi-parameter equations applying combinations of available parameters and recommended the best combination of the $E_T(30)$ parameter[10], the Kirkwood function of relative permittivity[6,7], and a function of refractive index[6,7]. Koppel and Palm[11,12] presumed the interaction between solvent and reacting molecules to be separable into specific and non-specific solvation. They suggested a four-parameter equation in the form:

$$A = A_0 + yY + pP + eE + bB , \qquad (1)$$

where A is a symbol for the physico-chemical property dependent on solvent effect, A_0 is value of the same property in gas phase, Y, P, E, B are parameters characterizing individual kinds of the solvent–solute interactions, and y, p, e, b are the regression coefficients characterizing sensitivity of the property A to the individual parameters. This equation was tested in 70 various examples[7]. Most of the correlations showed a single term to be statistically significant. In more than 50 cases the term of electrophilic solvation only appeared significant[7].

Krygowski and Fawcett[13–15] presumed the decisive role to be played by specific solvation of the substrate, and they suggested a two-parameter equation in the form:

$$A = A_0 + \alpha E_T(30) + \beta DN . \qquad (2)$$

This equation proved successful in 90% of the cases tested. Another multiparameter empirical relation, mainly for solvatochromic effects, was suggested by Kamlet and Taft[16–19] in the form:

$$A = A_0 + s \,.\, \pi^* + a \,.\, \alpha + b \,.\, \beta . \qquad (3)$$

For the cases with no significant contribution of the Lewis acidity α and basicity β this relation was complemented by the term characterizing polarizability to give[20]

$$A = A_0 + s(\pi^* + d\delta) . \qquad (4)$$

The equation was tested with data on solvatochromic shifts of various indicators and proved successful in this field. Mayer[21,22] used the so called donor-acceptor approach and the defined AN and DN scales and he suggested the relation

$$\Delta \Delta G = a \,.\, \Delta DN + b \,.\, \Delta AN + c \,.\, \Delta \Delta G^0_{ev} , \qquad (5)$$

where ΔG represents the Gibbs energy of the reaction or the Gibbs activation energy (ΔG^*), ΔG^0_{ev} is the standard Gibbs energy of evaporation, these values, as well as the

AN and DN values, being related to the reference solvent – acetonitrile. This model takes into account the cavity term described by means of ΔG^0_{cv} and connected with the idea of formation of empty cavities in the solvent with the magnitude corresponding to volume of solute molecules.

Dougherty[23] based his correlation Eq. (6) on a consideration of solute–solvent interactions using the frontier orbitals HOMO and LUMO:

$$E_{solv} = C_1(IP_{solv} + EA_{solv}) + C_2(IP_{solv}) + C_3(EA_{solv})^2 + C_4 , \qquad (6)$$

where IP_{solv} and EA_{solv} mean ionisation potential and electron affinity of the solvent, respectively, the C_1, C_2, C_3 constants being dependent on ionisation potential and electron affinity of the substrate. In Eq. (6) the term $(IP_{solv} + EA_{solv})$ reflects the ionisation strength of the solvent – an analogue of the Y parameter, whereas the IP_{solv} and $(EA_{solv})^2$ terms represent the electrophilicity and nucleophilicity of the solvent, respectively. This equation was tested with limited sets of data only.

These multi-parameter relations seem to be much more suitable and promissing in correlations of solvent effect as compared with the mono-parameter ones, because they express a greater part of the solvent–solute interactions. A certain imperfection of these relations or even unsuccessfulness in some cases of application to chemical problems is probably due to the fact that individual terms of the correlation equations are not mutually orthogonal. Therefore, definition of such set of parameters represents one of the main problems in this field.

The factor analysis analyzed in detail (inclusive of the solvent effect) in a book[24] by Malinowski and Howery seems to be a suitable method for the above purpose. Bohle and coworker[25] carried out the factor analysis for 35 solvents and 18 parameters and determined the minimum number of 4 factors, out of which the first is expressed best by means of the E or $E_T(30)$ parameters, the second, third, and fourth ones being expressed by the Kirkwood function of relative permittivity, function of refractive index, and parameter B, respectively. Chastrette[26] carried out the factor analysis for 24 solvents and 6 parameters and determined 5 factors, our of which one was assigned to dipole moment of the solvent, and the other ones were assigned similarly to ref.[25]. Chastrette suggested correlation of the solvent effect by means of abstract factors. Fawcett and Krygowski[15] determined (by the method of main components) the number of factors to be 2 and put them equal to DN and $E_T(30)$ (Eq. (2)). Finally, Wold[27] determined 2 main components using the method of main components for 7 parameters and 65 solvents and solvatochromic data only. So far, the factor analysis has been applied in chemistry to complete data sets only, whereby, of course, the number of the used parameters and solvents was considerably limited. The method, however, can be applied in principle to incomplete sets, too, which makes it possible to involve a greater amount of information in the source matrix.

The aim of our contribution was to adopt the factor analysis for classification of the solvent parameters suggested so far, for choice of the most suitable one for description of the solvent effect, and possibly for a suggestion of a new orthogonal set of parameters.

DATA AND DATA TREATMENT

Two sets of data were used for the analysis. The basic set 1 involved 35 parameters for 85 solvents (the matrix was filled to 43·5%). As this matrix was considerably incomplete, the set 2 involved 20 parameters for the greatest possible number of 51 solvents (the matrix was filled to 77·9%). Table I gives a survey of the parameters and number of their values used in the individual sets. Table II gives a list of the solvents used in the two sets. The parameter 20 — index of molecular connectivity $^{n}\chi$ of the n-th order (ref.[86]), where n means number of σ bonds in the solvent molecule minus the number of bonds to hydrogen — was calculated according to our own program.

TABLE I

The used parameters in the basic (set 1) and the selected (set 2) sets of data

No	Parameter	n (set 1)	n (set 2)	Ref.	No	Parameter	n (set 1)	Ref.
1	B	82	50	28	21	$\log k_1$	16	44
2	$E_T(30)$	63	50	10, 29, 79	22	$\log k_2$	12	45
3	Z	29	28	30	23	Ω	12	46, 47
4	S_1[a]	38	33	31	24	a_N/a_{NH}	11	48
5	S_2[b]	38	35	32	25	Y	9	49, 50—52
6	DN	32	29	33, 14	26	χ_B	11	41
7	ε	85	51	34	27	$\Delta G^0_{OCH_3}$	14	53
8	n_D^{20}	85	51	34	28	F	12	54
9	YP[c]	85	51	—	29	B_G	23	55—57
10	PP[d]	85	51	—	30	$\int_H^{NO}$	25	20
11	E	61	48	35	31	$\Delta\nu_{P=O}$	20	58
12	a^{14N}	27	27	36	32	ν_F	20	59
13	AN	26	25	6, 15	33	$\varepsilon_{Al_2O_3}$	25	60, 61
14	π^*	52	48	6, 37, 38	34	$\Delta I_{SO}^{Cl/Br}$	17	62
15	$\log P$	29	29	39	35	Φ	20	54
16	δ	32	31	40				
17	χ_R	38	37	41				
18	δ^2	32	29	42				
19	β	44	42	18, 43				
20	$^{n}\chi$[e]	84	50	—				

[a] S_1 the parameter S defined by Zelinski; [b] S_2 the parameter S defined by Brownstein; [c] the Kirkwood function of dielectric constant $YP = (\varepsilon - 1)/(2\varepsilon + 1)$; [d] the function of refractive index $PP = (n^2 - 1)/(n^2 + 1)$; [e] the index of molecular connectivity of the n-th order.

The factor analysis was carried out according to ref.[24]. The program was modified in such way that the calculation of elements of the correlation matrix from the normed data[24] was only carried out between two parameters for the solvents in which the two parameters were measured. In the cases where no such solvent was found the correlation coefficient was put equal to zero. This case only occurred for the parameters 25 and 32 in the basic set (set 1). For determination of the minimum number of the factors we used the factor indicator function IND by Malinowski[24]. The proper factor analysis was carried out by the method of iterative calculation of the communalities[63]. The rotation of the abstracts factor was carried out by the VARIMAX method[24].

TABLE II

The solvents used for the factor analysis, set 1 Nos 1–85, set 2 Nos 1–51

No	Solvent	No	Solvent	No	Solvent
1	Hexane	18	Diisopropyl ether	35	Water
2	Heptane	19	Anisol	36	Methanol
3	Cyclohexane	20	Phenetol	37	Ethanol
4	Benzene	21	Tetrahydrofurane	38	1-Butanol
5	Toluene	22	Dioxane	39	2-Propanol
6	*m*-Xylene	23	Acetone	40	t-Butyl alcohol
7	*p*-Xylene	24	Butanone	41	Benzyl alcohol
8	Mesitylene	25	Cyclohexanone	42	1,2-Ethandiol
9	Tetrachloromethane	26	Methyl acetate	43	2-Methoxyethanol
10	Chloroform	27	Ethyl acetate	44	Acetic acid
11	Dichloromethane	28	Acetanhydride	45	Triethylamine
12	1,2-Dichloroethane	29	Formamide	46	Pyridine
13	Chlorobenzene	30	N,N-Dimethylformamide	47	Nitromethane
14	Bromobenzene	31	N,N-Dimethylacetamide	48	Nitrobenzene
15	Fluorobenzene	32	HMPA[a]	49	Dimethyl sulphoxide
16	Diethyl ether	33	Acetonitrile	50	Sulfolane
17	Dibutyl ether	34	Benzonitrile	51	Carbon disulphide
52	Cyclohexene	64	Methyl formiate	76	Formic acid
53	Ethylbenzene	65	Ethyl formiate	77	n-Propylamine
54	t-Butyl chloride	66	Ethyl chloroacetate	78	Aniline
55	Benzyl chloride	67	Methyl benzoate	79	Piperidine
56	Iodobenzene	68	Ethyl benzoate	80	Pyrrole
57	n-Butyl iodide	69	Diethyl carbonate	81	N-Methylaniline
58	Dipropyl ether	70	Dimethyl sulphate	82	N,N-Dimethylaniline
59	Dipentyl ether	71	N-Methylformamide	83	Quinoline
60	Diphenyl ether	72	Hydrogen cyanide	84	Ammonia
61	Dimethoxymethane	73	i-Butyl alcohol	85	Diethyl sulphide
62	Furan	74	Cyclohexanol		
63	Acetophenone	75	Phenol		

[a] Hexamethylphosphoramide.

The cluster analysis was carried out by the method of the nearest neighbour[64]. The multi-fold linear regressions used for testing of the new set of parameters were carried out according to our own statistical program. All the calculations were carried out with an EC 1033 computer.

TABLE III

Coordinates of parameters in factor space of the basic set (set 1)

No[a]	F_1	F_2	F_3	F_4
1	−0·035	0·019	0·455	−0·039
2	0·210	0·122	0·014	0·106
3	0·261	−0·076	0·048	0·079
4	0·205	0·062	0·128	0·022
5	0·217	0·141	−0·016	0·036
6	0·071	−0·068	0·412	−0·067
7	0·120	0·068	−0·026	0·074
8	−0·007	0·143	−0 003	−0·509
9	0·041	0·269	0·075	0·110
10	−0·010	0·144	−0·001	−0·513
11	0·245	−0·002	−0·048	0·133
12	0·292	−0·003	0·021	−0·006
13	0·280	−0·010	−0·053	0·012
14	0·091	0·321	−0·031	−0·163
15	−0·134	−0·055	−0·174	−0·119
16	0·307	−0·003	0·011	−0·120
17	−0·023	−0·350	−0·040	0·023
18	0·303	−0·005	−0·046	−0·151
19	−0·052	0·084	0·412	0·155
20	−0·040	−0·082	0·118	−0·309
21	0·262	−0·031	−0·139	−0·094
22	0·019	−0·043	−0·020	−0·072
23	0·099	0·075	−0·174	0·224
24	−0·262	0·091	−0·095	−0·002
25	0·140	−0·010	−0·042	−0·237
26	0·255	−0·104	0·017	0·011
27	0·008	−0·274	0·022	−0·106
28	0·067	0·112	0·072	0·191
29	−0·007	−0·068	0·502	−0·093
30	−0·042	0·370	0·014	−0·051
31	−0·014	0·346	−0·102	−0·031
32	0·080	−0·312	−0·076	−0·010
33	0·043	0·149	0·187	0·157
34	−0·045	0·304	−0·044	0·106
35	0·293	0·012	0·030	−0·043

For numbers of the parameters see Table I.

RESULTS AND DISCUSSION

In both the treated sets we determined the minimum number of 4 factors, which agrees with the results obtained by Bohle and coworkers[25]. Tables III and IV summarize the coordinates of the individual parameters in the factor space for the two studied sets after completed rotation. From the data it is obvious that the parameters mostly localized on the first factor are those describing electrophilic solvation ability of the solvent, this being true (in the both sets) especially for the parameters AN (13) and $a(^{14}N)$ (12) which are orthogonal with the other factors. Distinctly localized on the second factor are then the factors characterizing the solvent polarity, especially the Kirkwood function of relative permittivity YP(9). The parameters expressing nucleophilic solvation abilities of solvent as the Lewis basicity – B (1), DN (6), β (19), and B_G (29) – are most localized on the third abstract factor. The parameter B (1) appears most orthogonal to the other factors. The last, fourth factor is most closely connected with the parameters describing the dispersion solvation forces –

TABLE IV

Coordinates of parameters in factor space of the selected set (set 2)

No[a]	F_1	F_2	F_3	F_4
1	−0·079	0·012	0·610	0·608
2	0·181	0·263	0·602	0·092
3	0·305	−0·018	0·021	0·133
4	0·261	0·078	0·144	0·014
5	0·225	0·208	−0·010	0·051
6	0·187	−0·208	0·560	−0·161
7	0·154	0·237	0·026	−0·047
8	−0·010	0·044	−0·010	−0·600
9	−0·097	0·473	0·090	0·068
10	−0·014	0·046	−0·608	−0·604
11	0·297	0·073	−0·042	0·124
12	0·355	−0·015	0·022	0·037
13	0·390	−0·066	−0·026	−0·014
14	0·026	0·413	−0·032	−0·250
15	−0·113	−0·103	−0·152	−0·167
16	0·373	0·024	−0·014	−0·114
17	0·094	−0·480	−0·046	0·106
18	0·363	−0·011	−0·071	−0·113
19	−0·137	0·169	0·472	0·140
20	0·028	−0·320	0·159	−0·222

[a] For numbers of the parameters see Table I.

refractive index n_D^{20} (8) and its function PP (10). The said localization is most distinct in the set 2, where the source matrix is filled much more, and the calculation is statistically more significant. Hence, the results obtained agree with the idea by Koppel and Palm[7]. The solvent effect must be described by using 4 parameters, out of which two describe general non-specific solvation of polar and dispersion character and two describe specific solvation of electrophilic and nucleophilic character. This division into 4 classes is also obvious from results of the cluster analysis carried out in the factor space. Table V gives results of this analysis. The best parameter for the correlation equations of solvent effect with one parameter seems to be the $E_T(30)$ parameter by Reichardt which has the highest communality for one factor in the factor matrix, involving thus the greatest part of variability of the source matrix.

From Table IV we can then suggest the following best parameters for description of the individual solvation types: the AN parameter (13) for specific solvation with electrophilic character, the B parameter (1) for specific solvation with nucleophilic character. The solvation of non-specific character is described best by the functions of dielectric constant YP (9) and refractive index PP (10) suggested earlier. The equation describing solvent effect in analogy to that by Koppel and Palm[7] (1) is transformed into Eq. (7).

$$A = A_0 + a \,.\, AN + b \,.\, B + y \,.\, YP + p \,.\, PP \qquad (7)$$

The equation defined in this way has a drawback in that the AN parameter (13) describing the specific electrophilic solvation was measured in a relatively small number of solvents, and its values are experimentally inaccessible in other solvents.

TABLE V
Results of the cluster analysis in the factor space

Class	Set 1	Set S
I	δ, $E_T(30)$, Z, $\log k_2$, Ω, S_1, S_2, a_N/a_{NH}, Y, ε, E, Φ, $a^{14}N$, AN, $\log P$, χ_B, F, δ^2	AN, Z, S_1, S_2, E, $a^{14}N$, $\log P$, δ, δ^2
II	$f_H^{p\text{-}NO}$, YP, π^*, χ_R, $\Delta G^0_{OCH_3}$, $\Delta\nu_{P=O}$, ν_F, $\varepsilon_{Al_2O_3}$, $\Delta I_{50}^{Cl/Br}$	χ_R, $E_T(30)$, ε, YP, π^*, $^n\chi$
III	B_G, B, DN, β	B, DN, β
IV	PP, n_D^{20}, $^n\chi$	PP, n_D^{20}

Therefore, for the correlation of the solvent effect it is more suitable to use the rotated abstract factors which were assigned the above-mentioned physical meaning. The parameter set defined in this way would have several advantages as compared with the parameters of Eq. (7). The newly suggested parameters would not be defined on a single model but would involve information on the given interaction common for all the models used. This set would have a great advantage in having the normed normal distribution, since the regression coefficients in the expression type Eq. (7) would express directly the significance of the individual terms, which is impossible in Eq. (7), because the parameters used differ in their scale factors, and at least partial correlation coefficients must be known for evaluation of significance of the individual terms. Also not negligible is the possibility to calculate certain values of the parameter for the solvents for which the parameters of Eq. (7) were experimentally inaccessible.

On the other hand, the thus suggested set of parameters has the drawback in that it is necessary to carry out – after each completion or extension of the source matrix – a new factor analysis and new calculation of these parameters. In our opinion, however, this drawback is sufficiently counterbalanced by the above-mentioned advantages of such set. Table VI gives values of this parameter set for the equation

$$A = A_0 + aAP + bBP + eEP + pPP , \qquad (8)$$

where AP means parameter of electrophilic solvation (acidity parameter), BP relates to nucleophilic solvation (basicity parameter), EP means polar solvation (electrostatic parameter), and PP relates to dispersion solvation (polarizability parameter). These parameters represent values of the rotated abstract factors obtained by calculation for the chosen set (set 2) of the solvent parameters. The regression coefficients a, e, p, b express sensitivity of the process to the given type of solvation, and A_0 is value of the correlated quantity in a medium in which the parameters AP, BP, EP, PP are equal to zero. In such solvent all types of interactions attain average values. From values of Table VI it follows that this requirement is practically fulfilled by cyclohexanone.

Table VII summarizes the correlation coefficients of Eq. (9),

$$Y = a + bX , \qquad (9)$$

where Y are values of individual solvent parameters defined earlier, and X are values of the AP, BP, EP, PP parameters defined by us, depending on the class into which Y was located by the cluster analysis. Values of correlation coefficients of the correlation of AN, $a(^{14}N)$, Z with AP parameter of electrophilic solvation, that of χ_R and $(\varepsilon - 1)/(2\varepsilon + 1)$ with EP parameter of polar solvation, that of B and DN with BP parameter of nucleophilic solvation, and that of $(n^2 - 1)/(n^2 + 1)$ and n_D^{20} with PP parameter indicate that the set defined by us reflects the individual types of solvent–solute interactions.

TABLE VI

Values of orthogonal set of parameters of solvents with normed normal distribution

No	AP[a]	BP[b]	EP[c]	PP[d]
1	−0·456	−0·391	−0·607	0·228
2	−0·002	−0·203	−0·464	0·053
3	−0·156	−0·251	−0·647	−0·026
4	−0·419	−0·373	−0·197	−0·216
5	−0·219	−0·236	−0·343	−0·258
6	0·015	−0·124	−0·338	−0·206
7	0·017	−0·132	−0·352	−0·200
8	−0·028	−0·094	−0·416	−0·254
9	−0·411	−0·465	−0·332	−0·021
10	−0·090	−0·257	0·010	−0·012
11	−0·065	−0·223	0·076	0·000
12	−0·212	−0·387	0·107	−0·019
13	−0·243	−0·240	−0·080	−0·348
14	−0·173	−0·199	−0·006	−0·410
15	−0·074	−0·173	−0·085	−0·144
16	−0·429	0·089	−0·269	0·295
17	−0·157	0·132	−0·410	0·059
18	−0·229	0·074	−0·356	0·235
19	−0·082	−0·071	−0·114	−0·273
20	−0·093	−0·056	−0·140	−0·278
21	−0·277	0·126	−0·047	0·098
22	−0·169	−0·014	−0·236	0·054
23	−0·188	0·059	0·121	0·251
24	−0·104	0·067	0·091	0·189
25	−0·065	0·091	0·078	−0·095
26	−0·102	−0·017	−0·030	0·253
27	−0·191	0·008	−0·103	0·194
28	−0·003	−0·104	0·111	0·130
29	0·708	0·108	0·541	−0·022
30	0·045	0·266	0·264	0·001
31	−0·022	0·308	0·237	−0·079
32	−0·166	0·501	0·136	−0·102
33	0·089	−0·073	0·215	0·310
34	−0·114	−0·059	0·207	−0·308
35	1·680	0·032	0·520	0·287
36	0·627	0·167	0·370	0·441
37	0·420	0·254	0·260	0·330
38	0·197	0·176	0·203	0·218
39	0·226	0·202	0·208	0·298
40	0·053	0·220	0·070	0·207
41	0·123	0·101	0·187	−0·265
42	0·540	0·160	0·602	0·151

TABLE VI
(*Continued*)

No	AP[a]	BP[b]	EP[c]	PP[d]
43	0·142	0·089	0·241	0·175
44	0·628	−0·008	0·136	0·303
45	−0·102	0·724	−0·567	0·048
46	−0·195	0·373	0·136	−0·248
47	0·057	−0·186	0·331	0·202
48	−0·169	−0·172	0·274	−0·409
49	0·053	0·261	0·372	−0·170
50	0·007	−0·004	0·152	−0·203
51	−0·222	−0·072	−0·115	−0·445

[a] The parameter of electrophilic solvation; [b] the parameter of nucleophilic solvation; [c] the parameter of polar solvation; [d] the parameter of dispersion solvation.

The parameter set thus defined was applied to some more extensive data sets published earlier. The results are given in Table VIII. It is obvious that a change in the reaction type is accompanied also by change in character of the solvation which affects the process with statistical significance. Out of the 21 examples tested we observed statistically significant electrophilic solvation in 11 cases, nucleophilic solvation in 8 cases, solvation by dispersion forces in 7 cases, and polar solvation in 18 cases. Thus the polar solvation operated practically in all the examples studied, which is obviously due to non-specific nature of this solvation based on electrostatic forces which act on any polar molecule dissolved in the solvent. This solvation type does not operate in dimerization of pentadiene (reaction 2) where two non-polar molecules react with each other, and the reaction goes through non-polar (or isopolar) transition state. The absence of polar solvation in the acid-induced decomposition of 1-phenyl-3-alkyltriazene (reaction 8) is due probably to the fact that nucleophilic solvation is decisive and affects strongly the whole process, which is confirmed by high value of regression coefficient of this term.

Values of the regression coefficients p of solvation by dispersion forces show that this solvation type is the more significant the less significant are the specific electrophilic and nucleophilic solvations. *E.g.* in reaction 6, in which specific solvation makes itself felt very distinctly, the said solvation type is insignificant. In reactions 3 and 7 specific solvation operates to lesser extent only (low values found for regression coefficients of this term). On the contrary, this type of solvation makes itself felt in the spectral measurements 17 and 19, where specific solvation is practically absent. Of course, also important here is polarizability of the reacting molecules, which is

seen in reactions 10–12, in which polarizability of the reactants will be lower than that of the substrates in cases 17 and 19 involving aromatic π-electronic system.

Reaction 1 belongs to those going through the free-radical transition state[6] which are usually little affected by solvent. The values of the regression coefficients in Table VIII show that the reaction is slowed down by polar and nucleophilic solvation of the starting substances. Introduction of *para*-amino group into aromatic ring radicals causes polarization of the radical[65] and, hence, its better solvation by polar solvents. The amino group is also responsible for nucleophilic solvation of the free radical. Fig. 1 gives a plot of logarithms of experimental *vs* calculated rate constants. Obviously, introduction of the term of nucleophilic solvation improves markedly the correlation of the effect of medium as compared with the correlation by Ito and Matsuda[65] (logarithm of rate constant *vs* $E_T(30)$); the correlation of solvents is not decomposed into three groups (which was observed by the said authors[65]).

The reactions 2 and 3 go through cyclic isopolar transition states. The former (dimerization of pentadiene) involves reaction of two molecules which are neither markedly polar, nor polarizable. Moreover, they contain no functional groups which could interact with solvent. Therefore, none of the solvation terms has statistically significant effect in the reaction. In reaction 3, one reacting molecule (maleinanhydride) has polar character, hence the reaction is affected by the medium. The regression coef-

TABLE VII

Values of correlation coefficients for relation Eq. (9)

Parameter (Y)	AP (X)	Parameter (Y)	EP (X)
AN	0·9257	χ_R	−0·9491
Z	0·9207	$E_T(30)$	0·8894
S_1	0·8289	ε	0·7467
S_2	0·8638	$(\varepsilon - 1)/(2\varepsilon + 1)$	0·9166
E	0·8946	π^*	0·8502
$a^{14}N$	0·9627	$^nX^v$	−0·6298
log *P*	0·8031		
δ	0·9108		
Parameter (Y)	**BP (X)**	**Parameter (Y)**	**PP (X)**
B	0·9480	$(n^2 - 1)/(n^2 + 1)$	−0·9712
DN	0·9560	n_D^{20}	−0·9659
β	0·8721		

ficients of the individual terms indicate that none of the interaction types operates too distinctly.

The reactions 4 and 5 go by S_N1 mechanism through dipolar transition state, hence they are considerably sensitive to a solvent change. The reaction is accelerated by solvation of the polar transition state by polar solvents and, furthermore, by electrophilic solvation of the anion being formed. From values of the regression coefficients it is obvious that the transition state of reaction 5 will be more polar, which indicates a more advanced bond splitting in the transition state of this reaction as compared with that of reaction 4. The higher regression coefficient of the term of electrophilic solvation in the reaction 4 indicates a more distinct solvation of the chloride ion being produced as compared with tosylate anion in reaction 5. The correlation was good in both the cases.

The transition states of the rate-limiting steps of reactions 6 and 7 involve the proton transfer[70-72]. The same arrangement of the transition state is indicated by values of the regression coefficients of polar solvation which are practically the same. In accordance with findings of the authors[70-72], the reaction 6 is affected by both electrophilic and nucleophilic solvation, the two types of specific solvation being decisive and predominant over non-specific solvation. The insignificance of electrophilic solvation in the reaction 7 can be explained by delocalization of the electron pair

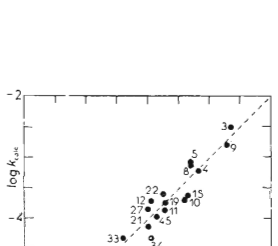

FIG. 1

Dependence of logarithm of the calculated rate constant (Eq. (8)) on logarithm of the rate constant observed for reaction 1 (Table VIII). For numbers of the solvents see Table II

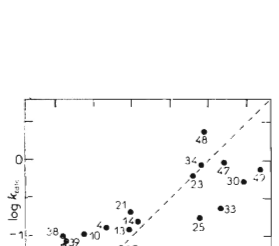

FIG. 2

Dependence of logarithm of the calculated rate constant on logarithm of the rate constant observed for reaction 15 (Table VIII). For numbers of the solvents see Table II

TABLE VIII

Examples of application of the new set of parameters according to the relation (8)

	A[a]	A_0[a]	a[a]	b[a]	e[a]	p[a]	n[b]	R[c]	s[d]	Solvents[e]
1.	log *k* of addition of *p*-aminobenzenethienyl radical to styrene[65]	−4·043 ±0·06	—	−1·338 ±0·199	−1·831 ±0·207	—	19	0·947	0·2473	3—5, 8—12, 15, 19, 21, 22, 27, 30, 33, 34, 45, 46
2.	log *k* of dimerization of pentadiene[66]	−5·462 ±0·131	—	—	—	—	14	—	—	4, 5, 9—11, 13, 16, 21—23, 36—38, 40
3.	log *k* of the Diels–Alder addition of maleinanhydride to 1,3-butadiene[67]	−1·022 ±0·027	0·419 ±0·167	−0·804 ±0·06	0·457 ±0·146	−0·295 ±0·040	7	0·994	0·0320	4, 9, 11, 16, 27, 47, 51
4.	log *k* of S_N1 solvolysis of tert-butyl chloride at 120°C[68]	−4·885 ±0·093	2·925 ±0·201	—	3·153 ±0·383	—	20	0·990	0·3905	1, 4, 13, 16, 23, 30, 33, 35—40, 44—49
5.	log *k* of S_N1 solvolysis of *p*-methoxyneophyltosylate at 75°C[69]	−5·187 ±0·185	1·574 ±0·137	—	3·710 ±0·865	—	11	0·972	0·4372	16, 23, 27, 30, 33, 35—37, 44, 47, 49
6.	log *k* of reaction of benzoic acid with diphenyldiazomethane[70–72]	—	3·123 ±0·602	−4·995 ±0·371	1·681 ±0·282	—	27	0·961	0·3140	4—15, 17—23, 25—27, 30, 31, 34, 48
7.	log *k* of reaction of 2,4-dinitrophenol with diphenyldiazomethane[70]	−1·198 ±0·044	—	−1·462 ±0·203	1·624 ±0·189	0·724 ±0·186	27	0·913	0·1950	4—15, 19—23, 26, 27, 29, 31, 33, 34, 46—49
8.	log *k* of acid-induced decomposition of 1-phenyl-3-alkyltriazene[73]	−1·040 ±0·137	—	−6·519 ±0·715	—	—	13	0·940	0·4558	4, 5, 8, 10, 11, 13, 16, 21—23, 27, 33, 49
9A.	log *k* of the S_N2 Menshutkin reaction of tripropylamine with methyl iodide[74]	−1·494 ±0·119	—	—	3·623 ±0·431	−1·469 ±0·477	32	0·846	0·6504	1, 3—14, 16, 17, 19—23, 25, 27, 30, 33, 34, 36—38, 41, 47, 48, 51

9B. log k of the same reaction, the solvents except for alcohol[74]	−0·974 ±0·122	1·339 ±0·629	—	4·105 ±0·352	—	28	0·941	0·4390	1, 3–14, 16, 17, 19–23, 25, 27, 30, 33, 34, 47, 48, 51
10. log k of the S_N2 Menshutkin reaction of triethylamine with ethyl bromoacetate[75]	−1·541 ±0·066	—	—	3·219 ±0·215	—	14	0·974	0·2348	3–5, 7–9, 12, 19, 20, 23, 33, 34, 47, 48
11. log k of the S_N2 Menshutkin reaction of triethylamine with ethyl iodoacetate[75]	−1·180 ±0·064	—	—	2·952 ±0·207	—	14	0·971	0·2271	3–5, 7–9, 12, 19, 20, 23, 33, 34, 47, 48
12. log k of the S_N2 Menshutkin reaction of triethylamine with ethyl iodide[76]	−4·356 ±0·036	—	—	3·094 ±0·274	—	9	0·974	0·0944	10, 11, 13–15, 23, 25, 34, 48
13. log k of reaction of diazabicyclo-[2,2,2]octane with 1-chloro-2-phenylethane[77]	−3·695 ±0·102	−1·640 ±0·495	—	3·749 ±0·579	—	22	0·837	0·3926	4, 5, 10, 13, 14, 19, 21–23, 25, 27, 30, 33, 34, 36–40, 47–49
14. log k of S_N2 reaction of diazabicyclo-[2,2,2]octane with 1-bromo-2-phenylethane[77]	−1·793 ±0·118	−2·332 ±0·614	—	4·238 ±0·654	—	24	0·822	0·4973	4, 5, 9, 10, 13, 14, 19, 21–23, 25, 27, 30, 33, 34, 36–40, 47–49
15. log k of S_N2 reaction of diazabicyclo-[2,2,2]octane with 1-iodo-2-phenylethane[77]	−1·299 ±0·143	−2·975 ±0·144	—	4·291 ±0·791	—	24	0·764	0·6017	as in 14
16. ν_{max} — $\pi \rightarrow \pi^*$ UV/VIS spectrum of p-nitroaniline (in cm^{-1}) (ref.[18])	27·900 ±0·074	0·545 ±0·229	−2·494 ±0·271	−3·883 ±0·315	—	27	0·975	0·3769	1, 3–5, 9, 11–13, 16, 19, 21–23, 27, 30–32, 35–40, 42, 45, 46, 49
17. ν_{max} — $\pi \rightarrow \pi^*$ UV/VIS spectrum of N,N-dimethyl-p-nitroaniline (in cm^{-1}) (ref.[18])	25·403 ±0·056	−0·475 ±0·184	—	−2·584 ±0·226	1·667 ±0·286	27	0·965	0·2784	as in 16
18. ν_{max} — $\pi \rightarrow \pi^*$ UV/VIS spectrum of p-nitrhopenol (in cm^{-1}) (ref.[18])	32·624 ±0·057	—	−2·693 ±0·257	−1·876 ±0·218	0·897 ±0·276	23	0·981	0·2566	1, 3, 4, 9, 11, 12, 16, 19, 21, 22, 27, 30–32, 35–40, 42, 46, 49

TABLE VIII
(*Continued*)

A[a]	A_0[a]	a[a]	b[a]	e[a]	p[a]	n[b]	R[c]	s[d]	Solvents[e]
19. $\nu_{max} - \pi \rightarrow \pi^*$ UV/VIS spectrum of *p*-nitroanisole (in cm^{-1}) (ref.[18])	32·641 ±0·054	—	—	−2·034 ±0·164	1·662 ±0·264	23	0·946	0·2447	as in 18
20. $\nu^{cis}_{(C=O)}$ IR spectrum of α-chloroacetophenone[78]	1 707·547 ±0·520	—	—	−11·176 ±1·483	—	12	0·922	1·4451	3—5, 7, 8, 13, 16, 22, 34, 45, 46, 48
21. $\nu^{gauche}_{(C=O)}$ IR spectrum of α-chloroacetophenone[78]	1 690·647 ±0·345	—	—	−5·377 ±0·983	—	12	0·866	0·9584	as in 20
22. pK_a of benzoic acid[80–85]	15·383 ±0·878	−6·118 ±1·489	−13·891 ±3·377	—	—	13	0·880	2·6110	12, 23, 24, 29, 30, 33, 35—38, 40, 42, 46, 47, 49

[a] The regression coefficients and the A_0 constant of the relation (*8*); significance of the coefficients was tested by the t test at the significance level $\alpha = 0{\cdot}05$; [b] number of the solvents taken into the regression; [c] the correlation coefficient of the relation (*8*); [d] the standard deviation; [e] for numbers of the solvents see Table II.

in the produced 2,4-dinitrophenoxide anion by strong mesomeric effect of nitro groups. Therefore, solvation of the phenoxide by medium will be less distinct than that of benzoate anion in the reaction 6.

Reactions 9–15 are the Menshutkin quaternizations of amine going by S_N2 mechanism. From Table VIII it follows that all these reactions are affected distinctly by polar solvation due to the charges formed in the transition complex. The correlation obtained for the reaction 9 in the greatest possible number of solvents (correlation 9A) is not too successful, the protic solvents 36–38 and 41 (capable of formation of hydrogen bonds with free amine) being markedly deviated from the relation. With these solvents excluded, the obtained correlation 9B was more successful. Also relatively unsuccessful is the correlation in the case of the reactions 13–15. Here again, the protic solvents 36–40 are markedly deviated, the same being true, moreover, of a group of solvents having no general common property. Figure 2 gives the plot of log k_{obs} *vs* the calculated logarithms for the reaction 15, which illustrates well the described facts. The second above-mentioned group involves the following solvents: 5, 19, 22, 25, 30, 33, 47, 49. The same decomposition of the correlation field is also observed with the reactions 13 and 14. The failure of this correlation can be due to the possibility of elimination reaction (phenethyl halogenide to styrene) accompanying the quaternization of the amine.

Solvatochromic effects are correlated quite frequently in literature. The data of examples 16–19 were used by Taft for definition of the basicity scale β based on the presumption that introduction of alkyl groups into hydroxy group of *p*-nitrophenol or into amino group of *p*-nitroaniline will prevent nucleophilic solvation of the substrates by solvent. This presumption is verified also by values of the regression coefficients in Table VIII for the examples 16, 17, 18, 19. Also clearly seen is operation of the term of dispersion solvation in the case of the indicators for which the specific nucleophilic solvation is prevented (cases 17 and 19). Practically the same value of the regression coefficient of this term in the two cases indicates comparable polarizability of the two substrates.

Comparison of the regression coefficients of the terms of polar solvation in the examples 20 and 21 indicates higher polarity of *cis* conformer of α-chloroacetophenone, which agrees with findings of Bilobrov and coworkers[78]. Also ratio of magnitudes of these regression coefficients agrees well with the value found by the authors cited.

The low correlation coefficient in the example 22 is due probably to great experimental error in determination of the dissociation constants of benzoic acid. The methods of titration in non-aqueous media are not fully unified yet, so the values of dissociation constants determined by various authors show a large scattering. In this case, too, as well as in the reaction 8, position of the equilibrium does not depend on polarity or polarizability of solvent, because it is highly sensitive to specific solvation – both nucleophilic and electrophilic. The both solvation types shift the equilibrium in favour of ion formation, the ions being much more strongly solvated than

the non-dissociated acid. Especially distinct is the solvation of the proton being split off, which is manifested by the high value of the regression coefficient of the term of nucleophilic solvation.

CONCLUSION

Application of the set of parameters defined by us to some chemical processes shows that this set can be used for correlation of solvent effect on these processes. The orthogonality and the normed normal distribution of this set of parameters allowed to discuss the mechanism by which solvent affect these processes and make comparisons between various reactions. Moreover, they enable to draw conclusions about the reaction mechanisms and arrangement of the transition state. In all the cases studied the correlation was as successful as or more successful than that carried out by the authors cited on the basis of empirical parameters. These facts show advantage of the thus defined set of parameters and vitality of the multi-parameter approach to correlations of solvent effect.

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