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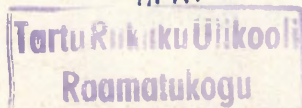
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NONLINEAR PARAMETRIZATION OF EQUATIONS FOR ATOMIC  
SPECTRAL TERMS. 2. DATA PROCESSING APPLYING THE  
MINIMIZATION OF RELATIVE STANDARD DEVIATION IN THE  
EQUATION WITH A REDUCED NUMBER OF PARAMETERS

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Parametrization of equation (3) has been carried out using a set of 332 values of atomic spectral terms for the first three electron shells as the basic experimental data. This equation describes the eigenvalues of hamiltonian for a single-electron hydrogen-like system considered as a model for multi-electron system (neutral atoms and positively charged ions). The above-mentioned system can be characterized by value  $z^*$  of the effective nucleus charge and by the additional nonshielding potential  $U$ . The latter takes into consideration this portion of the total energy of interaction between electrons which is not determined by  $z^*$ , as well as the components formally corresponding to the relativistic correction and Lamb shift for the corresponding hydrogen-like single-electron systems.

Both the  $z^*$  value and nonshielding potential  $U$  are expressed by orbital-orbital shielding constant  $\sigma_j(i)$  ( $i$  and  $j$  are the indexes of shielding and shielded orbitals respectively). Certain regularities dis-



tinguishing the dependence of the  $\sigma_{j(i)}$  values on the quantum numbers were established:

$$\begin{aligned}\sigma_{1s}^2 &= \sigma_{2s}^2 = \sigma_{3s}^2, \quad \sigma_{2p}^2 = \sigma_{3p}^2, \\ \sigma_{2p(2p)} &= \sigma_{3p(3p)}, \quad \sigma_{3d(1s^2)} = \sigma_{3d(2s^2)} = \\ &= \sigma_{3d(2p^2)} = 2, \quad \sigma_{3d}^2 = 1.\end{aligned}$$

The obtained parameters can be applied to form a hydrogen-like base for quantum-chemical calculations.

In our previous contribution<sup>1</sup> the results of the statistical treatment of spectral term values for the first three electronic shells are given according to the following equations:

$$I_j = \frac{I_H}{n^2} \left( z - \sum_{i=1}^{j-1} \sigma_{j(i)} \right)^2 - \frac{z}{n^2} \sum_{i=1}^{j-1} C_{j(i)} (N_1 - \sigma_{j(i)}) \quad (1)$$

$$\begin{aligned}I_j &= \frac{I_H}{n^2} \left( z - \sum_{i=1}^{j-1} \sigma_{j(i)} \right)^2 - \frac{z}{n^2} \sum_{i=1}^{j-1} C_{j(i)} (N_1 - \sigma_{j(i)}) + \\ &+ \delta \left( z - \sum_{i=1}^{j-1} \sigma_{j(i)} \right)^3, \quad (2)\end{aligned}$$

where  $I_j$  denotes the spectral terms (ionization potentials) of atoms and positively charged ions in ground as well as in various excited states;  $I_H$  is the ionization potential for the hydrogen atom;  $n$  is the principal quantum number of the  $j$ th electron removed in the course of ionization;  $z$  denotes the nuclear charge;  $\sigma_{j(i)}$  is the shielding constant of the  $j$ th electron by the  $N_1$  electrons (electron) on the  $i$ th orbital;  $C_{j(i)}$  is the proportionality coefficient, being to a certain extent independent of shielding orbital;  $\delta$  denotes the parameter to be determined.

Equation (1) enables one to achieve relatively good accuracy in describing the  $I_j$  values. Still better accuracy is reached if the term proportional to the  $z^3$  (eq.(2)) is

added to the right-hand side of the equation.

In our previous paper we suggested some possibilities of perfecting the parametrized scheme. This can be achieved by a considerable reduction of the total number of empirical parameters, proceeding from certain dependences of  $\zeta_j(1)$  and  $C_j(r)$  values on quantum numbers. It is also reasonable to use instead of the entirely formal last term of eq. (2) another way of expression which would be more consistent with the theory of hydrogen-like atom (the relativistic correction and the Lamb shift are taken into consideration). Instead of  $I_H$  the Rydberg constant for the given nucleus should be introduced.

Moreover, the maximum values of the relative and even the absolute deviations were observed for the first members of the corresponding isoelectronic series (for neutral atoms). The latter are actually of the greatest interest.

Due to this it would not be reasonable to minimize the sum of squares of absolute deviations but that of relative ones.

The present study was undertaken in order to check the possible ways of perfecting the type of the parametrized equation.

### The Technique of Data Processing

The initial way of writing down the parametrized function was modified to avoid an overparametrization. The elimination of the statistically nonsignificant parameters is granted by the algorithm of nonlinear least squares (NLLS) used.

Nevertheless, the situation of overparametrization may arise when two or more parameters to be estimated have indistinguishable values. In that case it is reasonable to substitute new parameters  $X'_1$ ,  $X'_2$ ,  $X'_3$ , etc. for  $X_1$ ,  $X_2$ ,  $X_3$ , etc. according to the following scheme:

$$\begin{aligned}X_1 &= X'_1 \\X_2 &= X'_1 + X'_2 \\X_3 &= X'_1 + X'_3\end{aligned}$$

The statistical indistinguishability of  $X_1, X_2, X_3$ , etc. causes the statistical insignificance of the  $X'_2, X'_3$ , etc. values. The latter are eliminated in the course of parametrization, resulting in  $X_1 = X_2 = X_3$ . As to the data processing technique, it is of no importance whether this equalization reflects some "real" intrinsic regularities or is purely incidental.

In order to minimize the sums of the squares of relative deviations the  $\ln I_j$  values were used as those described by the parametrized equation. Though the substitution of  $\ln I_j$  for  $I_j$  may lead to the increase of the standard deviation (within the range of  $I_j$ ) the absolute values of individual deviations for atoms and low-charged ions will be reduced.

More strict application of the hydrogen-like atom theory for multi-electron atoms and ions assumes such a form of expression which might adequately describe the energy of hydrogen-like atoms. The value of nucleus  $z$  is changed for its effective value  $z^\pi$ . The correction to the energy  $\frac{R}{n^2} z^2$  of a hydrogen-like atom which takes into consideration both the relativistic effect and the magnetic properties of an electron is in the first approximation proportional to  $z^{4.2a}$ . The expression for the Lamb shift<sup>2b</sup> contains also a member proportional to  $z^4$ . For S-states a contribution proportional to  $z^4 \ln z$  is added. Taking into account these contributions guarantees practically an adequate description of experimental values for hydrogen atom and single-electron ions. Therefore no further attempt to complicate the equation by inclusion of the additional terms was avoided.

Thus, proceeding from the aforesaid, the parametrized equation is as follows:

$$\ln I_j = \ln \left[ \frac{R}{n^2} z^\pi - \frac{z}{n^2} \sum_{i=1}^{j-1} C_j(x) (N_i - \zeta_{j(i)}) + \gamma_n z^\pi + \int_0^{\infty} z^\pi \ln z^\pi \right], \quad (3)$$

where  $z^\pi = z - \sum_{i=1}^{j-1} \zeta_{j(i)}$ ;  $R$  is the Rydberg constant calculated from value  $R_\infty = 13.6058$  eV and from the given atomic



mass;  $\gamma_n$  and  $\delta_n$  denote the parameters to be determined depending on the principal quantum number of the external electron.

In the terms of this equation the statistical treatment of the spectral term values for the first three electronic shells was carried out. The total number of processed  $I_j$  values for atoms and positively charged ions amounted to 332. The corresponding electronic configurations are presented in Table 1. Numerical values used for spectral terms were extracted from references<sup>3,4</sup>.

The  $I_j$  values for the lowest energy levels of the corresponding multiplets (the calculation of mean values turned out to be impossible as there was no necessary data concerning multiple-charged ions) were applied for the configurations of the ground states of atomic particles. Arithmetical mean values were used for the configurations that corresponded to the excited states of atoms and ions. The differences of the latter from the averaged values as well as from those corresponding to the lowest multiplet levels do not exceed the standard deviation for the relationship under discussion.

Due to this it is quite evident that the use of the strict equation for the hydrogen-like single-electron system for description of the  $I_j$  values for multi-electron atoms (as in eq. (3)) cannot be considered an entirely correct procedure. The Dirac equation<sup>2a</sup> as well as the correction for the Lamb shift<sup>2b</sup> depend on the total moment of the  $j$ th electron. As a result, the coefficients for higher powers of  $z$  have different values for separate sublevels of the term. This fact is ignored in Eq.(3) and only the general character of the dependence on  $z$  has been retained.

The parametrization of Eq. (3) was performed applying the algorithms and the programs of NLLS represented in contribution<sup>1</sup>. However, the calculation technique of the standard deviations for the estimated parameters was modified. For this purpose were used standard deviations  $SX(J)$  of corrections  $DX(J)$  (for the explanation of the denotations see Ref. 1) obtained by the multiple linear regressive analysis (MLRA), provided that the whole set of cor-



Table 1

## The Set of Spectral Terms

Subset of configura- tions	Seq. No	Electronic configura- tion	Term (Symbol)	Num- ber of points	Range of values $I_j$ (eV)
1	2	3	4	5	6
1s	1	1s <sup>2</sup>	<sup>1</sup> S	19	24.587-5129.045
	2	1s <sup>2</sup> 2s	<sup>2</sup> S	14	5.392-707.14
2s	3	1s <sup>2</sup> 2s <sup>2</sup>	<sup>1</sup> S	14	9.322-749.74
	4	1s <sup>2</sup> 2p	<sup>2</sup> P <sup>o</sup>	8	3.542-223.10
2p	5	1s <sup>2</sup> 2s <sup>2</sup> 2p	<sup>2</sup> P <sup>o</sup>	13	8.298-656.69
	6	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>	<sup>3</sup> P	13	11.260-686.09
	7	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>	<sup>4</sup> S <sup>o</sup>	13	14.534-714.02
	8	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>	<sup>3</sup> P	13	13.618-726.03
	9	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	<sup>2</sup> P <sup>o</sup>	13	17.422-755.47
	10	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>	<sup>1</sup> S	13	21.564-787.33
	11	1s <sup>2</sup> 3s	<sup>2</sup> S	8	2.022-102.73
3s	12	1s <sup>2</sup> 2s <sup>2</sup> 3s	<sup>2</sup> S	6	3.338-68.34
	13	I, II, 3s <sup>a</sup>	<sup>2</sup> S	14	5.139-384.30
	14	I, II, 3s <sup>2</sup>	<sup>1</sup> S	12	7.646-308.25
	15	1s <sup>2</sup> 3p	<sup>2</sup> P <sup>o</sup>	8	1.562-98.44
3p	16	1s <sup>2</sup> 2s <sup>2</sup> 3p	<sup>2</sup> P <sup>o</sup>	6	2.268-62.29
	17	I, II, 3p	<sup>2</sup> P <sup>o</sup>	6	3.039-74.846
	18	I, II, 3s <sup>2</sup> 3p	<sup>2</sup> P <sup>o</sup>	10	5.986-215.91
	19	I, II, 3s <sup>2</sup> 3p <sup>2</sup>	<sup>3</sup> P	10	8.151-230.5
	20	I, II, 3s <sup>2</sup> 3p <sup>3</sup>	<sup>4</sup> S <sup>o</sup>	10	10.486-244.4
	21	I, II, 3s <sup>2</sup> 3p <sup>4</sup>	<sup>3</sup> P	10	10.360-248.3
	22	I, II, 3s <sup>2</sup> 3p <sup>5</sup>	<sup>2</sup> P <sup>o</sup>	10	12.967-262.1
	23	I, II, 3s <sup>2</sup> 3p <sup>6</sup>	<sup>1</sup> S	10 <sup>b</sup>	15.759-321.2
	24	1s <sup>2</sup> 3d	<sup>2</sup> D	7	1.512-74.137
	25	1s <sup>2</sup> 2s <sup>2</sup> 3d	<sup>2</sup> D	6	1.508-56.71

Table 1 continued

1	2	3	4	5	6
	26	I,II,3d	$^2D$	6	1.519-57.371
	27	I,II,3s <sup>2</sup> 3d	$^2D$	6	1.966-63.902
	28	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>c</sup>	$^2D$	8	24.760-224.5
	29	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>2</sup>	$^3F$	6	27.491-157
3d	30	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>3</sup>	$^4F$	6	29.310-162
	31	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>4</sup>	$^5D$	6	14.65 -133
	32	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>5</sup>	$^6S$	6	16.50 -139
	33	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>6</sup>	$^5D$	5	30.651-134
	34	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>7</sup>	$^4F$	4	33.50 -108
	35	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>8</sup>	$^3F$	4	17.06 -82.6
	36	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>9</sup>	$^2D$	3	18.168-59.4
	37	I,II,3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup>	$^1S$	6 <sup>b</sup>	20.292-192.8

- a) I,II denote the completely filled first and second electronic shells
- b) One of the intermediate  $I_j$  values has been omitted
- c) From this configuration onward single- or double-charged positive ions are the first members of isoelectronic sets.

rections  $DX(J)$  (the statistically insignificant  $DX(J)$  values included) are established simultaneously. The resulting conventional values of standard deviation tend to exceed the corresponding values obtained by some other methods as a result of the statistical "overpumping" effect (of non-orthogonality).

Simultaneously into the treatment were involved the subsets of data related to the given combination of quantum numbers  $n$  and  $l$  for the external electron (for the configuration sets see Table 1).

In order to establish possible dependences (of numerical equality) between different parameters, a set of values to be determined was used in the form of additive corrections to some parameters considered as the basic ones, according to the scheme given above. The preliminary results of Ref.<sup>1</sup> and those obtained by the use of eq. (3), were taken into consideration. It is known that the final results got by the use of the NLS technique, depend to a certain extent on the initial approximation. Nevertheless, it was possible accurately enough to detect some dependences between the values of the parameters to be estimated. Introduction of those did not increase remarkably either the standard deviation of the description or the individual deviations for neutral atoms (we considered the latter to be the most significant criterion). Such solutions were accepted for the final results.

At first coefficients  $f$  and  $\delta$  were calculated separately for each  $nl$  subshell, employing for the representation of parameters the relationships as follows:  $\gamma_{2p} = \gamma_{2s} + X_j$ ,  $\delta_{3p} = \gamma_{3s} + X_j$ ,  $\delta_{3d} = \delta_{3p} + X_j$ , etc. The validity of equalities  $\delta_{2p} = \delta_{2s}$ ,  $\delta_{3p} = \delta_{3s}$ ,  $\delta_{2p} = \delta_{2s}$  and  $\delta_{3p} = \delta_{3s}$  was established reliably enough, while the differences between values  $\gamma_{3p} - \gamma_{3d}$  and  $\delta_{3p} - \delta_{3d}$  appeared to be statistically significant. As the experimental data for the subset  $3d$  are relatively unreliable, and having the general logical integrity of the model in mind, relationships  $\gamma_{3s} = \gamma_{3p} = \gamma_{3d} (= \gamma_3)$  and  $\delta_{3s} = \delta_{3p} = \delta_{3d} (= \delta_3)$  were fixed a priori.



The preliminary results demonstrated that during the treatment of the logarithms of the  $I_j$  values, it were mostly the data concerning neutral atoms and single-charged ions that belonged to the significantly deviating points. At the same time the corresponding absolute deviations were rather negligible. Therefore, when carrying out the final version of data treatment, the significantly deviating points were not excluded.

### Discussion

The results of the parametrization of eq.(3) are presented in Table 2. They show that a simple single-electron approximation as e.g. in eq. (3), leads to an unexpectedly accurate description of the  $I_j$  values for multi-electron atoms with different charges and electronic configurations. This is confirmed by the values of statistics  $S$  and  $S_0$  representing the accuracy of description. It should also be emphasized that it is the deviations for multiple-charged ions that mostly influence the value of  $S$ . Considerably lower values specifying the results of the treatment within the natural scale of  $I_j$  values are always accompanied by significant deviations for atoms and low-charged ions.

The obtained results confirm the existence of the following relationships which enable to reduce the total number of the parameters to be estimated:

$$\sigma_{1s^2} = \sigma_{2s^2} = \sigma_{3s^2} \quad (4)$$

$$\sigma_{2p(2s^2)} = 2 \cdot \sigma_{2s^2} \quad (5)$$

$$\sigma_{2p(1s^2)} = \sigma_{3p(1s^2)} \quad (6)$$

$$\sigma_{2p(2p)} = \sigma_{3p(3p)} \quad (7)$$

$$\sigma_{2p^2} = \sigma_{3p^2} \quad (8)$$

$$\sigma_{3d(1s^2)} = \sigma_{3d(2s^2)} = \sigma_{3d(2p^2)} = 2 \quad (9)$$

$$c_{1s(1s)} = c_{2s(1s)} = c_{3s(1s)} \quad (10)$$



$$C_{3s(2s)} = C_{3s(2p)} \quad (C_{3s(2s,p)}) \quad (11)$$

$$\gamma_{2s} = \gamma_{2p} \quad (\gamma_2) \quad (12)$$

$$\gamma_{3s} = \gamma_{3p} = \gamma_{3d} \quad (\gamma_3) \quad (13)$$

$$\delta_{2s} = \delta_{2p} \quad (\delta_2) \quad (14)$$

$$\delta_{3s} = \delta_{3p} = \delta_{3d} \quad (\delta_3) \quad (15)$$

The total number of independent parameters  $\sigma_{j(i)}$  decreases from 24 (Ref. 1) to 15\*, and that of the independent  $C_j(f)$  values from 13 to 11. The total number of the coefficients at higher than second powers of  $z^*$  remained the same ( 6 and 3 + 3 respectively).

Some of the given relationships ( e.g. (5) and (6)) have, most probably, incidental character ( according to the inner logics of the model) and, thus, they can hardly be used for extrapolations. The relationships which could be reasoned somehow are of special interest. The conclusion<sup>1</sup> that constants  $\sigma$  related to the interaction of the two electrons located on a single orbital do not depend on the principal quantum number, has been confirmed (relationships (4) and (8)). In order to prove the validity of the similar statement concerning  $\sigma$  values related to the interaction between the two electrons located on the different orbitals of the same subshell (eq. (7)) an additional confirmation based on the data for subsequent electronic shells is required. At any rate, these relationships could serve as a certain point of departure when specifying the equation for higher electron-shells.

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\* Parameters  $\sigma_{2p(2s)}^{\uparrow\uparrow}$  and  $\sigma_{3p(3s)}^{\uparrow\uparrow}$  that occurred in Ref. 1 were not taken into account here. In the present study the corresponding electronic configurations were excluded from the treated set of data.

Table 2

The Results of Parametrization of Eq.(3). The dimensions of  $C_{j(f)}$ ,  $\gamma_n$ ,  $\delta_n$  and  $S$  are in eV;  $\sigma_{j(i)}$  is given in elementary charge units.

$j(i)^a$	$\sigma_{j(i)}$	$C_{j(f)}$	$\gamma_n, \delta_n$	$S_o, S^b$	$n^c$
1	2	3	4	5	6
$1s^2$	$0.55122 \pm 0.00023$	$C_{1s(1s)} = 4.4196 \pm 0.0084$	$\gamma_1 = 0$ $\delta_1 = 5.311 \cdot 10^{-5} \pm$ $\pm 2.8 \cdot 10^{-7}$	$S_o = 5.35 \cdot 10^{-5}$ $S = 0.085$	19
$2s(1s^2)$	$1.58589 \pm 0.00380$	$C_{2s(1s)} = C_{1s(1s)}$	$\gamma_2 = 2.913 \cdot 10^{-3} \pm$	$S_o = 0.0047$	28
$2s^2$	$\sigma_{2s^2} = \sigma_{1s^2}$	$C_{2s(2s)} = 1.3034 \pm 0.1178$	$\pm 4.63 \cdot 10^{-4}$ $\delta_2 = -1.039 \cdot 10^{-3} \pm$ $\pm 1.81 \cdot 10^{-4}$	$S = 1.069$	
$2p(1s^2)$	$1.94474 \pm 0.00362$	$C_{2p(s)} = 3.9152 \pm 0.0417$	$\gamma_2$	$S_o = 0.0076$	86
$2p(2s^2)$	$1.10244 \pm 0.00046$	$C_{2p(p)} = 3.4036 \pm 0.1074$	$\delta_2$	$S = 1.703$	
$2p(2p)$	$0.60229 \pm 0.00355$				
$2p^2$	$0.92351 \pm 0.00600$				

Table 2 continued

1	2	3	4	5	6
$3s(1s^2)$	$1.73867 \pm 0.00444$	$C_{3s(1s)} = C_{1s(1s)}$	$\gamma_3 = 1.038 \cdot 10^{-3} \pm$	$S_0 = 0.0070$	40
$3s(2s^2)$	$1.41771 \pm 0.00745$	$C_{3s(2s,p)} = 3.5795 \pm 0.0577$	$\pm 2.66 \cdot 10^{-4}$	$S = 0.721$	
$3s(2p^2)$	$1.58275 \pm 0.00673$	$C_{3s(3s)} = 1.9168 \pm 0.1481$	$\delta_3 = -2.904 \cdot 10^{-4} \pm$		
$3s^2$	$\bar{G}_{3s^2} = \bar{G}_{1s^2}$		$\pm 9.68 \cdot 10^{-5}$		
$3p(1s^2)$	$\bar{G}_{3p(1s^2)} = \bar{G}_{2p(1s^2)}$	$C_{3p(s)} = 3.8026 \pm 0.0687$	$\gamma_3$	$S_0 = 0.0154$	80
$3p(2s^2)$	$1.58715 \pm 0.00978$	$C_{3p(p)} = 2.1032 \pm 0.1172$	$\delta_3$	$S = 1.189$	
$3p(2p^2)$	$1.77161 \pm 0.00426$				
$3p(3s^2)$	$0.78601 \pm 0.01445$				
$3p(3p)$	$\bar{G}_{3p(3p)} = \bar{G}_{2p(2p)}$				
$3p^2$	$\bar{G}_{3p^2} = \bar{G}_{2p^2}$				



Table 2 continued

	1	2	3	4	5	6
3d(1s <sup>2</sup> )		2.0	$C_{3d(s)} = 1.3026 \pm 0.2892$	$\gamma_3$	$S_0 = 0.0269$	79
3d(2s <sup>2</sup> )		2.0	$C_{3d(p)} = 4.2110 \pm 0.1454$	$\delta_3$	$S = 1.352$	
3d(2p <sup>2</sup> )		2.0	$C_{3d(d)} = 1.9000 \pm 0.5423$			
3d(3s <sup>2</sup> )		$1.72323 \pm 0.04224$				
3d(3p <sup>2</sup> )		$1.14880 \pm 0.03454$				
3d(3d)		$0.78360 \pm 0.02161$				
3d <sup>2</sup>		1.0				

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- a) In the indices of constant  $\sigma$  parenthesis are omitted if two interacting electrons are situated on the same orbital
- b)  $S$ —standard deviation in the scale of  $I_j$  values;  $S_0$  denotes the corresponding standard deviation in the normalized scale ( $S_0 = S/\sigma$ , where  $\sigma^2$  is the dispersion of  $I_j$  values) Standard deviations in  $\ln I_j$  units are not given.
- c)  $n$  is the number of points.



Coefficients  $\gamma_n$  and  $\delta_n$  differ from their analogues in the single-electron atom theory both by their absolute value as well as by the sign of the term proportional to  $z^4 \ln z$ . Thus, e.g. it is known<sup>2</sup> that at  $n=2$  for an hydrogen-like atom the total coefficient before  $z^4$  for  $2s$  level equals  $5.229 \cdot 10^{-5}$  eV, for  $2p_{1/2}$   $5.665 \cdot 10^{-5}$  eV and for  $2p_{3/2}$  it is equal to  $1.128 \cdot 10^{-5}$  eV. For the same  $2s_{1/2}$  term the coefficient before  $z^4 \ln z$  equals  $1.121 \cdot 10^{-6}$  eV. In the equations for P-states this member is not present. These values are but loosely connected with values  $\gamma_2 = 2.913 \cdot 10^{-3}$  eV and  $\delta_2 = -1.039 \cdot 10^{-3}$  eV, presented in Table 2. One should also keep in mind that the numerical values of  $\gamma_n$  and  $\delta_n$  have to be considered as vague ones due to the "overpumping" effect caused by the high correlation between arguments  $z^{\pm 4}$  and  $z^{\pm 4} \ln z^{\pm}$ . The aforesaid confirms that the two last items of eq. (3) should be taken only as the formal additional members permitting to achieve a better accuracy in the data description. Therefore the substitution of  $\delta z^{\pm 3}$  (eq. (2)) by members proportional to  $z^{\pm 4}$  and  $z^{\pm 4} \ln z^{\pm}$  in eq. (3) should not be commented upon proceeding from any conceptual aspects of these items.

Data processing within the logarithmic scale of the  $I_j$  value guarantees considerably small absolute deviations for atoms and low-charged ions. The latter will grow with the increase of the  $I_j$  values. Still, such a good absolute accuracy in the description of atoms and single-charged positive ions is not always achieved. The following numerical deviation values<sup>\*</sup> (in eV) for the ground states of atoms were obtained:

He	0.000 (-0.031)	Na	0.024 (0.426)
Li	-0.046 (0.034)	Mg	-0.008 (0.564)
Be	-0.093 (0.041)	Al	0.077 (0.003)
B	-0.041 (0.010)	Si	0.083 (0.233)
C	0.032 (0.195)	P	-0.046 (0.295)
N	0.004 (0.315)	S	0.186 (0.255)
O	-0.242 (-0.346)	Cl	0.037 (0.259)
F	0.035 (0.001)	Ar	-0.236 (0.106)
Ne	0.230 (0.336)		

\* Differences between the experimental and calculated values.

The values corresponding to eq. (2) are given in parenthesis. It can be seen that the maximum absolute deviation for the atoms of the second period decreases from 0.346 to 0.242 eV and that of the third period from 0.564 to 0.236 eV. The corresponding mean square value decreases from 0.269 to 0.121. The highest deviations were observed for the atoms of O, Ne, S and Ar. However, there is no statistical ground for any reasonable interpretation of these deviations. None of them exceeds the critical value (0.256) according to Student's criterion, corresponding to risk level 0.05. Moreover, the general distribution of deviations corresponds to the criteria of the normal statistical distribution.<sup>\*</sup>

It should be pointed out that a substantial reduction of the processed data set (highly-ionized atoms are excluded) did not have any remarkable effect on the description accuracy of neutral atoms. The variations of values  $\sigma_{j(i)}$  and  $\sigma_{j(r)}$  conditioned by the restriction of the data set are insignificant. Values  $\delta_n$  and  $\delta_n$  undergo a much greater change (at the same time for  $n = 2$  and  $n = 3$   $\delta_n = 0$ ). The latter does not especially influence the description adequacy of neutral atoms.

A sufficient description adequacy of ionization potentials  $I_j$  of atoms and positively charged ions does not guarantee that the application of eq. (3) could give a satisfactory account of the corresponding experimental values for negative ions i.e. the values of the electron affinities (EA) of atoms. This can be seen from the comparison of values EA (in eV) for stable negative ions, calculated according to this equation and experimental values<sup>6</sup> (the latter are given in parenthesis):

<sup>\*</sup> Using the symbols of Ref.5 (pp.28-29), index  $\sqrt{(\text{mean absolute deviation})/\bar{S} - 0.7979} - 0.4/\sqrt{n} = 0.0106$ ; the unbiased estimations of asymmetry indices  $G_1 = -0.084$  (the mean square deviation equals 0.55) and of excess  $G_2 = 0.233$  (the mean square deviation is 1.06).  $\bar{S} = 0.121$  denotes the mean square deviation value;  $n = 17$ , is the total number of deviations. Only the former formally indicates an insignificant deviation from the normal distribution.



H <sup>-</sup> ( <sup>1</sup> s)	0.755 (0.754)	Na <sup>-</sup> ( <sup>1</sup> s)	-0.670 (0.548)
Li <sup>-</sup> ( <sup>1</sup> s)	0.723 (0.609)	Al <sup>-</sup> ( <sup>3</sup> p)	-0.928 (0.5)
B <sup>-</sup> ( <sup>3</sup> p)	-0.143 (0.3)	Si <sup>-</sup> ( <sup>4</sup> s)	0.398 (1.394)
C <sup>-</sup> ( <sup>4</sup> s)	0.761 (1.27)	P <sup>-</sup> ( <sup>3</sup> p)	-0.180 (0.77)
O <sup>-</sup> ( <sup>2</sup> p)	0.747 (1.465)	S <sup>-</sup> ( <sup>2</sup> p)	1.431 (2.077)
F <sup>-</sup> ( <sup>1</sup> s)	2.279 (3.400)	Cl <sup>-</sup> ( <sup>1</sup> s)	3.348 (3.62)

For H<sup>-</sup> and Li<sup>-</sup> the calculated and experimental values EA coincide. As to the rest of the ions, the values calculated by eq. (3) are constantly lower than the experimental ones. As the inclusion of experimental values EA into the set of processed data did not eliminate this shortcoming we tested some additional modifications of eq. (3)<sup>8</sup>. Unfortunately, we must admit that we have not reached any positive results as yet.

The values of the parameters in eq.(3), presented in Table 2, could be applied to create a hydrogen-like base for quantum-chemical calculations within the methods of ab initio, CNDO/2 and others<sup>8</sup>. We suppose that this base has several advantages, e.g. the correlation energy of interactions between electrons at one and the same nucleus is taken into account, as well as the electron density of AO while calculating the effective nuclear charges and the potential of nonshielding electronic interaction.

We have started to study the results of employing such a base in the quantum-chemical calculations for molecules.

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<sup>8</sup> Additional terms of different types inversely proportional to the first and greater powers of  $z^{\pm 7}$  were introduced.

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THE INFLUENCE OF STRONG ELECTROLYTES ON  $E_T$ -PARAMETERS  
OF SOME NONAQUEOUS SOLVENTS

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The investigation of the nature and concentration of some salts ( $Bu_4NBr$ ,  $Me_4NCl$ ,  $Me_4NClO_4$ ,  $Et_4NClO_4$ ,  $Bu_4NClO_4$ ,  $KBr$ ,  $NaClO_4$ ,  $NaCl$ ,  $CsCl$ ) on the  $E_T$  values of polar nonaqueous solvents - DMSO and methanol. In the apolar aprotic solvent benzene the influence of two quaternary ammonium salts -  $Bu_4NBr$  and  $Bu_4NClO_4$  - on the long-wavelength absorption maximum of the pyridinium-N-phenoxide betaine dye was also studied.  $E_T$ -parameters of electrolyte solutions of the binary mixtures  $MeOH-H_2O$ ,  $t-BuOH$ -DMSO, and  $t-BuOH$ -MeCN were determined.

It was found that most of the salts considered independently of the chemical nature enhance the energy of  $\pi \rightarrow \pi^*$  transition of the betaine dye in the dimethyl sulfoxide medium.

The same conclusion can evidently be drawn also from the study of the salt effects on the  $E_T$ -values of the salt solutions in methanol.

In its turn, in the apolar aprotic solvent - benzene - dominate the effects of the complex-formation between the pyridinium-N-phenoxide betaine and quaternary ammonium salts -  $Bu_4NBr$  and  $Bu_4NClO_4$ .

Earlier<sup>1</sup> the influence of the nature and concentration of some strong electrolytes on the  $E_T$ -values of their solutions in water and aqueous methanol was studied. It was

shown that the behavior of the solutions of inorganic salts in these media differs qualitatively from such in the aqueous solutions of some quaternary ammonium salts ( $\text{Bu}_4\text{NBr}$ ,  $\text{Me}_4\text{NCl}$ ). It was suggested that the specific trends of salt effects displayed by these two classes of electrolytes is closely related to differences of their influence (structure-breaking or structure-making effects) on the structure of aqueous medium.

The goal of the present study was to extend the study of the effects of different inorganic and organic electrolytes on the  $E_T$ -parameters of some nonaqueous solvents (DMSO, methanol, benzene).

### Experimental.

The technique of determining of  $E_T$ -values was described in our earlier papers<sup>1,2</sup>. The same sample of pyridinium-N-phenoxide dye as in these studies was used.

Tetramethyl- and tetrabutylammonium perchlorates were synthesized from 10 per cent perchloric acid and the aqueous solution of the corresponding quaternary ammonium hydroxide and purified by repeated recrystallization from the hot aqueous solutions.  $\text{Bu}_4\text{NBr}$  was repeatedly recrystallized from the mixture of the anhydrous ethyl acetate and ethyl ether as described in Refs. 1, 3 and 4. In accordance with Ref. 4 it was found that some properties of carefully purified  $\text{Bu}_4\text{NBr}$  differ very drastically\* from those characteristic to the solutions of nonpurified salt.

The results of the study of the effects of the nature and concentration of different electrolytes on the  $E_T$ -values of the  $\pi \rightarrow \pi^*$  transition of the long-wavelength band of pyridinium-N-phenoxide dye in dimethyl sulfoxide and methanol are given in Tables 1 and 2 and displayed in Figs. 1 and 2.

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\* E.g., the value of  $\lambda_{\text{max}}$  of the long-wavelength band of the  $\pi \rightarrow \pi^*$  transition of betaine dye in DMSO changes up to 100-150 nm depending on the concentration and purity of that salt.

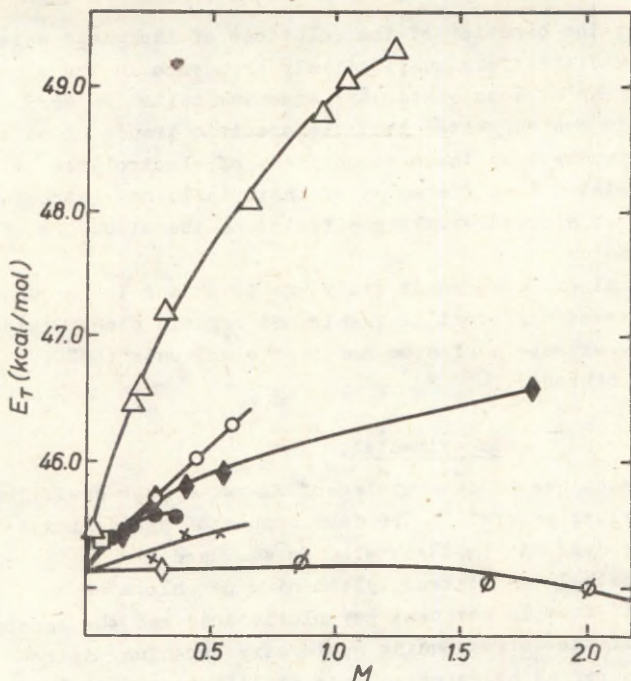


Fig. 1. The dependence of halochromic shifts of  $E_T$ -value of DMSO on the nature and concentration of different electrolytes.  $\Delta$  -  $\text{NaClO}_4$ ,  $\circ$  -  $\text{Me}_4\text{NClO}_4$ ,  $\square$  -  $\text{NaCl}$ ,  $\bullet$  -  $\text{KBr}$ ,  $\blacklozenge$  -  $\text{Et}_4\text{NClO}_4$ ,  $\diamond$  -  $\text{Me}_4\text{NCl}$ ,  $\emptyset$  -  $\text{Bu}_4\text{NBr}$ ,  $\times$  -  $\text{Bu}_4\text{NClO}_4$ .

For the sake of comparison with the previous<sup>1,2</sup> as well as with the present work the  $E_T$ -parameters of a few aqueous and aqueous-organic mixtures ( $\text{Me}_4\text{NClO}_4$  and  $\text{Bu}_4\text{NClO}_4$  in aqueous methanol,  $\text{Bu}_4\text{NBr}$  in aqueous DMSO, etc.) were also determined. The corresponding data are given in the footnotes to Tables 1 and 2.<sup>3</sup>

<sup>3</sup> The  $E_T$ -value for the 20 per cent aqueous  $\text{Bu}_4\text{NOH}$  was also determined - it equals 56.7 kcal/mol.



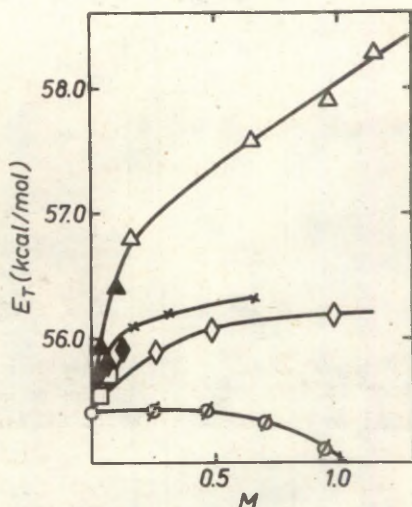


Fig. 2. The dependence of the halochromic shifts of  $E_T$ -values of MeOH on the nature and concentration of the different electrolytes (for notation of points see Fig. 1, ▲ - CsCl).

Also the preliminary semiquantitative experiments for the study of the effects of two quaternary ammonium salts -  $\text{Bu}_4\text{NBr}$  and  $\text{Bu}_4\text{NClO}_4$  - on the long-wavelength absorption maximum of the  $\pi \rightarrow \pi^*$  transition of pyridinium-N-phenoxy dye in aprotic and apolar solvent benzene were performed.

The typical dependences of the absorption spectrum of the dye on the concentration of the corresponding ammonium salts is given in Figs. 3 and 4\*.

\* More detailed analysis of this data will be given in one of the forthcoming publications in this series.

The Dependence of  $E_T$  Values on Nature and Concentration of Some Salts in DMSO at 25°C<sup>a</sup>

Table 1 continued

Bu <sub>4</sub> NClO <sub>4</sub>			Bu <sub>4</sub> NBr			NaCl			KBr		
M	$\lambda_{\max}$	E <sub>T</sub>	M	$\lambda_{\max}$	E <sub>T</sub>	M	$\lambda_{\max}$	E <sub>T</sub>	M	$\lambda_{\max}$	E <sub>T</sub>
1. 0	634	45.1	1. 0	634	45.1	1. 0	634	45.1	1. 0	634	45.1
2. 0.27	632	45.2	2. 0.85	632	45.2	2. Saturated solution	627	45.6	2. 0.093	630	45.4
3. 0.40	630	45.4	3. 1.35	634	45.1				3. 0.182	628.5	45.5
4. 0.53	630	45.4	4. 1.58	635	45.0				4. 0.27	627	45.6
			5. 1.98	637	44.9				5. 0.36	628	45.5
									6. Satur. soln.	619	46.2

<sup>2</sup> In mixture of DMSO with t-BuOH ( $N_{\text{ROH}}=0.49$ )  $E_{\text{T}}=49.5$  kcal/mol, and in its 0.73 M solution of Bu<sub>4</sub>NBr  $E_{\text{T}}=46.9$  kcal/mol. In binary mixture t-BuOH-MeCN ( $N_{\text{ROH}}=0.40$ )  $E_{\text{T}}=47.4$  kcal/mol, whereas in 0.7 M solution of Bu<sub>4</sub>NPr  $E_{\text{T}}=47.5$  kcal/mol.

In aqueous DMSO ( $N_{\text{HOH}}=0.504$ ,  $E_{\text{T}}=50.0$  kcal/mol) in the presence of Bu<sub>4</sub>NBr the significant red shift of  $\lambda_{\max}$  was observed (compare with Refs. 1,2): in its 0.315 M solution  $E_{\text{T}}=46.1$  kcal/mol.



Table 2  
The Dependence of  $E_T$ -Parameters on Nature and Concentration of Some Salts in  
MeOH at 25°C.

M	$\text{NaClO}_4$ $\lambda_{\text{max}}$	$E_T$	M	$\text{Bu}_4\text{NClO}_4^a$ $\lambda_{\text{max}}$	$E_T$	M	$\text{Me}_4\text{NCl}$ $\lambda_{\text{max}}$	$E_T$	M	$\text{NaCl}^b$ $\lambda_{\text{max}}$	$E_T$
1. 0	516	55.4	1. 0	516	55.4	1. 0	516	55.4	1. 0	516	55.4
2. 0.34	503	56.8	2. 0.03	512	55.8	2.0.26	511	55.9	2. 0.029	514.5	55.6
3. 0.65	496	57.6	3. 0.06	511	55.9	3.0.49	510	56.1	3. 0.056	513	55.7
4. 0.97	494	57.9	4. 0.17	510	56.1	4.0.99	509	56.2			
5. 1.30	490	58.3	5. 0.32	509	56.2						
			6. 0.66	508	56.3						

Table 2 continued

Bu <sub>4</sub> NBr				Me <sub>4</sub> NClO <sub>4</sub> <sup>c</sup>			Et <sub>4</sub> NClO <sub>4</sub>				
N	λ <sub>max</sub>	E <sub>T</sub>	M	λ <sub>max</sub>	E <sub>T</sub>	M	λ <sub>max</sub>	E <sub>T</sub>			
1.	0	516	55.4	1.	0	516	55.4	1.	0	515	55.5
2.	0.25	516	55.4	2. saturated solution	516	55.4	2.	0.027	513	55.7	
3.	0.47	516	55.4		3.	0.058	512	55.8			
4.	0.69	517	55.3		4.	0.087	510	56.1			
5.	0.94	519	55.1		5.	0.118	511	55.9			

e - In saturated solution of this salt in aqueous methanol ( $N_{\text{ROH}}=0.238$ )  $E_T=58.9$  whereas in the absence of that salt  $E_T=59.1$  kcal/mol.

b - In saturated CsCl solution ( $M \leq 0.1$ )  $\lambda_{\max}=507$  nm and  $E_T=56.4$  kcal/mol;  
at  $M=0.05$   $E_T=55.9$  kcal/mol.

c - In aqueous methanolic ( $N_{\text{MeOH}}=0.238$ ) solution of this salt at  $M=0.0366$   $E_T=59.3$  kcal/mol  
and at  $M=0.0556$   $E_T=59.3$  kcal/mol (at  $M=0$   $E_T=59.1$  kcal/mol).

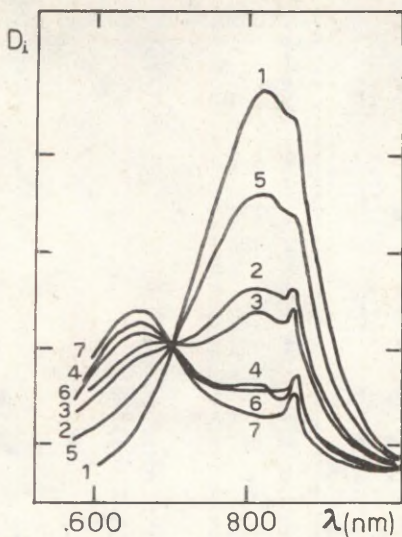


Fig. 3.

The influence of  $\text{Bu}_4\text{NBr}$  on the long-wavelength maximum of the  $\pi \rightarrow \pi^*$  transition of the pyridinium-N-phenoxide betaine dye in benzene at  $25^\circ\text{C}$ . The reference cell with the blank solution was not used in this experiment and, therefore, the additional absorption maximum at  $\lambda_{\text{max}} = 860 \text{ nm}$  belongs to the solvent - benzene. The following concentrations (in mol/l units) of the salt were used: 1 - 0.0; 5 - 0.00081; 2 - 0.00161; 3 - 0.0024; 6 - 0.0054; 4 - 0.0061; 7 - 0.0095.

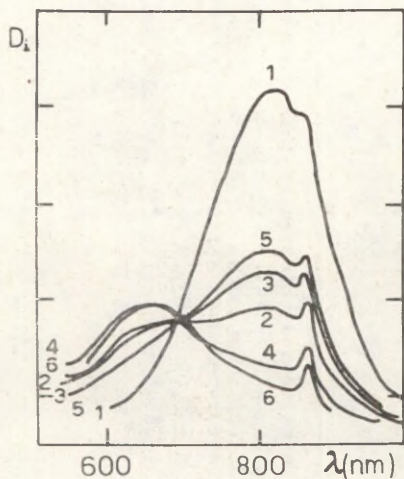


Fig. 4.

The influence of  $\text{Bu}_4\text{NClO}_4$  on the long-wavelength maximum of the  $\pi \rightarrow \pi^*$  transition of the pyridinium-N-phenoxide betaine dye in benzene at  $25^\circ\text{C}$ . The additional maximum at  $\lambda_{\text{max}} = 860 \text{ nm}$  belongs to the solvent (see Fig. 3.). The following concentrations (in mol/l) of the salt were used: 1 - 0.0; 5 - 0.00054; 3 - 0.00073; 2 - 0.0014; 4 - 0.0035; 6 - 0.0092.



## Discussion

### 1. Dimethylsulfoxid and Methanol.

The comparison of the data from Tables 1 and 2 with the results of our previous work<sup>1</sup> (see also Figs. 1 and 2) shows that the qualitative as well as quantitative picture of the influence of the concentration and nature of various electrolytes on the  $E_T$ -values of nonaqueous (DMSO and methanol) solvents differ very significantly. As a matter of fact, one can see from Fig. 1 and 2 that unlike the media of the latter type, practically all salts increase the energy (i.e. the solvent gross polarity) of the long-wavelength  $\pi \rightarrow \pi^*$  transition band of pyridinium-N-phenoxide dye in DMSO as well as in methanol.

From the viewpoint of the rather probable guess about the nonsignificant and monotonous relative changes of the electrolyte induced shifts of the solvent polarity<sup>5</sup> and polarizability<sup>5</sup> the above-mentioned facts are essentially supporting the suggestion that this increase of  $E_T$ -parameters is at least formally connected to the increase of the specific solvating power (electrophilicity?) of the medium (see also Ref. 1,2).

As in the case of aqueous and aqueous methanolic ( $N_{ROH} = 0.218$ ) solutions<sup>2</sup> the largest specific (in unimolar solution of the salt) effect of increase of  $E_T$  values belongs to  $NaClO_4$  where the  $\Delta E_T = E_T(M=1) - E_T(M=0)$  equals 3.8 kcal/mol for DMSO and 2.6 kcal/mol for methanol. Both of these two values are significantly higher than the corresponding value (+1.8 kcal/mol) for the aqueous methanolic solution of  $NaClO_4$ . As compared with the latter salt, the increase of the gross polarity of the solvent by various tetraalkylammonium salts is much less significant. So, in DMSO the monotonous decrease of the capacity of the salt to increase the  $E_T$ -parameter is connected with the gradual increase of the dimensions of the quaternary ammonium cation (in 0.5 M the increase of  $E_T$ -value is 1.2 kcal/mol for  $Me_4NClO_4$ , 0.8 kcal/mol for  $Et_4NClO_4$ , and only 0.3 kcal/mol for  $Bu_4NClO_4$ ).

In methanol the addition of  $\text{Bu}_4\text{NClO}_4$  (0.5 M) increases the  $E_T$ -value by 0.8 kcal/mol<sup>xx</sup>, whereas the comparable effect is displayed by  $\text{Et}_4\text{NClO}_4$  in the same medium. The solubility of NaCl and CsCl in both solvents is rather low and, therefore, the measured  $E_T$  values for the solutions of these salts suffer from some increased uncertainty<sup>xxx</sup>. Nevertheless, it is evident that in both cases the definite hypsochromic shift of long-wavelength maximum of the betaine dye is observed.

Moderate blue shift is displayed also by KBr in DMSO (0.5 kcal<sup>xxx</sup> in 0.5 M solution of KBr).

In water and aqueous methanol the additions of  $\text{Bu}_4\text{NBr}^2$  induced very significant decrease of the gross-polarity of the medium (in unimolar aqueous solution  $\Delta E_T = -8.1$  kcal/mol and in aqueous methanol  $\Delta E_T = -4.0$  kcal/mol) mainly because of its structure-making effect on the threedimensional structure of water. The structure of DMSO solutions is mainly determined by the dipolar association of highly polar molecules of this aprotic solvent into the long chain-like aggregates<sup>6</sup>. The association of dipoles into cyclic complexes  $a^+ \cdot b^-$  is also possible. In both of these cases one should  $b^- \cdot a^+$

expect the structure-making effect of  $\text{Bu}_4\text{NBr}$  which was characteristic to aqueous solutions. The latter conclusion might not be necessarily true for the pure methanol. However, as one can see from Fig. 1 and 2 in DMSO and MeOH in the similar conditions (unimolar solution) the bathochromic shift of the maximum of the  $\pi \rightarrow \pi^*$  transition of the betaine dye is either absent ( $\Delta E_T = 0$ ) or exceeds only

\* In the saturated solution of this salt in aqueous methanol ( $N_{\text{MeOH}} = 0.238$ ) a very weak bathochromic shift of the absorption maximum  $\lambda_{\text{max}}$  of the betaine dye was observed.

\*\* The concentrations of these salts given in Tables 1 and 2 are theoretical and refer to the weighed initial amount of the salt: no attempt has been made to determine their exact real concentrations by argentometric titration or by some other technique.

\*\*\* In aqueous methanol ( $N_{\text{ROH}} = 0.218$ ) this value does not exceed 0.1 - 0.2 kcal/mol.



slightly the errors of the determination of  $E_T$ -parameters (in MeOH 1 M Bu<sub>4</sub>NBr solution  $\Delta E_T = -0.3$  kcal/mol).

Unfortunately, the present results give only very limited information about the nature of the solvent-solute interactions which are responsible for the halochromic blue shifts of the maximum of the  $\pi \rightarrow \pi^*$  transition of the pyridinium-N-phenoxide dye. The relative stabilization of the highly polar and rather basic initial (non-excited) state of that transfer might, in principle, take place both via the mechanism of specific solvation, as well as by the mechanism of nonspecific solvation. In the first case, besides the interactions between the betaine dye and molecules of DMSO or MeOH the interaction between the phenoxide dye and moieties of the electrolyte. The latter can be either in the form of ion-pairs  $E^+N^-$  or more complicated associates of the latter or in the form of free ions  $E^+$  and  $N^-$  (where  $E^+$  - cation,  $N^-$  - anion). Naturally the linear complexes  $a^+-b^- \dots \dots E^+N^-$  (where  $a^+-b^-$  denotes the dipolar dye) as well as cyclic associates of the type  $a^+-b^- \dots \dots N^-E^+$  might be present. Naturally, such associates can form between the dye and dipolar molecules of DMSO (in MeOH, probably the complexes of the type  $a^+-b^- \dots (HOMe)_n$  are rather common). In other words, the addition of the salts to the polar non-aqueous solvent, the oversolvation of the solvates of the betaine dye by even more polar (or electrophilic) moieties of the electrolyte takes place. In the case of quaternary ammonium salts one also can hardly deny the possibility of formation of complexes between the latter and betaine dye via the hydrophobic interactions (vide infra).

We are not aware of the data on the dependence of the dielectric constants of DMSO and MeOH on the nature and concentration of electrolytes. Therefore, it is hard to make any suggestions about the possible trend of operation of the nonspecific solute - solvent interactions (especially, the polarity of the medium) on  $E_T$ -values while going over to the electrolytic solutions in these media. Concluding the analysis of the halochromic effects on  $E_T$ -parameters of polar nonaqueous solvents one has to notify that (see Footnote a



to Table 1) that in the mixture of DMSO with t-BuOH ( $N_{ROH}=0.49$ ) the addition of  $Bu_4NBr$  indeed leads to the significant red shift of the long-wavelength maximum of the  $\pi \rightarrow \pi^*$  band. At the same time, the same effect is absent in the binary mixture of acetonitrile with t-BuOH ( $N_{ROH} = 0.40$ ). Keeping in mind that the influence of both these pure (no electrolyte added) binary solvents on the  $E_T$ -values is qualitatively similar (their gross polarity is higher than the additive value of the pure components)<sup>1</sup>, the difference in their halochromic effects ( $Bu_4NBr$ ) on  $E_T$ -values seems hard to explain. In its turn, analogously to the aqueous methanol and binary mixture of t-BuOH-DMSO in the aqueous dimethyl-sulfoxide the addition of  $Bu_4NBr$  again results in the significant (almost 4 kcal/mol) decrease of the gross polarity of that mixed solvent (compare with Ref. 2).

## 2. $Bu_4NBr$ and $Bu_4NClO_4$ in Benzene

In the case of all the above-mentioned highly polar non-aqueous, aqueous and aqueous organic solvents (see also Ref. 2) the variation of the concentration and nature of the additions of electrolytes results only in the "ordinary" solvatochromic (halochromic) shift of the long-wavelength maximum of the  $\pi \rightarrow \pi^*$  transition of pyridinium-N-phenoxide dye. It does not change qualitatively (the presence, number and character of maxima, etc.) the absorption spectrum of this dye.

However, one can see from Figs. 3 and 4 that the influence of the addition of two quaternary ammonium salts  $Bu_4NClO_4$  and  $Bu_4NBr$  on the behavior of the pyridinium-N-phenoxide dye in the apolar aprotic solvent benzene ( $\epsilon = 2.2$ ) has rather different character and evidences about the strong complex formation between betaine-like dye and tetraalkylammonium salts.\*

Those figures show that the gradual increase of the concentration of these quaternary ammonium salts converts the free (i.e., solvated by the molecules of benzene predominantly by the mechanism of the nonspecific solvent-solvate). The solubility of inorganic salts in benzene is too low for the study of this problem.

lute interactions) betaine dye into its complex (associate) with the salt. Formally, this process is evidenced by the gradual decrease of the intensity of the absorption band at  $\lambda_{\text{max}} \approx 820 \text{ nm}$  (pure benzene)<sup>2,7</sup> up to its total absence. On the other hand, simultaneously the new, more short-wave-length absorption band ( $\lambda_{\text{max}} = 650\text{--}660 \text{ nm}$ ) corresponding to the dye-salt complex appears.

Figs 3 and 4 show that the dependence of the optical density ( $D_{\lambda}$ )-wavelength plots on the concentration of the salt (the concentration of the dye is constant) is characterized by the presence of the clearly pronounced isobestic point at  $\lambda_{\text{max}} \approx 700 \text{ nm}$ .

One can see that the transfer of the indicator dye into the complex is accompanied with the rather significant increase of its  $\pi \rightarrow \pi^*$  excitation energy ( $E_T \approx 44 \text{ kcal/mol}$  for the complex and  $34.5 \text{ kcal/mol}$  for the free dye in benzene<sup>1</sup>). At the same time the location of the absorption maximum of the complex depends only moderately<sup>8</sup> on the nature of the anionic part ( $\text{Br}^-$  or  $\text{ClO}_4^-$ ) of the salt as well as on the concentration of the electrolyte.

On the other hand, the estimation of the constants of the association equilibria between quaternary salt and betaine dye shows that the latter forms somewhat more stable complexes with the  $\text{Bu}_4\text{NClO}_4$  ( $\log K_{\text{ass}} = 3.3 \pm 0.2$ ) than with  $\text{Bu}_4\text{NBr}$  ( $\log K_{\text{ass}} = 2.8 \pm 0.1$ ). The mechanism of the interaction of quaternary ammonium salts in benzene is, probably, even more complicated than that of the halochromic effects in polar aqueous or nonaqueous solvents.

First of all it is probably heavily dependent on the interactions of the highly polar dipolar (with  $\mu = 14.6 \text{ D}$ ) dye with the similarly polar moieties (ion pairs) of the electrolyte the dipole moments of  $\text{Bu}_4\text{NBr}$  and  $\text{Bu}_4\text{NClO}_4$  in benzene media were reported<sup>8</sup> as 11.6 and 14.1 D, respectively) via the association of dipoles and formation of linear or cyclic

<sup>8</sup>  $\lambda_{\text{max}}$  for the saturated solution of  $\text{Bu}_4\text{NClO}_4$  is about 650 nm whereas  $\lambda_{\text{max}}$  for  $\text{Bu}_4\text{NBr}$  is somewhat higher (ca 658–660 nm).



complexes (vide supra). Here, alongside with the purely electrostatic interactions, significant role should also be played by the hydrophobic interactions between betaine dye and quaternary ammonium salt.

These specific interactions between betaine dye and electrolyte are probably accompanied by the effects connected with the influence of the concentration of the added salt on the nonspecific solvating power (polarity) of the benzene itself. Indeed, it was shown<sup>8-10</sup> that the addition of the moderate amounts of different tertiary and quaternary ammonium salts to the benzene results in a rather significant increase of its dielectric permittivity (e.g., in c. 0.1 M solution of  $(i-C_5H_{11})_4N^+SCN^-$  in  $C_6H_6$  has<sup>8,9</sup>  $\epsilon = 3.60$ , etc.). The enhanced polarity of the solvent leads to some extra-stabilization of the highly polar ground state of the  $\pi \rightarrow \pi^*$  transition of the pyridinium-N-phenoxide dye. It should, in its turn, result in some increase of  $E_T$ -values.

On the other hand, the increase of the macroscopic dielectric constant of the solvent should also decrease the electrostatic interaction between betaine dye and salts ion pair which to some extent must compensate the former effect of the increased (solvent) polarity. According to the net halochromic effect (the significant blue shift of the absorption maxima) the latter effect is evidently overrun by the consequences of the complex formation and influence of the increased polarity of the solvent on the stabilization of the ground state of the betaine dye. This conclusion is also supported by the fact that the energy of the spectral  $\pi \rightarrow \pi^*$  transition of the complex between betaine dye and quaternary ammonium salt is practically identical to that of dipolar aprotic solvents (DMSO, MeCN, MeNO<sub>2</sub>)<sup>2,7</sup> or pure molten electrolytes ( $C_6H_5COON(n\text{-Hex})_4$ ,  $Bu_4NBr$ )<sup>2,7</sup>.

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THE STRUCTURAL THEORY OF ELECTROLYTE SOLUTIONS  
I. INTRODUCTION

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A theory of electrolyte solutions based on the separate examination of physically independent interionic and ion-solvent interactions, is proposed. Preliminary experimental verification of the theory is made on the basis of the activity coefficients concentration-dependence. Also the limits of the theory are discussed.

1. Introduction.

The theoretical description of the strong electrolyte solutions has been a major goal for many physical chemists for a long time.<sup>1-7</sup> During a number of decades a big variety of theoretical approaches proposed by various authors have had the well-known Debye-Hückel electrostatic theory<sup>8,9</sup> as their cornerstone. The mathematical structure of the latter restricts its use only for the extremely diluted solutions. As a result of detailed criticism of the Debye-Hückel theory the validity of it is moved down to the more diluted than  $10^{-3}$  molar<sup>10,11</sup> or even  $10^{-7}$  molar<sup>12</sup> solutions. For that reason almost all the experimental work in electrolyte chemistry was restricted by the dilute solutions with minor concentration variations.

However, a search for the models valid for the wider range of electrolyte concentration was initiated by the needs of a number of chemical problems. In the first place it was done by the addition of semiempirical terms to the



Debye-Hückel limiting law. Those had to take into account various possible physical effects besides the interionic electrostatic interaction,<sup>13-15</sup> e.g., the finite size of ions and other hard-core effects, ionic dehydration in solutions,<sup>16</sup> dielectric saturation of the solvent in the vicinity of ion<sup>13,17-18</sup> etc. These extended theoretical equations are often unjustified because of the incorrect use of the basic Debye-Hückel electrostatic model for the more concentrated solutions. It can be simply shown that even at a moderate electrolyte concentration this model leads to absurd results. For instance, the number of counterions having intimate contact with the given central ion in 0.5 molar solution of the 2:2 electrolyte, calculated from the charge distribution around an ion according to the Maxwell-Boltzmann statistics used in Debye-Hückel theory, is approximately 50. At the same time the geometrically possible maximum number of ions in contact with the given central ion is only 12 in case of close packing. Therefore it is obvious that such nonsenses make meaningless every discussion about the "real" ion size parameters, calculated on the basis of the extended Debye-Hückel theories.

In this work a different, simple model of electrolyte solutions is proposed, which proceeds from their structural features. The preliminary experimental verification of this model is provided on the basis of the activity coefficient data in aqueous solutions.

The existence of a regular structure of the nearest neighbours around a given particle in liquids and solutions is well-known from X-ray<sup>19,20</sup> and neutron<sup>21-23</sup> scattering experiments and also from the Monte Carlo or molecular dynamics simulations of dense fluids.<sup>24-27</sup> In principle two different types of organization between particles may be distinguished in electrolyte solutions. First of all, there is a regularity in statistically average distribution of ions due to the long-range electrostatic interaction between them. Secondly, the solvent is characterized by its internal structure which could be perturbed by solute particles, e.g. ions.



According to this picture we define two formally independent interaction types in electrolyte solutions:

- 1) ion-ion interaction, which is essentially of electrostatic nature at all real concentrations,
- 2) ion-solvent interaction, characterized by the influence of an ion on the solvent structure.

Both interactions correspond to the independent contributions in the excess free energy  $\Delta G_{ex}$  of electrolyte in solution:

$$\Delta G_{ex} = RT \ln \gamma_{el}$$

where  $\gamma_{el}$  is the activity coefficient of electrolyte, i.e.

$$\Delta G_{ex} = \Delta G_{ii} + \Delta G_{is} \quad (1)$$

The derivation of the quantitative mathematical form of the interionic excess free energy  $\Delta G_{ii}$  and ion-solvent excess free energy  $\Delta G_{is}$  is the subject of our following discussion.

## 2. The Ion-Ion Interaction in Electrolyte Solutions.

An assumption about the spatial distribution of ions in solution is requisite for the calculation of the first term in Eq. (1). The Poisson-Boltzmann distribution is not valid for the wide range of concentration,<sup>1-3</sup> and therefore it is not recommended as the basis for the calculation of interionic electrostatic interaction. Alternatively we assume the so-called "disordered lattice" structure model, which have had a constant popularity among the investigators<sup>28-32</sup> and which does not have serious internal restrictions on its use at different electrolyte concentration regions. The attractive feature of this model is also its utmost simplicity at simultaneous good consistency with experimental data. The following necessary and sufficient conditions must be satisfied for the calculation of the interionic electrostatic interaction energy according to this model:

- 1) a statistically uniform distribution of ions in solution is assumed, where the average reciprocal value of the distance between any of the two ions is equal to the similar quantity in perfectly ordered ionic lattice at the number density which corresponds to the ion concentration in solution,
- 2) the average number of ions in every coordination sphere around any ion in solution is equal to that in the above-mentioned perfect ionic lattice.

Provided that these conditions are satisfied, the electrostatic energy of lattice is to be found by the direct Madelung summation of ion-ion interactions. Correspondingly the electrostatic excess free energy of a binary electrolyte is equal to:

$$\Delta G_{ii} = \frac{331 A_M z_1 z_2 e^2}{\epsilon \bar{r}} \quad (\text{kcal/mole}), \quad (2)$$

where  $A_M$  denotes the theoretical Madelung constant for a given lattice type,  $z_1$  and  $z_2$  are the ionic charges,  $e$  is the electronic charge and  $\epsilon$  - the macroscopic dielectric constant of the pure solvent. The quantity  $\bar{r}$  is the mean distance between the nearest neighbouring counterions, i.e. the lattice constant. The latter is essentially concentration - dependent as the distance between ions is enhancing if the concentration of ions is lowering in solution. In the case of binary electrolytes the distance  $\bar{r}$  is a reciprocal function on the cube-root of electrolyte molar concentration  $c$ :

$$\bar{r} = \frac{9.3999}{\sqrt[3]{c}} \quad (\text{\AA}) \quad (3)$$

As a result the electrostatic excess free energy of a binary electrolyte in solution is expressed by the following formula:

$$\Delta G_{ii} = \frac{35.21 z_1 z_2 A_M}{\epsilon} \sqrt[3]{c} \quad \left( \frac{\text{kcal}}{\text{mol}} \right) \quad (4)$$



Due to the absence of freedom inside the model a macroscopic dielectric constant  $\epsilon$  of the pure solvent must be assumed.

### 3. The Structural Model of the Solute-Solvent Interactions .

To describe the ion-solvent interactions in solutions we proceed from the simplest structural model of dense fluids, i.e. from the two-state theory.<sup>34-38</sup> According to this concept every particle (ion or molecule) can exist in one of two different states in the solution. A fast dynamic equilibrium, characterized by the relaxation time  $10^{-11} - 10^{-12}$  sec is established between them. The particles at the given state have uniform properties and the energy level of them in state II is assumed to be equal to  $\epsilon$  ( $\epsilon < 0$ ), taking the level of those in state I as zero. The properties of particles in state II correspond to those in a hypothetical perfect crystal, where the solute particle is surrounded by solvent molecules in ordered solid lattice. State I is the state of ideal or real gas. The number density of particles in both states is equal to the mean number density of the solute in solution. Therefore the relative population in these states is uniquely determined by the volumes of solution occupied by the molecules in these.

The formulation of the partition function  $Z_N$  for a system of  $N$  particles of which fraction  $x$  is in state I, is made as follows<sup>35</sup> :

$$Z_N = \frac{N!}{(Nx)! \{N(1-x)\}!} f_I^{Nx} (f_{II} e^{-\epsilon/RT})^{N(1-x)}, \quad (5)$$

where  $f_I$  and  $f_{II}$  are internal partition functions of every species in state I and II, respectively. The mole fraction  $x$  of the particles in the equilibrium mixture is determined by the maximization of  $Z_N$  concerning  $x$  as variable, i.e.:

$$\left( \frac{\partial Z_N}{\partial x} \right)_{eq} = 0 \quad (6)$$



Using Stirling's approximation, equilibrium value  $x_{eq}$  is formulated as follows:

$$x_{eq} = \frac{f_I}{f_I + f_{II}e^{-\varepsilon/RT}} \quad (7)$$

and the partition function

$$Z_N = (f_I + f_{II}e^{-\varepsilon/RT})^N \quad (8)$$

In the system of variable number of particles the grand canonical partition function is defined as<sup>39</sup>:

$$Q = N! Z_N \quad (9)$$

and the chemical potential of this system is :

$$\mu = kT \left( \frac{\partial \ln Q}{\partial N} \right)_{T,V,N_j} = RT \left( \frac{\partial \ln Q}{\partial N} \right)_{T,V,N_j} \quad (10)$$

A simple derivation of  $\mu$  as a function of the number of particles  $N$  can be proceeded from the Eq. (7-10).

Obviously, for a system of a given  $N$ , using again Stirling's approximation, we get:

$$\ln Q = N \ln N - N + \ln Z_N = N \ln N - N + N \ln f_I - N \ln x_{eq} \quad (11)$$

The equilibrium mole fraction of particles in state I at the given solute molar concentration  $e$  is determined by the Čeleda law<sup>40</sup>:

$$x_{eq} = x_0 \frac{V_F}{V_0} = x_0 \exp(-V_S c), \quad (12)$$

Here  $x_0$  denotes the mole fraction of state I at standard conditions (infinite dilution), and  $V_F$  is the part of the total volume  $V_0$  of the solution whose structure is not influenced by the solute particles. These are characterized by the molar structure-changing volume  $V_S$  (cm<sup>3</sup>/mole), which is the volume in the vicinity of the solute particle where the solution is transformed from state I to state II (for the positive values of  $V_S$ , and otherwise round in the case of its negative values). Naturally, volume  $V_S$  does not correspond to an "iceberg" around the solute molecule, but it is only

the statistically average measure of the solute influence on the solvent structure. Correspondingly the volumes  $V_s$  for different solute particles can overlap without restriction. By transforming the molar concentration  $c$  to the function of the number of particles  $N$  in a constant volume  $V_0$

$$c = \frac{N}{N_A V_0} \quad (13)$$

( $N_A$  is the Avogadro's number), Eq. (12) can be rewritten as

$$x_{eq} = x_0 \exp\left(-\frac{V_s}{N_A V_0} N\right) = x_0 \exp(-\alpha_s N), \quad (14)$$

where  $\alpha_s$  is now a constant uniquely connected with the  $V_s$ . After substituting the last equation into Eq. (11) we get:

$$\ln Q = N \ln N - N + N \ln f_I - N \ln x_0 + \alpha_s N^2 \quad (15)$$

and consequently

$$\mu = RT \ln N + RT \ln (f_I + f_{II} e^{-\epsilon/RT}) + 2 \alpha_s N RT \quad (16)$$

or

$$\mu = RT \ln N_A V_0 + RT \ln (f_I + f_{II} e^{-\epsilon/RT}) + RT \ln c + \quad (17)$$

$$+ 2 \alpha_s RT N_A V_0 c = \mu_0 + RT \ln c + 2 RT V_s c,$$

where  $\mu_0 = RT [\ln N_A V_0 + \ln (f_I + f_{II} e^{-\epsilon/RT})]$  is the standard chemical potential of the solute.

The thermodynamic definition of the chemical potential of the real solution, is however<sup>41</sup>:

$$\mu = \mu_0 + RT \ln c + RT \ln \gamma_s, \quad (18)$$

where  $\gamma_s$  is the solute activity coefficient.

Consequently, the partial excess free energy of the dissolved substance caused by the solvent structure transformation is as a result of the comparison of two last equations as follows:

$$\Delta G_{is} = RT \ln \gamma_s = 2 RT V_s c \quad (19)$$



Noteworthy the formulation of the solute-solvent interaction excess free energy  $G_{is}$  is independent of the electrical nature of the solute particle, i.e. it can be equally ionic or neutral molecule.

#### 4. Preliminary Comparison of the Theory with the Experimental Activity Coefficients.

For the electrolyte solutions both interionic and ion-solvent interactions are to be taken into account and therefore the final formula of its partial molar excess free energy is as follows

$$\Delta G_{ex} = \frac{35.21 \cdot Z_1 Z_2 A_M}{\epsilon} \sqrt{c} + 2RTV_g c \quad (20)$$

or shortly

$$\Delta G_{ex} = a_t \sqrt{c} + b_1 c. \quad (21)$$

In the last formula  $a_t$  is a constant for the electrolytes of the same charge type in the given solvent and  $b_1$  is a characteristic parameter of the electrolyte. The sign of the latter defines essentially the nature of the solute effect on the solvent structure. Thus, the positive  $b_1$  values (the positive volumes  $V_g$ ) correspond to the structuremaking solutes, whereas the negative  $b_1$ -s are characteristic to structure-breakers. The absolute value of  $b_1$  (and respectively,  $V_g$ ) is the quantitative measure of the solute-solvent interaction intensity.

According to the final equation of the structural theory of electrolyte solutions given here, Eq. (21), the partial molar excess free energy of electrolyte in solution consists of two physically and formally independent terms.

The former, the electrostatic interionic interaction energy is always negative. Consequently, depending upon the sign of parameter  $b_1$ , function  $\Delta G_{ex}$  may have an extremum (minimum) point. This is in the case of  $b_1 > 0$ , indeed.

The solution concentration  $c_0$  at the minimum excess free



energy is determined from the condition

$$\left( \frac{d \Delta G_{ex}}{dc} \right)_{c=c_0} = 0 \quad (22)$$

$$\text{as } \frac{1}{3} a_t c_0^{-2/3} + b_1 = 0 \quad (23)$$

and thus:

$$\Delta G_{ex}(c_0) = a_t c_0^{1/3} - \frac{1}{3} a_t c_0^{1/3} = -\frac{2a_t}{3} \sqrt[3]{c_0} \quad (24)$$

As to the second derivative  $d^2 \Delta G_{ex}/dc^2 > 0$ , we have a minimum.

The minima on experimental curves of activity coefficients and therefore on the partial excess molar free energies of many electrolytes in aqueous solutions are well-known. According to the Eq. (24) these are uniquely determined by the molar concentration of electrolyte at minimum and the theoretical ion-ion interaction constant  $a_t$  for a given electrolyte type (cf. Eq. 20 and 21).

Following the numerous compilations of experimental activity coefficients of many electrolytes<sup>42-46</sup> the location of minima on their concentration curves could be well evaluated. Thus the experimental minimal partial excess free energies at 25°C in water were compared with the cube root of the concentrations at the minima. The validity of the linear relationships (24) is illustrated by graphs in Fig. 1. (1 : 1 electrolytes) and Fig. 2. (other electrolyte types). Respective statistical parameters of the linear regression treatment are given in Table 1. The fit with the theory may be estimated good, keeping in mind that the activity coefficients of different electrolytes at quite different concentrations were used for data analysis. For instance, the minimum concentration for the hydrochloric acid is estimated as 0.38M whereas for potassium chloride it is 2.78M. We have also to mention a remarkable coincidence of the experimental 'Madelung' constants  $A_M$  with the similar theoretical quantities of the corresponding perfect crystals for a given electrolyte charge type.

Table 1.

The Results of the Partial Molar Excess Free Energy  
Minima Data Treatment For the Aqueous Electrolyte Solutions  
at 25°C.

Electro- lyte type	$a_t$	$\Delta G_o$	(2) $r$	(3) $s$	(4) $s_o$	$\Delta H$ (calc.)	$\Delta H$ (theor.) <sup>(47)</sup>
1 : 1	0.656 $\pm$ 0.021	0.058 $\pm$ 0.015	0.992	0.024	0.026	1.750 $\pm$ 0.033	1.748 (NaCl)
2 : 1	1.517 $\pm$ 0.030	-0.015 $\pm$ 0.023	0.993	0.014	0.020	2.634 $\pm$ 0.052	2.520 (CaF <sub>2</sub> )
3 : 1	2.347 $\pm$ 0.033	0.041 $\pm$ 0.025	0.990	0.026	0.033	3.297 $\pm$ 0.046	3.322 (AlF <sub>3</sub> )

1) The treatment was actually carried out by the modified  
Eq. 24:

$$\Delta G_{ex}(c_o) = \Delta G_o + \frac{2 a_t}{3} \sqrt[3]{c_o},$$

where  $\Delta G_o$  describes a small correction to the experimental values of  $\Delta G_{ex}(c_o)$ . This is due to the different standardization of canonized activity coefficients, as the standard state for them is usually determined by the extrapolation of experimental data as the linear function from the square-root of the concentration instead of the cube-root of the concentration.

2) The correlation coefficient

3) The standard deviation (kcal/mol)

4) The weighted standard deviation  $s_o = s / \sqrt{\delta}$ , where  $\delta$  is the dispersion of the function  $\Delta G_{ex}(c_o)$



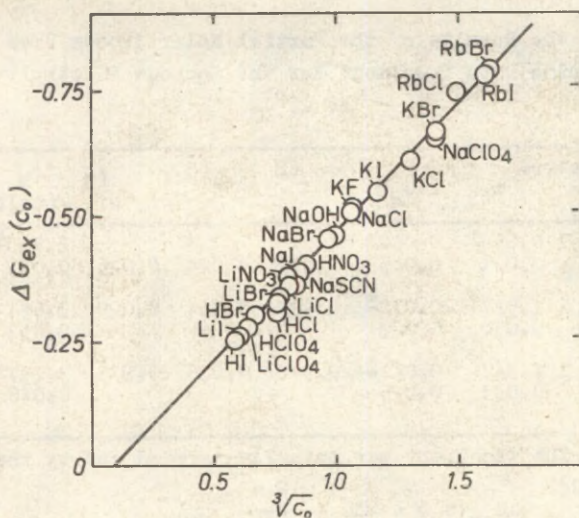


Fig. 1. The relationship between the minimal partial molar excess free energy and the cube-root of the electrolyte molar concentration in minimum for the 1:1 electrolytes



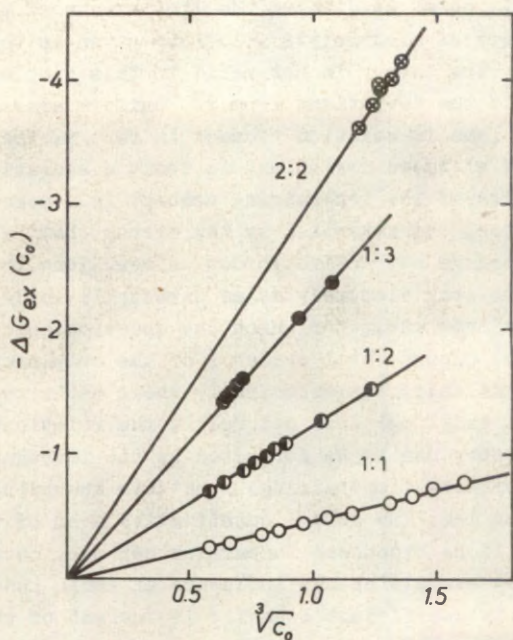


Fig. 2. The relationship between the minimal partial molar free energy and the cube-root of the electrolyte molar concentration for the different electrolytes.

## 5. The Limitations of the Model.

At this point we discuss the limitations of the structural theory of electrolyte solutions given in this paper.

First, the theory is not valid in this simple form in the case of the deviations from the uniform average distribution of ions in solution assumed in Part 2. The most dramatic form of these deviations is ionic association. The introduction of the ion-pairing concept is necessary for all electrolytes, characterized by the strong chemical or physical short-range attractive forces between ions. This is the case of the weak electrolytes as carboxylic acids, transition metal complexes etc., for which the spectroscopic or other independent experimental evidence of the complexation between ions is available. Correspondingly their activity coefficient minima (if existing) does not follow the relationship (24), and the theory has to be corrected by the introduction of ion-complexation (ion-pairing) constants according to the mass-action law. The actual quantitative form of this correction will be discussed in our further publications. An interesting example of the influence of ionic association on the activity coefficient behavior is the set of the alkali monocarboxylates<sup>48</sup>. Assuming the theoretical Madelung constant for the 1:1 electrolyte ( $A_M=1.748$ ), the electrostatic term in the partial molar excess free energy  $\Delta G_{ex}$  (Eq.20.) can be calculated independently. By subtraction of this term from both sides of Eq. 21, a simple linearity between the quantities  $\Delta G_{ex} - a_t \sqrt[3]{c}$  and the molar concentration of electrolyte solution is obtained:

$$\Delta G_{ex} - a_t \sqrt[3]{c} = b_1 c \quad (25)$$

As illustrated on Fig. 3, such linear relationship holds in the case of lower members of the monocarboxylate homologous series  $H(CH_2)_nCOONa$ . The statistical parameters of the corresponding linear regression treatment are given in Table 2.

Table 2.

The Results of the Activity Coefficient Data Treatment  
for the Sodium Monocarboxylates in Aqueous Solutions  
at 25°C (1)

Electrolyte	$\Delta G_o$	$b_1$	$r^{(2)}$	$s^{(3)}$	$s_o^{(4)}$
HCOONa	-0.028 $\pm$ 0.003	0.176 $\pm$ 0.002	0.999	0.0040	0.010
CH <sub>3</sub> COONa	-0.028 $\pm$ 0.008	0.317 $\pm$ 0.005	0.992	0.0202	0.016
C <sub>2</sub> H <sub>5</sub> COONa	-0.013 $\pm$ 0.004	0.380 $\pm$ 0.003	0.999	0.0072	0.008
C <sub>3</sub> H <sub>7</sub> COONa	-0.008 $\pm$ 0.019	0.433 $\pm$ 0.014	0.998	0.0301	0.028
C <sub>4</sub> H <sub>9</sub> COONa	-0.029 $\pm$ 0.007	0.493 $\pm$ 0.012	0.999	0.0078	0.024

(1) The data were treated according to the modified Eq. (25):

$$\Delta G_{ex} - a_t \sqrt[3]{c} = \Delta G_o + b_1 c,$$

where  $\Delta G_o$  is a small correction due to the differences  
in experimental activity coefficient standardization  
( See footnote (1) in Table 1.)

(2) The correlation coefficient

(3) The standard deviation (kcal/mol)

(4) The weighted standard deviation (See footnote (4) in  
Table 1.)

However, the successively larger deviations from the linearities (25) are observable for the higher members of monocarboxylate series (of Fig. 3). In our opinion, this is due to the association between the carboxylate anions induced by the hydrophobic interaction between alkyl chains. This ion-like association causes the lowering of the activity coefficients as the real concentration of particles is decreasing in solution whereas their size is enlarging. In limit of large alkyl substituents this association leads to the formation of soap micelles.



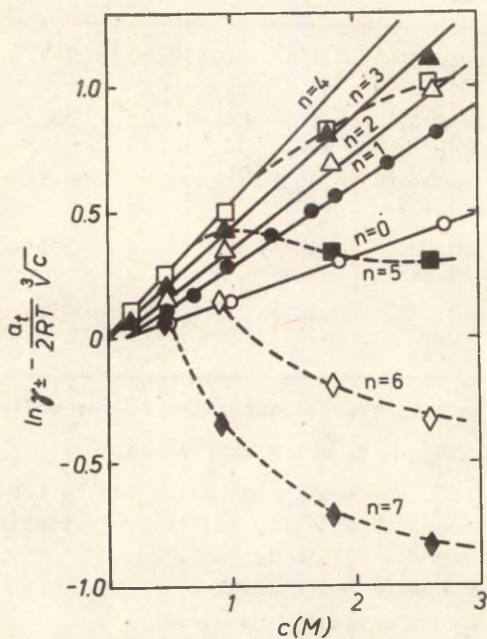


Fig. 3. The concentration dependence of the ion-solvent partial molar excess free energy  $\Delta G_{is} = \Delta G_{ex} - a_t \sqrt[3]{c}$  of the sodium monocarboxylate  $H(CH_2)_nCOONa$  aqueous solutions.

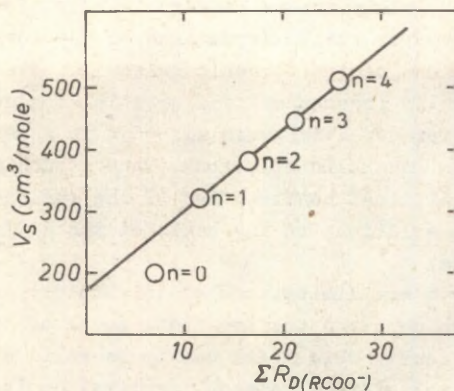


Fig. 4. The relationship between the structure-formation volumes  $V_s$  in aqueous solutions and intrinsic volumes of sodium monocarboxylates.

Finally, the existence of an interesting regularity between the structure-formation volumes  $V_s$ , calculated from the  $b_1$ -parameters, and intrinsic volumes of lighter monocarboxylate anions is observed. The latter are estimated from the additive bond molar refractions of the respective anions as  $\Sigma R_D$ . Then this regularity is described by the following linear relationship (see Fig. 4.) for  $n=1\dots 4$ :

$$V_s = (167.93 \pm 3.16) + (12.53 \pm 0.16) \Sigma R_D$$

$$r = 0.999$$

$$s = 1.68$$

$$s_0 = 0.013$$

The intercept of this linearity could be interpreted as the  $V_s$  for the sodium salt with anion having zero intrinsic volume. (This is not necessarily the  $V_s$  value for sodium ion itself). The sensitivity of  $V_s$ -parameters to the intrinsic volumes of carboxylate anions is surprisingly close to the similar quantity for the  $V_s$  dependence on the intrinsic volumes of various neutral organic molecules, evaluated from the experimentally independent differential-conduotometric data. This latter sensitivity is  $11.8 \pm 0.4$  in aqueous and  $12.2 \pm 0.4$  <sup>(50)</sup> in ethanolic solutions. Thus it could be estimated as an additional confirmation of the structural theory of electrolyte solutions on the basis of the different experimental data.

Returning to the limitations of this theory, another restriction which concerns the two-state model of the solution should be mentioned. This model has to be valid as far as state II ("crystal state") remains identical on the change of the solute concentration. However, at very large concentrations the mole fractions of solute and solvent become comparable and consequently the distribution of the particles around a given solute molecule becomes more similar to that in molten solute. This is naturally different from the assumingly constant distribution in diluted solutions where mainly solvent molecules are in the proximity of solute molecule. Thus there is a difference in partition function  $f_{II}$  in concentrated solutions which leads to the deviations from the simple relationship (19) due to the change in parameters  $X_0$  and  $\xi$  (See Eq. (7) and (16), respectively). Such deviations of experimental data from the theory could be foreseen for highly concentrated electrolyte solutions, e.g. for the molten crystal hydrates.

The results of the detailed experimental verification of the structural theory of electrolyte solutions given here on the basis of the whole variety of the activity coefficients and other experimental data will be given in separate publications.



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INFRARED SPECTRA AND ELECTRONIC EFFECTS.

I. TRANSMISSION OF SUBSTITUENT EFFECT TO THE ELECTRON -  
WITHDRAWING REACTION CENTER IN DIPHENYL SYSTEMS WITH  
HETEROBRIDGES.

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The substituent effect on the nitro group stretching frequencies in diphenyl systems with hetero - bridges (M) in between the rings has been studied. The established mechanism of conduction of electronic effects in such systems (biphenylene  $>O>S>SO_2>CO>NHCO$ ) does not depend either on the electron-releasing or electron-withdrawing nature of the reaction center. In diphenyl systems exists a direct polar conjugation between the nitro group and the electron - releasing substituents of the other ring. The same mechanism also accounts for the fact that heterobridges (M) interact both with the electron - releasing and electron withdrawing reaction centers. With the increase of conjugation the corresponding diphenyl systems are more inclined to transmit the effects of substituent (X) from one ring to the reaction center in another ring.

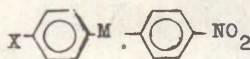
The transmission mechanism of electronic substituent effects in diphenyl systems with heterobridges connecting the rings, amino group forming the electron-releasing reaction center, has been studied previously<sup>1,2</sup>. It has been shown

that the attenuation of the electronic effects depends on the nature of a heterobridge as well as on the state of the reaction series. Thus, with diphenyl, a direct polar conjugation between amino group in one ring and electron - withdrawing substituent in another can be observed; while in case of some other heterobridges already examined (e.g. O, S, SO<sub>2</sub>, CO) the conjugation does not exist.

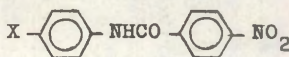
It was interesting to study the attenuation of electronic effects in the same systems where a nitro group formed the electron-withdrawing reaction center with the opposite electronic nature.

As Boček, Mangini and Zahradnic (3) have already shown, stretching frequencies of nitro groups can only slightly be affected by the substituent change in diphenyl systems which have oxygen and sulphur atoms in between the rings. Litvinenko et al.<sup>4</sup> have connected these results with the unsatisfactory sensitivity of the  $\nu_{\text{NO}_2}$  frequencies, caused by the equality of the atomic masses of nitrogen and oxygen, participating in the band stretching. However, according to the data on nitrobenzenes and anilines the sensitivity constants for asymmetric stretching bands of nitro- ( $\nu_{\text{asNO}_2}$ ) and amino groups ( $\nu_{\text{asNH}_2}$ ) have similar values, i.e.  $\sim 30.5 \text{ cm}^{-1}$ <sup>5,6</sup>, which contradicts to the above mentioned statement.

In the current work we have studied the effect of substituents (X) on the frequencies of symmetric ( $\nu_{\text{s}}$ ) and asymmetric ( $\nu_{\text{as}}$ ) stretching bands of nitro group for the compounds with general structure I - VI,



I-V



VI

where bridge M is a simple bond (I), -O- (II); -S- (III), -SO<sub>2</sub>- (IV), -CO- (V); X denotes a variable substituent: NH<sub>2</sub>, OCH<sub>3</sub>, CH<sub>3</sub>, HO, H, Cl, I, COOCH<sub>3</sub>, Br, NHCOCH<sub>3</sub>, COCH<sub>3</sub>, and NO<sub>2</sub>. The band frequencies were determined on an infrared spectrophotometer Perkin-Elmer 180, to within  $0.2 \text{ cm}^{-1}$ .

Table 1

The Values of  $\nu_{asNO_2}$  and  $\nu_{sNO_2}$  (in  $cm^{-1}$ ) in Compounds I - VI in DMSO

X M	$\nu_{NO_2}$		-O-		-S-		-SO <sub>2</sub> -		-CO-		-NHCO <sup>b</sup>	
	$\nu_{as}$	$\nu_s$	$\nu_{as}$	$\nu_s$	$\nu_{as}$	$\nu_s$	$\nu_{as}$	$\nu_s$	$\nu_{as}$	$\nu_s$	$\nu_{as}$	$\nu_s$
NH <sub>2</sub>	1509.0	1334.0	1510.5	1341.0	1512.0	1335.5	1530.5	1350.0	1522.5	1350.0	1525 <sup>c</sup>	1348 <sup>c</sup>
OCH <sub>3</sub>	-	-	1510.0 <sup>a</sup>	1342.0	-	-	-	-	1526.0	1351.0	1526 <sup>d</sup>	1347 <sup>d</sup>
CH <sub>3</sub>	-	-	1516.0	1342.5	1513.0	1337.0	1532.5	1352.0	1526.0	1352.5	1527	1348
H	1518.0	1344.0	1516.5	1342.5	1515.5	1337.5	1533.0	1353.0	1525.5	1353.5	1527	1349
NHCOCH <sub>3</sub>	-	-	-	-	1515.0	1336.5	1532.5	1351.0	-	-	-	-
Cl	1518.0 <sup>e</sup>	1341.0 <sup>e</sup>	1519.5	1343.0	1514.5	1338.0	1533.0	1351.0	1527.0	1350.5	1529 <sup>f</sup>	1349 <sup>f</sup>
COOH	1520.5	1344.0	1517.0	1341.5	-	-	-	-	1527.5	1350.0	1529	1350
COOCH <sub>3</sub>	1520.5	1342.0	1520.0	1343.5	1518.0	1338.0	-	-	-	-	-	-
COCH <sub>3</sub>	1522.0	1345.5	1520.5	1343.5	-	-	-	-	-	-	-	-
NO <sub>2</sub>	1524.0	1343.0	1521.5	1343.5	1520.0	1341.5	1536.5	1351.5	1527.5	1352.0	1529 <sup>g</sup>	1349 <sup>g</sup>

<sup>a</sup> was not taken into consideration in correlation calculations;

<sup>b</sup> a spectrophotometer UR-20 was used;

<sup>c</sup> X = N(CH<sub>3</sub>)<sub>2</sub>; <sup>d</sup> OH; <sup>e</sup> I; <sup>f</sup> Br; <sup>g</sup> 3'-NO<sub>2</sub>.



Dimethylsulfoxide (DMSO), permitting to examine the whole set of series (diphenylsulfone derivatives with a lower solubility included) under similar conditions, served as a solvent.

The experimental data from Table 1 show that the frequencies of both  $\nu_{as}NO_2$  and  $\nu_sNO_2$  within separate series grow proportionally to the increasing of the electron - withdrawing character of the solvents (Fig. 1.).

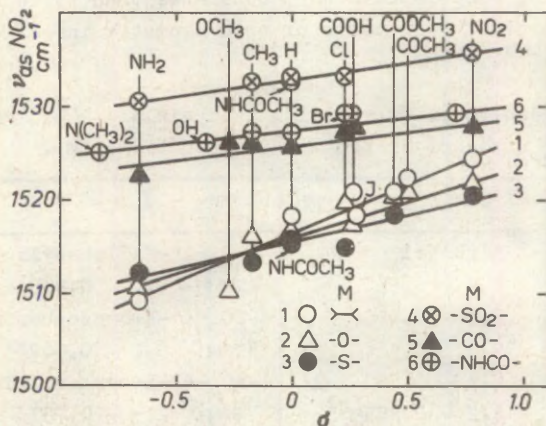


Fig. 1. Relationship between the  $\nu_{as}NO_2$  frequencies and Hammett  $\sigma$ -constants.

This relationship is due to the attraction of the electronic density from the oxygen atoms of nitro group. As a result of it, the polarity of the N=O bonds decreases and the state of their bonds order increases.

Table 2 presents the values of sensitivity constants ( $\rho$ ) for equation  $\nu = \nu_0 + \rho\sigma$  calculated by means of correlation treatment, using the least squares method<sup>7</sup>. The comparison of this data with the previously calculated values of the  $\nu_{NH_2}$  frequencies for the analogous diphenyl systems<sup>2</sup> shows that the sensitivity of the reaction center to the substituent effect remains the same in the diphenyl systems despite the nature of the reaction center. The seem-

ing absence of the shift of  $\nu_{\text{NO}_2}$  bonds in Ref. (3) can, probably be explained by the fact that only the substituents with an insignificant variation range of  $\sigma$ -constants (i.e. electron-releasing substituents only) were studied. Also the application of IR spectrometers with a relatively weak resolution accounts for the phenomenon.

According to the results of correlation treatment (Table 2) the correlation coefficient for diphenyl series is higher when using electrophilic  $\sigma^+$  constants than it is either with the Hammett  $\sigma$ -constants or with aromatic induction constants  $\sigma^B$ .

Table 2

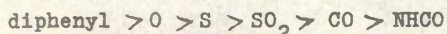
The Results of Correlation Analysis of  $\nu_{\text{NO}_2}$  Frequencies for Diphenyl System with Heterobridge (M).

Correlation	$\rho$	r	$\pi'$	Correlation	$\rho$	r	$\pi'$
4-NO <sub>2</sub> -4'-X-diphenyl				4-NO <sub>2</sub> -4'-X-diphenylsulfone			
$\nu_{\text{as}}; \sigma$	8.7	0.950	1	$\nu_{\text{as}}; \sigma^+$	4.0	0.968	0.46
$\sigma^+$	6.1	0.990		4-NO <sub>2</sub> -4'-X-benzophenone			
$\sigma^B$	9.8	0.914		$\nu_{\text{as}}; \sigma^+$	3.2	0.902	0.37
$\nu_{\text{s}}; \sigma$	6.5	0.783	1	4-NO <sub>2</sub> -4'-X-benzanilide			
$\sigma^+$	4.2	0.889		$\nu_{\text{as}}; \sigma^+$	2.9	0.937	0.33
$\sigma^B$	6.7	0.709		4-(ArM)-nitrobenzene			
4-NO <sub>2</sub> -4'-X-diphenyloxide				$\nu_{\text{as}}; \sigma$	16.9	0.912	1.95
$\nu_{\text{as}}; \sigma^+$	7.3	0.964	0.84	$\sigma^+$	13.4	0.972	-
4-NO <sub>2</sub> -4'-X-diphenylsulfide				4-(ArM)-aniline			
$\nu_{\text{as}}; \sigma^+$	5.7	0.946	0.65	$\sigma$	38.7	0.959	-
				$\sigma^+$	31.3	0.985	

Consequently, there is a direct polar conjugation between the reaction center and the substituent of another ring with an opposite electronic nature in both 4-nitro-4'-X-diphenyl and the earlier examined 4-amino-4'-X-diphenyl systems. Table 2 does not contain the correlation results for symmetric frequencies  $\nu_{\text{s}}\text{NO}_2$ . The corresponding correlation coefficients are unsatisfactory (0.7-0.8) because of the narrow variation range of band frequencies (for a number of systems it did not exceed 3-4 cm<sup>-1</sup>). The values of transmission fac-



tors  $\pi' = \rho/\rho$  reference obtained by frequencies  $\nu_{as}^{NO_2}$  (diphenyl was used as a standard series) show that the attenuation of substituent electronic effect to the  $\nu_{as}^{NO_2}$  band in the systems studied can be expressed as follows:



Thus, the existence of the electron-withdrawing reaction center in diphenyl bridge systems of nitro group refers to the regular conductivity, observed already with the electron-releasing reaction center of amino group. Since the data has been obtained using IR-spectroscopy, it reflects the equal attenuation of the systems in their ground states.

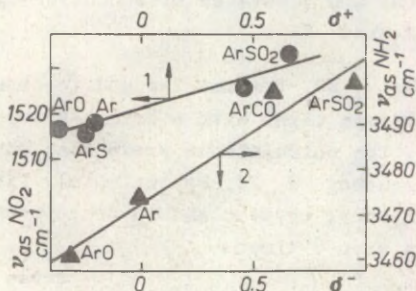


Fig. 2. Correlation between  $\nu_{as}^{NO_2}$  frequencies and  $\sigma^+$  (1); between  $\nu_{as}^{NH_2}$  and  $\sigma^-$ -constants (2) for p - ArM in para-substituted nitrobenzenes and anilines.

As can be seen, in figure 1 the change of M bridges' character has a considerably greater effect on the  $\nu_{NO_2}$  frequencies than that of substituent X within each separate series. This is quite natural, as the heterobridge itself, if taken as a substituent, stands much closer to the reaction center. The obtained data (see Table 1) enables one to quantitatively estimate the interaction between bridge groups and the reaction center. With this end in view has been carried out the correlation treatment of the relation-



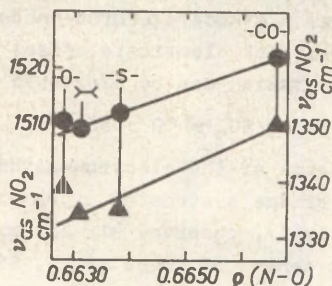


Fig. 3. Correlation between  $\nu_{as}NO_2$  frequencies (1) and  $\nu_sNO_2$  (2) and  $\pi$ -states of bonds P(N-O) for 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-M-O-4'-NH<sub>2</sub>.

ship between the  $\nu_{as}NO_2$  frequencies and  $\delta$ -constants of complex substituents (ArM) with a bridge-group and aromatic ring (Table 3). The calculations prove that the effect of bridge M on frequency  $\nu_{as}NO_2$  approximately twice exceeds that of X in diphenyl system; and in benzophenone and benzanilide systems even 6 times.

Table 3.

The Values of Frequencies  $\nu_{as}NO_2$  and  $\nu_{as}NH_2$  for p - ArM - C<sub>6</sub>H<sub>4</sub>-Y(Y=NO<sub>2</sub> and NH<sub>2</sub>) and Constants  $\delta$ ,  $\delta^+$  and  $\delta^-$  for Substituents p=ArM (from Ref.<sup>8</sup>, if there is no special reference) and of the  $\pi$ -State bond N=O.

ArM	$\nu_{as}NO_2$ cm $^{-1}$	$\nu_{as}NH_2$ cm $^{-1}$ , 2	$\delta_{ArM}$	$\delta^+_{ArM}$	$\delta^-_{ArM}$	P <sub>N=O</sub> <sup>e</sup>
Ar <sup>-</sup>	1518.0	3474.0	-0.01	-0.207 <sup>b</sup>	-0.01	0.6631
ArO	1516.5	3461.0	-0.320	-0.370 <sup>c</sup>	-0.320	0.6628
ArS	1515.5	3485.5	0.075 <sup>a</sup>	-0.247 <sup>c</sup>	-	0.6638
ArCO	1525.5	3497.0	0.459	0.459	0.586	0.6666
ArSO <sub>2</sub>	1533.0	3499.0	0.66	0.66	0.95 <sup>d</sup>	-

Values  $\delta$ ,  $\delta^+$  and  $\delta^-$  for a, b, c, d are taken from 9, 10, 11, 12 respectively; <sup>d</sup> is taken for compounds 4-NH<sub>2</sub>-Ph-M-Ph-NO<sub>2</sub>-4'.

As has already been mentioned, the direct polar conjugation can be observed between the nitro group and electron-releasing substituents in the 4-nitro-4'-X-diphenyl system. This effect will, probably, still stronger be expressed in case of substituted nitrobenzenes. If the established constants (Table 3) are used for electron-releasing bridge groups a relatively good linear correlation can be achieved (Table 2, fig. 2.). One can also notice a direct polar conjugation between electron-withdrawing substituents and the electron-releasing ( $\text{NH}_2$ )-reaction center<sup>1,2</sup> (correlation coefficient  $r$  is greater if the scale of nucleophilic substituent constants  $\sigma^-$  (Table 2) is used). The expression of a complex mechanism of the direct polar conjugation of bridge systems with nitro group forming the electron-withdrawing reaction center is also proved by the fact that in the dependency graph of  $\nu_s$  and  $\nu_{as}\text{NO}_2$  states on the N-O bond  $\pi$ -state, the data for the whole set of heterobridges is situated on the same single line (fig. 3). The strengthening of electron-withdrawing qualities of the M bridge results in the growth of the N-O bond  $\pi$ -state which corresponds to the increase of the bonds strength constant and that of the  $\nu_s$  and  $\nu_{as}\text{NO}_2$  frequencies. On the other hand, the ability of diphenyl systems to transmit the effect of substituent X on the reaction center of the other ring decreases.

Thus, the direct polar conjugation of bridge group with the reaction center is of particular importance in the transmission mechanism of substituent (X) effect on the electron-withdrawing reaction center  $\text{NO}_2$ , which is situated in the other ring of the diphenyl system with a heterobridge. The greater the interaction between the bridge and the reaction center, the more is the system inclined to transmit substituent effect X from one ring to the reaction center in another ring.

#### Experimental

IR-spectra were recorded at least 5 times under the following conditions: the concentration of compounds in



DMSO was 15-20 g/l, the thickness of the absorbing layer of cell from  $\text{CaF}_2$  equalled 0.064 mm, the scanning rate was 8-10  $\text{cm}^{-1}/\text{min}$ ; the spectral width of the layers was 1.5  $\text{cm}^{-1}$ , the calibration of spectrometer Perkin-Elmer 180 was regularly checked by polystyrene and the vapor of atmospheric moisture. Under these conditions the deviation of the  $\nu_{\text{NO}_2}$  frequency measurements did not exceed 0.2 - 0.3  $\text{cm}^{-1}$ . To be on the safe side, the values in Table 1 are rounded to 0.5  $\text{cm}^{-1}$ . Quantum - chemical calculations of  $\pi$ -states of the bonds were performed according to the SCF method in the approximation of Pariser-Parr-Pople (PPP) at a computer BESM-4 applying program<sup>13</sup>.

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SOME NEW VALUES OF BASICITIES

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The values of basicities, i.e. the changes in phenol IR spectrum were determined for 20 solvents. The obtained data were interpreted in connection with the known values for other solvents and with the peculiarities of their chemical structure.

The basicity of substances is one of the important characteristics which determines their behavior in various physico-chemical processes at present. The most wide-spread basicity scales are the spectroscopic one by Koppel-Palm-Paju<sup>1</sup> and by Kamlet-Taft<sup>2</sup> and the calorimetric donor number DN scale by Gutmann<sup>3</sup>. The first scale is preferable both owing to the great exactness of obtaining the suitable IR spectroscopic data and on account of the availability of a great number of basicity values: in the paper<sup>1</sup> only the basicity values for more than 200 solvents are cited.

Basicities "B" are used as one of the fundamental factors in the Koppel-Palm four-parameter equation which is widely spread for accounting the medium influence on the kinetic parameters and spectral processes<sup>4</sup>. Lately the possibility of using this equation for generalization of solvent influence data on such thermodynamical processes as the gases solubility<sup>5</sup> or the distribution of substances between two liquid phases<sup>6</sup> has been indicated. Therefore, it is important to expand the above-mentioned basicity scale "B" to the new substances possessing no known basicity values and to precise the present data as well.

We have determined the changes of phenol OH band  $\Delta \nu_{\text{PhOH}}$



i.e. basicity values "B" in the  $\text{CCl}_4$  solution in the presence of 20 substances. These measurements were carried out according to method<sup>7</sup> on a spectrophotometer IKS 14 A. In the case of the OH bond illegibly the concentration of the investigated donor was increased up to the measurements in extremal cases in the medium of the pure donor without  $\text{CCl}_4$ . The concentration of phenol was always invariable and equal to 0.01. The obtained data are given in the Table.

It is expedient to consider some data in detail in order to establish the connection between the substances' structure and their basicities "B". Thus, the basicities of the chloroethanes diminishing in the series dichloroethane (40) > tetrachloroethane (29) > pentachloroethane (12) agree with the growth of the electrophilicity of substances with the increase of halogen atoms number and with a noticeable acidity of pentachloroethane. In the paper<sup>8</sup> for the tetrachloroethane the authors give the change of frequency  $\Delta\nu_{\text{N-H}}$  for pyrrole as equal to  $55 \text{ cm}^{-1}$ . However, this value seems to be doubtful as according to Ref.1 the calculated "B" value is ca.120., i.e. similar with that of moderate strength donors: ethylbenzoate, ethylchloroacetate, furane.

The "B" value for tetrachloroethylene of  $2 \text{ cm}^{-1}$  is close to  $B=7$  calculated in<sup>9</sup> on the basis of the change of  $\Delta\nu_{\text{OH}}$  frequency of acetic acid in  $\text{CCl}_2=\text{CCl}_2$  medium. According to<sup>10</sup> for tetrachloroethylene  $B=0$ . The authors<sup>11</sup> give for o-nitrophenol the  $\Delta\nu_{\text{OH}}$  change  $4 \text{ cm}^{-1}$  but for this substance no satisfactory linearity exists between  $\Delta\nu_{\text{OH}}$  and "B" values probably as a result of the orto-effect. For trichloroethylene  $\Delta\nu_{\text{PhOH}}=B \cdot 10 \text{ cm}^{-1}$ , and the calculated value is equal to  $B=17$ .<sup>9</sup>

The basicities for  $\text{C}_2\text{H}_5\text{Br}$  (79),  $\alpha$ -methylnapthalene (37), m-bromotoluene (53), and p-chlorotoluene (41) are close to the similar values for n-BuBr (68), bromobenzene (40), and chlorobenzene (40)<sup>1</sup>.

The obtained basicity value for bromoform  $B=53$  is significantly greater than that for  $\text{CHCl}_3$  ( $B=14$ ), which coincides with the known fact of the halogenderivatives basicity in-



creasing in the rank  $I > Br > Cl$ . Nevertheless, the obtained value is smaller than  $B=67$  given in <sup>10</sup>.

These data confirm that the "B" scale is more differentiated than that of the Kamlet-Taft one in which <sup>12</sup> the B values for all the above-mentioned compounds are equal to zero.

The obtained  $\Delta \chi_{PhOH}$  value for  $\alpha$ -methylnaphtalene  $B=64$  is insignificantly greater than the values  $B=52, 53$  of <sup>13,14</sup>.

Butylacetate and tri-n-butylphosphate are widely used as extragents and therefore their B-values obtained could be used for the extraction processes equilibria calculations. The low basicity value for  $CCl_3COOMe$  agrees with the above-mentioned regularity - namely the decrease of B values with introduction of electronegative substituents into the molecule: thus for  $CH_2ClCOOEt$   $B=125$ , for  $CHCl_2COOEt$   $B=119$ <sup>1</sup>; for  $CH_3CONMe_2$   $B=345$ , for  $CCl_3CONMe_2$   $B=172$ <sup>15</sup>.

The basicity value for N-methylpyrrolidone is precised by us to  $B=357$  in comparison with  $B=341$  in <sup>15</sup>. In the same paper one may observe a number of considerable deviations from the average values calculated in <sup>1</sup>, e.g. for tetrahydrofuran  $B=365$ <sup>15</sup> and in <sup>1</sup>  $B=287$ , for acetone correspondingly  $193$ <sup>15</sup> and  $224$ <sup>1</sup>, for MeCN  $178$ <sup>15</sup> and  $160$ <sup>1</sup>, etc.

The basicity values for N,N-dialkylsulfamides  $B=150-160$  are close to the determined in the paper <sup>16</sup> value for allied compound  $MeSO_2NMe_2$   $B=139$ . For the corresponding phenylderivatives the basicity values are slightly lower. It may be pointed out that the experimentally established b-value for  $EtSO_2NMe_2$   $158$  coincides with the corresponding value calculated for this compound on the basis of dissolving  $CHClF_2$   $B=157$  in this solvent <sup>17</sup>. This once more confirms the universality of LFER-principles. Though, for the three other sulfamides such a high agreement between the spectrometrically determined basicities and the values calculated on the basis of solubility data does not exist, which probably may be caused by the use of simplified equation for calculations which does not take into account the influence of the medium electrophilicity on the dissolving  $CHClF_2$  solvation.

Table I

## SOLVENT BASICITIES

N°	Solvent	B	N°	Solvent	B
<u>Halogenoalkanes</u>			<u>Esters</u>		
1	Trichloroethylene	10	11	Butylacetate	158
2	Tetrachloroethane	29	12	$\text{CCl}_3\text{COOMe}$	87
3	Tetrachloroethylene	2	13	Tri-n-butylfosfate	336
4	Pentachloroethane	12	14	$\beta$ -Propiolactone	160
5	p-Chlorotoluene	41	15	$\gamma$ -Propansulfone	135
6	Ethylbromide	79	<u>Amides and sulfoamides</u>		
7	Bromoform	32	16	N-Methylpyrrolidone	357
8	m-Bromotoluene	53	17	$\text{CH}_3\text{SO}_2\text{N}(\text{C}_2\text{H}_5)_2$	152
9	$\alpha$ -Bromonaphtalene	37	18	$\text{C}_2\text{H}_5\text{SO}_2\text{N}(\text{CH}_3)_2$	158
<u>Hydrocarbons</u>			19	$\text{C}_2\text{H}_5\text{SO}_2\text{N}(\text{C}_2\text{H}_5)_2$	159
10	$\alpha$ -methylnaphtalene	64	20	$(\text{C}_2\text{H}_5)_2\text{NSO}_2\text{N}(\text{C}_2\text{H}_5)_2$	152

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THE STUDY OF SODIUM 1,1-DIMETHOXY-2,4,6-TRINITROCYCLO-  
HEXADIENATE-2,5 IN ALCOHOLS

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The decomposition kinetics of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienate in alcohols  $C_1-C_4$  has been measured spectrophotometrically. A satisfactory correlation between  $\log k$  and  $pK_a$  of alcohol as well as  $\delta^{\pi}$  was observed. As the process is controlled mainly by activation entropy, it was assumed that steric factors might have an essential importance in it. Thus, an excellent correlation between  $\log k$  and  $E_s^c$  of alcohol's radical R has been established.

Conductometric studies demonstrated that at the concentrations used in kinetic experiments ( $10^{-4}$ - $10^{-5}$  M) the apparent dissociation level is close to unity and consequently, the anions in the  $\delta$ -complex act as certain reactants. At concentrations  $1 \cdot 10^{-3}$  M and more the ion pairs whose significance is growing with the decrease of the alcohol's polarity tend to appear in the solution.

It is known that the rate of the activated nucleophilic substitution is determined by the stability of intermediate

$\delta$ -complexes which in its turn depends to a great extent on the composition and nature of the medium. Particularly, in low-polar aprotic solvents the ionic aggregates play a significant role.<sup>2</sup> In aqueous solutions pH of the medium

becomes an important factor.<sup>1</sup> However, up to now there is no data about the influence of the nature of protic solvents on the decomposition rate of the anionic Jackson-Meisenheimer  $\sigma$ -complexes.

Therefore, the aim of this work was the investigation of the decomposition kinetics of sodium 2,4,6-trinitro-cyclohexadienate-2,5 in aliphatic alcohols. The reaction rate was measured spectrophotometrically, monitoring the change of the optical density of the solution, watching the short-wave length absorption maximum which is characterized by the greater intensity ( $\lambda_{\max}=414-420$  nm). The linear character of the optical density logarithm dependence on time is indicative of the reaction's first order on the decomposing complex. Besides, the value of the calculated rate constant remains dependent on the initial concentration of the product. The pseudofirst order  $\sigma$ -complex decomposition reaction was observed for the alcohols studied.

The results of the measurements are given in Table 1. They show that the rate of the decomposition reaction of 2,4,6-trinitroanisole  $\sigma$ -complexes with sodium methylete decreases in series  $\text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{C}_3\text{H}_7\text{OH} > \text{C}_4\text{H}_9\text{OH}$  iso- $\text{C}_3\text{H}_7\text{OH} > \text{iso} - \text{C}_4\text{H}_9\text{OH}$ .

For the analogous reaction in low-alkaline solution Murto suggested a bimolecular decomposition mechanism, confirmed also by the negative values of activation volume and entropy<sup>1</sup>:

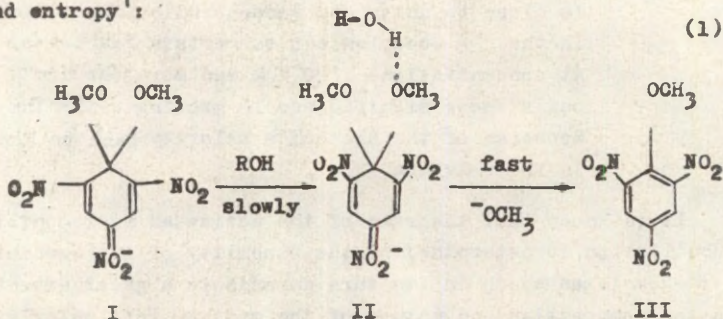




Table 1.

Rate Constants of  $\sigma$ -complex Decomposition (1).

No	ROH	$pK_a^3$	$\sigma^{*4}$	$E_s^c^5$	$k \cdot 10^4, c^{-1}$
1	$CH_3OH$	15.09	0.000	0.000	$18.0^6$
2	$C_2H_5OH$	15.93	-0.100	-0.38	10.5
3	$C_3H_7OH$	16.10	-0.115	-0.67	8.20
4	$C_4H_9OH$	-	-0.130	-0.70	6.30
5	1- $C_3H_7OH$	17.10	-0.190	-1.08	4.37
6	1- $C_4H_9OH$	-	-0.210	-1.24	3.60
7	$H_2O$	15.74	-0.490	0.32	$5.75^6$

If such a mechanism is supposed to work also in alcoholic solutions one should expect that the reaction is influenced by the alcohol acidity, which in its turn is connected with the electron donor. properties of the alkyl groups.

As a result of least squares treatment<sup>7</sup> has been established a correlation dependence of the logarithm of decomposition rate constant ( $\log k$ ) of  $\sigma$ -complex (1) on alcohol radicals ( $\delta^{\pi}$ )  $\sigma$ -constant values, the correlation coefficient being 0.985 ( $s=0.048$ ).

The obtained positive values of reaction constant  $\rho$  in equation  $\log k = -2.75 + 3.39 \sigma^{\pi}$  demonstrate that the process studied is relative to the electrophilic substrate. Therefore,  $\sigma$ -complex acts in the reaction as a nucleophile and forms in the solution ion pairs which should be less reactive than the free anions.

Thus, the decrease in the reaction rate may be caused by the increase of the concentration of ion pairs in transition while changing methanol for its less polar homologues. However, the analysis showed that there is no satisfactory correlation between the values of the decomposition rate constant logarithm ( $\log k$ ) and the value of the alcohol's reciprocal dielectric permittivity ( $1/D$ ) ( $r=0.924, s=0.152$ ).



A direct conductometric determination of the dissociation of the complex studied in the alcoholic solutions indicates that at concentrations  $1 \cdot 10^{-4} - 1 \cdot 10^{-5}$  M used for kinetic measurements the sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienate -2,5 was completely dissociated. At the same time when its concentration exceeds  $2 \cdot 10^{-4}$  M, the apparent dissociation degree ( $\alpha$ ) becomes less than a unity even in methanol and sharply falls with the decrease of dielectric permittivity of alcohol (Table II).

Table II.  
Conductometric and Spectral Study of  $\epsilon$ -Complex (I)  
in Alcohols

No	Alcohol	$D^{10}$	$K_d \cdot 10^4 M$	$\alpha_1$ $C=1 \cdot 10^{-3} M$	$\alpha_2$ $C=1 \cdot 10^{-5} M$	$\lambda_{max}$
1	$CH_3OH$	32.6	40.0	0.82	1.00	419
2	$C_2H_5OH$	24.3	27.2	0.78	1.00	418
3	$C_3H_7OH$	20.1	2.80	0.41	0.85	417
4	$C_3H_7OH$	18.3	2.06	0.38	0.84	416
5	$C_4H_9OH$	17.9	1.41	0.31	0.84	415
6	$C_4H_9OH$	17.2	0.84	0.26	0.75	4.4

Hence, at high concentrations the decomposition rate will be greatly dependent also on this medium factor.

The investigation into the temperature dependence of the decomposition of the  $\epsilon$ -complex (I) allowed to determine the activation parameters of the reaction. As it is seen from Table III, the nature of alcohol changes the activation energy of the process only insignificantly depending on the nature of the alcohol. It shows that the decomposition is controlled by the entropy factor. The latter allows to expect a sufficient contribution of the steric effects to the reaction rate. Really, the statistical analysis leads to an excellent correlation between  $\log k$  and  $E_S^C$  values of alcohol's alkyl radicals ( $r=0.992$ ;  $s=0.036$ ). The data obtained argue with the supposed reaction mechanism: the branching of

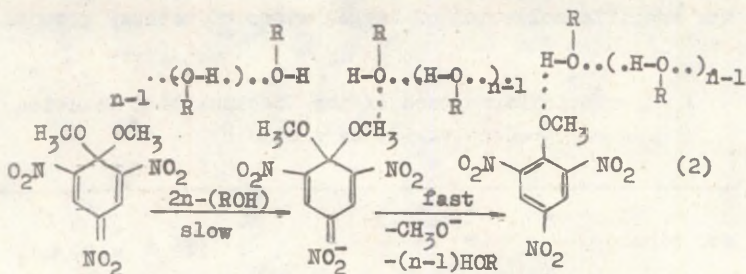
the alcohol alkyl radical should decrease the intensity of the specific solvation of oxygen atoms of methoxy groups.

Table III.

Energetic Parameters of the Decomposition Reaction  
of  $\sigma$ -Complex (1) by Alcohols

No	Alcohol	$k \cdot 10^4; s^{-1}$			E kJ/mol	log A	$S^\ddagger$ kJ/mol
		15°C	25°C	35°C			
1	C <sub>2</sub> H <sub>5</sub> OH	4.60	10.5	23.4	61.09	41.88	-96.57
2	C <sub>3</sub> H <sub>7</sub> OH	3.16	8.20	15.8	59.04	40.27	-105.39
3	C <sub>4</sub> H <sub>9</sub> OH	-	6.30	13.5	58.12	39.48	-110.83
4	C <sub>3</sub> H <sub>7</sub> OH	-	4.37	9.30	57.57	38.91	-115.69
5	C <sub>4</sub> H <sub>9</sub> OH	-	3.16	6.50	54.98	36.87	-128.49

From the correlation dependences of log k on all factors studied deviate only the corresponding values for water. From our viewpoint it is connected with the structure of the latter in the liquid state. It is known that water forms three-dimensional tetrahedral ice-like clusters in which every molecule is strongly enough connected with four adjacent ones by the hydrogen bonds.<sup>11</sup> Therefore, their activity in the hydration of the reaction center is lowered as compared to the solvation by the alcohol molecules which have only linear chains<sup>12</sup> due to the hydrogen bonds formation. Thus, in reaction of  $\sigma$ -complex with proton-donor solvent which is simultaneously an attacking agent and the medium, the structure of the latter also plays a rather important role. Hence, this factor should be taken into consideration in the reaction mechanism. Particularly, the decomposition process in alcohols may be represented by the following scheme (2):



Naturally, the solvation of all oxygen atoms of nitro groups takes place simultaneously. However, it has a considerably smaller effect on the decomposition rate. Moreover, the solvation must act also in the opposite direction to stabilize the complex. Therefore, for the sake of simplicity, it is not shown in scheme (2). From our viewpoint, the solvent structure must also be taken into consideration while studying the mechanism of decomposition of  $\sigma$ -complex by water.

Thus, the decomposition rate of sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienate-2,5 depends mainly on the acidity and the structure of the solvent. The role of the medium polarity may become significant at high concentrations of  $\sigma$ -complexes or at low values of solvent dielectric permittivity.

### Experimental

The  $\sigma$ -complex (I) was obtained according to the methods described earlier<sup>13</sup>. The solvents used were purified in accordance with the known methods<sup>13</sup>. The technique of kinetic measurements was previously described<sup>6</sup>. The obtained experimental data were processed according to the first order kinetic equation:

$$kt = 2.303(\log \Delta_0 - \log \Delta).$$



The activation parameters were calculated according to equation:

$$E = \frac{4.57 \cdot T_1 \cdot T_2 \cdot (\log k_1 - \log k_2)}{T_1 - T_2}$$

$$\log A = \log k + \frac{E}{4.57 \cdot T} \quad \Delta S^\ddagger/R \cdot -E/RT \quad 15$$

$$k = 2.0845 \cdot 10^{10} \cdot T \cdot \Delta S^\ddagger/R \cdot -E/RT$$

Equilibrium constants for dissociation of  $\sigma$ -complex (I) in alcohols were determined by the Kraus - Bray graphical method<sup>16</sup>. Conductance measurements were carried out according to the known method in a Jones-Bollinger pyrex cell<sup>17</sup>. The calculations of correlation parameters were conducted by means of the least-squares technique.

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ON THE "ORTHO EFFECT" IN A SERIES OF BASES OF  
TRIARYLCARBINOL TYPE

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From the analysis of the acid-base equilibrium constants of carbinol bases with ortho substituents of 10 reaction series a conclusion has been drawn about the electron nature of the ortho effect. Measure of alteration in the ortho substituents ( $\text{CH}_3$ ,  $\text{CH}_3\text{O}$ ,  $\text{Cl}$ ,  $\text{Br}$ ) effects during transition from one reaction series to another has been estimated quantitatively.

A number of studies<sup>1-4</sup> on the effect of different structural fragments on the stability of dyes of triphenyl methane series (derivatives of Malachite Green, Antipyrine Orange, 3,3'-dimethoxybenzaurin) have shown that the ortho position of sulfo-, nitro groups, halogen atoms and other substituents which are directly bound to the carbonium center of aryl decrease the hydrolysis of the dyes. It has been postulated<sup>5</sup> on the basis of these data that both electron-releasing and electron-withdrawing substituents, localized in the ortho position of aryl, raise the stability of the dyes to the hydrolysis as compared to the compounds containing no substituents in the benzene ring, or to para-isomers. The increase in the stability to the hydrolysis of the dyes with such electron-withdrawing ortho groups as halogen atoms,  $\text{NO}_2$ ,  $\text{SO}_3\text{H}$  can be explained by a stronger, opposite in sign and proportional to the volume of the group screening effect on the central carbon atom.

Analogous effect of the ortho substituents was also ob-



served in the series of isoindolynium ions<sup>6</sup> which are similar in their conjugation and molarization mechanism to the ions of triphenyl methane type. However, the studies on the stability of oxygen<sup>7-11</sup> and sulphuric<sup>12</sup> analogs of isoindolynium ions have shown that the above regularity is not always observed with these compounds. For example, although 3,3-(R)<sub>2</sub>-1-arylphthalylum- (R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, iso-C<sub>3</sub>H<sub>7</sub>, C<sub>6</sub>H<sub>5</sub>) and 3,3-dimethyl-1-arylthiophthalylum cations containing CH<sub>3</sub> and CH<sub>3</sub>O groups in the ortho position of 1-aryl are more stable than the corresponding 1-phenyl(thio)phthalylum cations, o-tolyl does stabilize the ions more efficiently than p-tolyl, whereas for o- and p-methoxyphenyls takes place the opposite dependence. But chlorine and bromine atoms in the ortho position of aryl in 3,3-dimethyl-1-arylphthalylum ions induce destabilization of the latter as compared to both their para-isomers and cations with non-substituted phenyl. It should be mentioned that for the series of 3,3-(R)<sub>2</sub>-1-arylphthalylum ions the differences in pK<sub>R</sub><sup>+</sup> values for the ortho- and para isomers of tolyls increase and for anisidines- decrease with the decrease of the effective electronegativity of the R group in order C<sub>6</sub>H<sub>5</sub>, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, which in its turn leads to the delocalization of the positive charge on the central carbon atom.

Finally, the studies on the effect of ortho substituents on the acid-base equilibrium involving such pseudobases as triarylcarbinols showed<sup>12</sup> that none of the ortho substituents investigated (CH<sub>3</sub>, CH<sub>3</sub>O, Cl, Br) increases the stability of the ions in this reaction series as opposed to the para-isomers. Only o-tolyl has a slight stabilizing effect with respect to the non-substituted cations.

Thus, the effect of ortho substituents on the stability of the ionized forms in the series of bases of triarylcarbinol type is not unequivocal, and in this context it should not only be considered as the steric interaction of the adjacent groups. In terms of the data presented and the results of the work<sup>14</sup> which have shown that the logarithms of the equilibrium constants for the ortho substituted derivatives

of the Antipyrine Orange are in linear relationship with the corresponding induction constants, we can draw the following conclusion. In the series of carbinol bases the "ortho effect" is mostly the electron effect involving a "normal" component (the induction effect) and a component related to the approximation of the ortho groups (the resonance effect)<sup>15</sup>. When considering acid-base transformations of weak carbinol bases, one cannot but take into account the formation of tight intramolecular hydrogen bonds in pseudobases between the ortho substituents and hydroxyl group attached to C<sup>1</sup> that shifts the equilibrium in the direction of covalent forms<sup>11-13,16</sup>.

Since for the bases of triarylcarbinol type the effect of ortho substituents had been shown to depend on the type of a reaction series and to be determined by the electron factors, so in order to quantitatively estimate the ortho effect in this work, we used the same approach based on the functional dependence of the substituent effect on the state of the reaction center as was applied earlier<sup>17</sup> while interpreting the effects of para- and meta-substituted aryls.

To this end we analysed the  $\lg K_R$  values for ortho substituted and non-substituted cations in 10 reaction series of triarylcarbinol type bases as follows:

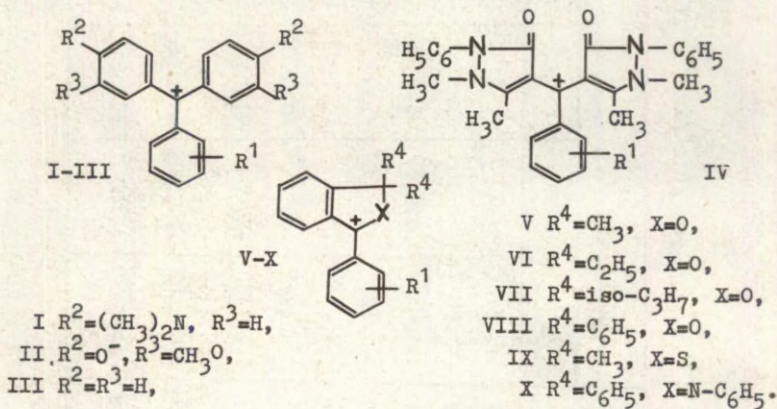




Table 1

VALUES FOR ACID-BASE EQUILIBRIUM CONSTANTS FOR DERIVATIVES OF SERIES I-X

Serial No	$R^1, \lg K_{R^+}$								
	H	o-CH <sub>3</sub>	p-CH <sub>3</sub>	o-CH <sub>3</sub> O	p-CH <sub>3</sub> O	o-Cl	p-Cl	o-Br	p-Br
I	-6.94 <sup>18</sup>	-9.03 <sup>19</sup>	-7.27 <sup>3</sup>	-	-	-7.5 <sup>5</sup>	-6.7 <sup>20</sup>	-8.3 <sup>21</sup>	-6.65 <sup>22</sup>
II	-10.98 <sup>4</sup>	-	-	-	-	-12.21 <sup>4</sup>	-10.88 <sup>4</sup>	-12.54 <sup>4</sup>	-
III	+6.63 <sup>23</sup>	+5.97 <sup>13</sup>	+5.41 <sup>23</sup>	+6.75 <sup>13</sup>	+3.40 <sup>23</sup>	+8.37 <sup>13</sup>	+7.08 <sup>13</sup>	+8.24 <sup>13</sup>	+7.25 <sup>13</sup>
IV	-6.60 <sup>24</sup>	-7.92 <sup>25</sup>	-7.00 <sup>25</sup>	-7.50 <sup>1</sup>	-7.48 <sup>25</sup>	-6.85 <sup>1</sup>	-6.13 <sup>24</sup>	-7.17 <sup>25</sup>	-6.00 <sup>25</sup>
V	+1.77 <sup>26</sup>	+0.31 <sup>7</sup>	+0.83 <sup>26</sup>	+0.98 <sup>7</sup>	-0.56 <sup>26</sup>	+2.91 <sup>7</sup>	+2.18 <sup>27</sup>	+2.73 <sup>7</sup>	+2.37 <sup>28</sup>
VI	+0.94 <sup>8</sup>	-0.72 <sup>8</sup>	-0.05 <sup>8</sup>	-0.03 <sup>9</sup>	-1.38 <sup>9</sup>	-	+1.59 <sup>9</sup>	-	+1.76 <sup>9</sup>
VII	-0.71 <sup>10</sup>	-2.06 <sup>10</sup>	-1.64 <sup>10</sup>	-	-	-	-	-	-
VIII	+3.74 <sup>29</sup>	+2.27 <sup>11</sup>	+2.74 <sup>11</sup>	+2.80 <sup>11</sup>	+1.06 <sup>11</sup>	-	+4.12 <sup>11</sup>	-	-
IX	+0.72 <sup>30</sup>	-0.34 <sup>12</sup>	-0.22 <sup>31</sup>	-0.76 <sup>9</sup>	-1.22 <sup>31</sup>	-	+1.24 <sup>31</sup>	-	+1.34 <sup>31</sup>
X	-7.30 <sup>32</sup>	-9.80 <sup>6</sup>	-7.66 <sup>32</sup>	-9.66 <sup>6</sup>	-8.20 <sup>32</sup>	-	-	-	-



Both electron-releasing and electron-withdrawing substituents were chosen for the analysis:  $R^1 = o\text{-CH}_3$ ,  $o\text{-CH}_3\text{O}$ ,  $o\text{-Cl}$ ,  $o\text{-Br}$  (Table 1). For comparison, Table 1 also lists the values for  $\lg K_{R^+}$  of their para-isomers. As in the paper<sup>17</sup>, the values of  $\lg K_{R^+}$  for the derivatives with non-substituted phenyl reflecting to some extent the  $+\delta$ -charge on the central carbon atom were taken as a criterion of the state of the reaction center.

The analysis of the data in Table 1 shows that, as in the case of their para-isomers<sup>17</sup>,  $\lg K_{R^+}$  for the compounds with ortho substituents<sup>\*)</sup> are in linear relationship with the  $\lg K_{R^+}$  values for the derivatives with non-substituted phenyl:

$$\lg K_{R^+}(R^1) = d \cdot \lg K_{R^+}(H) + \lg K_{R^+}^0(R^1), \quad (1)$$

which substantiates the electron nature of the ortho effect.

Parameters of Eq.(1) are listed in Table 2. As the table shows, the total effects of all of the ortho substituents studied are very sensitive (d) to the value of  $+\delta$ -charge localized on  $C^1$  and exceed the para-isomers in sensitivity

Table 2

PARAMETERS OF EQUATION (1)

$R^1$	$d \pm S_d$	$\lg K_{R^+}^0(R^1) \pm S$	r	n	Range of $\lg K_{R^+}$ (H) alteration, log unite
$o\text{-CH}_3$	$1.08 \pm 0.03$	$-1.44 \pm 0.39$	0.998	9	13.9
$o\text{-CH}_3\text{O}$	$1.17 \pm 0.03$	$-1.25 \pm 0.29$	0.999	6	13.9
$o\text{-Cl}$	$1.17 \pm 0.01$	$+0.71 \pm 0.15$	1.000	5	17.6
$o\text{-Br}$	$1.19 \pm 0.02$	$+0.43 \pm 0.34$	0.999	5	17.6

\*) The  $\lg K_{R^+}$  value for the compound with  $o\text{-CH}_3\text{O}$  in series IV shows a considerable deviation from the regression line, therefore it was not used in determining parameters of Eq.(1) and further calculations.

(Ref. 17). It is the different tendency of varying the total effect according to the state of the reaction center for ortho- and para- substituted phenyl that results in the ortho substituents of one reaction series or another being capable of stabilizing or destabilizing cations as compared to the non-substituted compounds or para-isomers. This is evident from Fig.1 which shows  $\lg K_R + (R^1) = f[\lg K_R + (H)]$  relationship as an illustration. Thus, the introduction of chlorine into the ortho position of aryl will result in

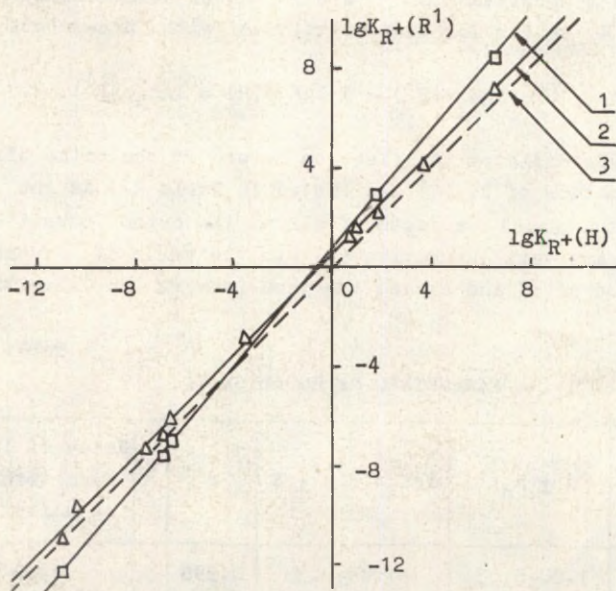


Fig.1.  $\lg K_R + (R^1) = f[\lg K_R + (H)]$  dependence  
for  $R^1 = o\text{-Cl}$ (1),  $R^1 = p\text{-Cl}$ (2) and  $R^1 = H$ (3)

the stabilization of cations as compared to the compounds with non-substituted phenyl for reaction series having  $\lg K_R + (H) < -4.2$ , while in comparison with para-isomers for series with  $\lg K_R + (H) < -1.3$

The linear correlation between the values of  $\lg K_R + (R^1)$



and  $\lg K_{R^+}(H)$  for the substituents of triarylcarbinol type bases enables us to calculate their constants by Eq.2<sup>17</sup> in terms of the changes of the effects of these substituents with the state of the reaction center. They will make a common scale with the respective constants for meta- and para-substituted aryls:

$$\sigma_d^+ = 0.227 \cdot [(d-1) \cdot \lg K_{R^+}(H) + \lg K_{R^+}^0(R^1)] \quad (2)$$

We have demonstrated for reaction series I-X that the values of  $\lg K_{R^+}$  for the ortho-, meta- and para-substituted compounds show a common correlation with the  $\sigma_d^+$  values (Fig. 2).

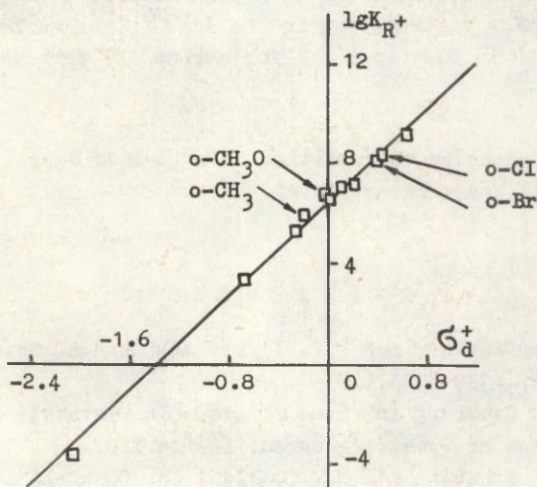


Fig.2.  $\lg K_{R^+}(R) = f(\sigma_d^+)$  dependence for reaction series III

Table 3 represents the obtained values of correlation  $r$  and standard deviation  $S$  coefficients. As shown in Table 3 and Fig.2, the  $\sigma_d^+$  values found for  $o\text{-CH}_3$ ,  $o\text{-CH}_3\text{O}$ ,  $o\text{-Cl}$  and  $o\text{-Br}$  sufficiently reflect the overall effect of these



Table 3

PARAMETERS OF CORRELATION EQUATION

$$\lg K_{R+}(R) = \rho \cdot \sigma_d^+ + \lg K_{R+}(H)$$

Serial No	n	r	S	Serial No	n	r	S
I	13	0.984	0.20	VI	12	0.997	0.17
II	6	0.992	0.12	VII	4	0.972	0.18
III	11	0.998	0.25	VIII	8	0.996	0.23
IV	14	0.983	0.26	IX	12	0.996	0.18
V	14	0.999	0.10	X	7	0.985	0.22

Note. In addition to the  $\lg K_{R+}$  values listed in Table 1 the  $\lg K_{R+}$  values given in the work<sup>17</sup> (for series I, III-X) and in the paper<sup>4</sup> (for series II) were used.

substituents on the position of acid-base equilibria of the carbinol bases investigated.

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INTERNAL SUBSTITUENT PARAMETERS AND CORRELATION  
OF PROTON AFFINITIES

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The correlation of the proton affinities of the compounds of various classes has been done using the internal (intrinsic) operational substituent parameters. On the bases of that approach it was shown that the substituent effects on the proton affinities are in several cases better described by the non-additive model. However, by the analogy with the ionization potentials the isoparametric value of the substituent parameter cannot be realized in any of the studied reaction series on the basis of the existing experimental data.

In the two other communications<sup>1,2</sup> the so called internal substituent parameters<sup>3-6</sup>  $X'_1$  and  $Y'_j$  were used for the quantitative correlation of the simultaneous non-additive substituent effects on the ionization potentials  $IP(X_1, Y_j)$  of the compounds  $X_1ZY_j$ , where Z is the ionization center using the equation of the following type:

$$IP(X_1, Y_j) = a_0 + a_1 X'_1 + a_2 Y'_j + \alpha X'_1 Y'_j \quad (1)$$

where  $a_0$ ,  $a_1$ ,  $a_2$ , and  $\alpha$  - are the constants

and

$$X'_1 = IP(X_1, Y_0) - IP(X_0, Y_0) \quad (2)$$

$$\text{and } Y_j' = IP(X_0, Y_j) - IP(X_0, Y_0) \quad (3)$$

By the definition  $a_0 = IP(X_0, Y_0)$  and  $a_1 = a_2 = 1.0$

The latter conditions make this simple method very convenient for the study of the relatively weak non-additive homogeneous or quasi-homogeneous influence of some factors (in the given case - substituents  $X_1$  and  $Y_j$ ) on the response function.

Earlier the correlation of the substituent effects on the proton affinity of neutral and anionic bases was performed<sup>7</sup> using the external (conventional) substituent characteristics (their inductive and resonance constants, substituent polarizability and the number of hydrogen atoms attached immediately or to the  $\alpha$ -position relative to the reaction center). It was demonstrated that in some rather satisfactory approximation the experimental data could be described in terms of equation which assumes the additivity of the substituent effects. For the comparison, in the present work the analysis of the structural effects on the PH values will be based on the approach which stems from Eq. (1) and uses the internal substituent constants as calculated from the proton affinity data by the analogy with Eqns.(2) and (3) substituting there the corresponding PA values for the ionization potentials IP.

The proton affinity data used throughout the present analysis are mostly taken from our earlier work.<sup>8</sup>

Both alkyl and electronegative substituents were involved.

The statistical data processing was performed according to the method of least squares using the program written by Prof. V.A. Palm. The major features of the program are described in Ref. 9.

The inclusion of the substituent scales and that of the cross term was performed according to the Fisher's test (at the 95 per cent level). The inclusion of the data points in its turn was done using the Student's t-test (95 per cent level).

Table 1  
Correlation of Substituent Effects on Proton Affinities of Various Classes of Neutral  
and Anionic Bases in Terms of Eqn.(1).<sup>a</sup>

Series		a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	α	n	R	s
1	2	3	4	5	6	7	8	9
1.1.	X <sub>1</sub> OY <sub>j</sub> <sup>b</sup>	187.1 (1.1)	0.886 (0.029)	0.905 (0.033)		29 (8)	0.987	1.1
1.2.	"	187.1 (1.1)	0.929 (0.038)	0.924 (0.034)	-0.0589 (0.0299)	29 (7)	0.988	1.1
1.3. <sup>c</sup>	"	186.8 (0.32)	0.996 (0.012)	0.968 (0.011)	-0.0155 (0.0017)	25 (4)	0.999	0.3
2.1. <sup>d</sup>	X <sub>1</sub> COY <sub>j</sub> <sup>e</sup>	189.9 (3.3)	0.755 (0.050)	0.798 (0.055)	-	51 (26)	0.910	3.3
2.2. <sup>d,f</sup>	"	189.5 (0.44)	1.000 (0.011)	0.995 (0.011)	-	28 (5)	0.998	0.4
2.3. <sup>d</sup>	"	189.1 (2.4)	0.928 (0.044)	0.963 (0.049)	-0.026 (0.004)	51 (25)	0.954	2.4
2.4. <sup>d,g</sup>		189.2 (1.0)	1.024 (0.022)	0.972 (0.023)	-0.028 (0.002)	39 (14)	0.991	1.0
2.5. <sup>h</sup>		190.0 (3.1)	0.832 (0.075)	0.755 (0.111)	-	18 (2)	0.932	3.0
2.6. <sup>h,i</sup>		189.6 (0.59)	0.995 (0.017)	1.004 (0.024)	-0.0426 (0.0021)	17	0.997	0.6



Table 1 continued

1	2	3	4	5	6	7	8	9
2.7.	$X_i \text{COOY}_j^j$	177.7 (1.1)	1.041 (0.034)	1.084 (0.048)		22 (9)	0.982	1.0
2.8.	"	177.8 (1.3)	1.023 (0.060)	1.060 (0.082)	0.003 (0.008)	22 (8)	0.981	1.0
3.1.	$X_i Y_j \text{CH}^{-k}$	376.3 (4.8)	1.033 (0.118)	1.158 (0.202)	-	13 (2)	0.872	4.7
3.2. <sup>1</sup>	"	374.3 (1.3)	1.010 (0.034)	0.931 (0.062)	-0.063 (0.016)	12 (0)	0.988	1.3
4.1.	$X_i Y_j Z_k R^{n,m}$	224.4 (2.4)	1.139 (0.161)	0.972 (0.096)	0.817 <sup>n</sup> (0.217)	22 (6)	0.919	2.4
4.2.	"	224.3 (2.5)	1.033 (0.228)	0.956 (0.100)	0.826 <sup>n,o</sup> (0.221)	22 (1)	0.916	2.4
4.3.	"	224.6 (0.8)	0.980 (0.073)	0.982 (0.032)	1.018 <sup>n,p</sup> (0.072)	21 (0)	0.992	0.8

## Footnotes:

a -  $a_0, a_1, a_2$  and  $\alpha$  are the regression coefficients; under their values in the parenthesis are given the corresponding error limits; n - is the number of the points in the regression whereas in the same (7th) column under its value in the parenthesis is shown the number of the degrees of the freedom  $f=n$  minus the number of the regression coefficients minus the number of data points used for the calculation of internal substituent constants  $X_i'$  and  $Y_j'$ ; R - is the multiple correlation coefficient; s - the standard deviation (in kcal/mol). The dash in the 6th column means

that the cross-term was not included into Eqn.(1) from the very beginning.

- b - Reference compound - methanol ( $PA(X_o, Y_o)=186.9$  kcal/mol).
- c - As compared with series 1.1 and 1.2 the points for  $t\text{-Bu}_2\text{O}$ ,  $\text{CH}_2=\text{CHOEt}$  and  $i\text{-Pr}_2\text{O}$  were excluded.
- d - Formal simultaneous correlation of aldehydes, ketones, carboxylic acids, esters, and amides.
- e - Reference compound - acetaldehyde ( $PA(X_o, Y_o)=189.7$  kcal/mol).
- f - As compared with series 2.1 the points for  $(\text{Me}_2\text{N})_2\text{CO}$ ,  $\text{PhCOOMe}$ ,  $\text{Ph}_2\text{CO}$ ,  $\text{Me}_2\text{NCOOEt}$ ,  $t\text{-BuCOOMe}$ ,  $\text{Me}_2\text{NCOOMe}$ ,  $t\text{-BuCOMe}$ ,  $\text{cy-PrCOMe}$ ,  $\text{CF}_3\text{COOPr}$ ,  $\text{CF}_3\text{COOBu}$ ,  $\text{CF}_3\text{COOEt}$ ,  $\text{CF}_3\text{COOH}$ ,  $\text{MeCONH}_2$ ,  $\text{EtCOOH}$ ,  $\text{CF}_3\text{COCF}_3$ ,  $\text{MeCOOPr}$ ,  $i\text{-PrCOOMe}$ ,  $\text{MeCOOEt}$ ,  $\text{EtCOOMe}$ ,  $\text{FCH}_2\text{COOH}$ ,  $\text{EtOCOOME}$ ,  $\text{FCH}_2\text{COOEt}$  were excluded.
- g - As compared with series 2.1 and 2.3 the points for  $\text{PhCOOMe}$ ,  $\text{MeCONH}_2$ ,  $\text{CF}_3\text{COCF}_3$ ,  $\text{CF}_3\text{COOBu}$ ,  $\text{CF}_3\text{COOPr}$ ,  $\text{CF}_3\text{COOEt}$ ,  $\text{Ph}_2\text{CO}$ ,  $\text{EtCOOH}$ ,  $\text{PrCOOMe}$ ,  $t\text{-BuCOOMe}$ ,  $t\text{-BuCOMe}$ ,  $\text{cy-PrCOMe}$  were excluded.
- h - Only the PA data for the aldehydes and ketones were included.
- i - As compared with series 2.5 the point for  $\text{CF}_3\text{COCF}_3$  was excluded.
- j - Reference compound -  $\text{CF}_3\text{COOH}$  ( $PA(X_o, Y_o)=178.0$  kcal/mol ).
- k - Reference compound -  $\text{Me}(\text{CN})\text{CH}^-$  ( $PA(X_o, Y_o)=373.7$  kcal/mol).
- l - As compared with series 3.2 the point for  $\text{FCH}_2^-$  was excluded.

- m - Reference compound - MeEtNH ( $PA(X_0, Y_0, Z_0) = 224.7$  kcal/mol).
- n - For this reaction series in the 6th column of the Table the regression coefficient  $a_3$  is given.
- o - Only one pair-wise cross term of substituent constants  $X_i'$  and  $Y_j'$  was taken into account:  $\alpha = -0.022 \pm 0.033$  (see also the text)
- p - As compared with series 4.2 the point for  $CF_3CH_2NMe_2$  was excluded. Only one pair-wise cross term of substituent constants  $X_i'$  and  $Y_j'$  was taken into account:  $\alpha = -0.026 \pm 0.010$ . (see also the text).



The results of the statistical least squares treatment of the data in terms of Eqn.(1) are given in Table 1.

### Discussion

Due to the more limited and less representative experimental material on the gas phase proton affinities of compounds of various classes the statistical verification of Eqn.(1) is much more difficult than in the case of the analogous analysis of non-additive substituent effects on the ionization potentials in terms of Eqn.(1). The situation is even more so complicated in the case when more than two substituents are involved. So, by the analogy of Ref.2 the study of the influence of three substituents  $X_1, Y_j$  and  $Z_k$  on the IP-s of tertiary amines  $X_1Y_jZ_kN$  it turned out that because of the statistically insufficiently representative set of substituents all three pair-wise product cross terms of internal substituent parameters  $X_1', Y_j'$  and  $Z_k'$  (i.e.  $X_1'Y_j'$ ,  $X_1'Z_k'$  and  $Y_j'Z_k'$ ) are mutually dependent on each other as well as on the triple product cross-term  $X_1'Y_j'Z_k'$ . Therefore, as earlier<sup>2</sup> the formal analysis of the non-additive substituent effects of these three substituents on PA-s of amines  $X_1Y_jZ_kN$  was performed in terms of equation which includes only one pair-wise cross term of substituent constants and no triple cross term at all:

$$PA(X_1, Y_j, Z_k) = a_0 + a_1X_1' + a_2Y_j' + a_3Z_k' + \alpha X_1' \cdot Y_j' \quad (4)$$

The survey of the correlation statistics from Table 1 shows that with the exception of the series 2.1 (formal simultaneous correlation of data for aldehydes, ketones, carboxylic acids, esters and amides according to the additive scheme), 2.5 (the additive correlation of the data for aldehydes and ketones only) and 3.1 (the additive correlation of proton affinities of carbanions  $X_1Y_jCH^-$ ) the reported correlations can be considered by their statistical characteristics as at least satisfactory or even good (e.g., series 1.1-1.3, 2.2, 2.4, 2.6-2.8, 3.2, and 4.3).

As in the case of ionization potentials<sup>2</sup> the approach which uses the internal operational substituent parameters leads, most frequently to the conclusion that, as a rule, the simultaneous influence of two or more substituents on the proton affinities is also non-additive. At the same time, depending on the reaction series and on the nature of the concrete representatives of the latter the deviations from the additive scheme might vary in a rather broad range. So, for the process of protonization of carboxylic acids and their esters (series 2.7 and 2.8) the cross term seems to be insignificant. In its turn, for the protonization of aldehydes and ketones (series 2.6), ethers and alcohols (1.3), carbanions  $X_1Y_jCH^-$  (3.2) and amines (4.3) the cross term is statistically significant.

For all series without exception the sign of regression coefficient  $\alpha$  is negative, i.e. on condition that the signs of internal parameters  $X_1$  and  $Y_j$  are the same the proton affinity of the base  $X_1ZY_j$  is less than predicted on the basis of the additive scheme for  $a_1=a_2=1$  and  $\alpha=0$ .

The analysis of the concrete experimental data for the reaction series recorded in Table 1 shows that, as a rule, the contribution of the cross term does not exceed 1-2 kcal/mol whereas the overall substituent effect for different reaction series often amounts up to several electron volts. However, as in the case of IP-s for some series and combinations of substituents the non-additivity effect is significantly larger. So, for the series of aldehydes and ketones (series 2.6) the contribution from the cross term for  $Ph_2CO$  is - 16 kcal/mol whereas the protonization of  $Ph_2CH^-$  carbanion deviates from additivity by - 6 kcal/mol.

Similarly, as in the case of the behavior of the IP-s of carbonyl compound of the general formula  $X_1COY_j$  (aldehydes, ketones, amides, carboxylic acids and esters), the analysis of PA-s of these compounds in terms of Eqn.(1) shows (see series 2.1-2.4) that aldehydes and ketones (No 2.5 and 2.6) don't belong to the same homogenous reaction series

with the carbonyl compounds (amides, esters, carboxylic acids) which have the lone pair of electrons located on the atom adjacent to the carbonyl group (see e.g. No 2.7 and 2.8).

For the conclusion one has to underline the urgent need for the significant purposeful and systematic extension of the experimental material on the gas phase proton affinities of several classes of neutral and anionic bases in order to conduct a more strict and statistically more founded study of the mutually perturbing influence of two or more substituents on their gas phase basicity.

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INTERNAL SUBSTITUENT PARAMETERS AND  
CORRELATION OF IONIZATION POTENTIALS

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The correlation of the ionization potentials of the compounds of various classes with the so called internal (intrinsic) substituent parameters has been made. It was shown that in several cases the substituent effects on the ionization potentials are non-additive. However, in any of the reaction series considered the actual realization and crossing of the isoparametric point was impossible on the basis of the existing experimental data.

The analysis of the structure effects on the ionization potentials of several classes of aliphatic compounds in terms of correlation scheme which includes the so called external or conventional substituent constants (Taft's inductive and resonance constants, the polarizability of the substituent and the number of hydrogen atoms attached immediately and in the  $\alpha$ -position to the ionization center) was used in the earlier paper of the present authors. Alongside of this approach the correlation of the substituent effects on the ionization potentials of 1,4-disubstituted benzenes  $X_1C_6H_4Y_j$  ( $\pi$ -orbitals of  $b_1$ -symmetry) was also performed<sup>2</sup> using the internal operational scales<sup>3-5</sup> of the substituent parameters. The use of the latter is especially

convenient for the study of the mutual non-additive influence of the structural, medium, temperature etc., effects on some function of response (ionization potential, proton affinity,  $pK_a$  of acids or bases, etc.) which characterizes the compounds studied.

In the framework of the latter approach for example, the simplest case of the influence of the simultaneous non-additive homogenous or quasihomogenous interaction of the two substituents  $X_1$  and  $Y_j$  on the ionization potentials of the compounds  $X_1ZY_j$ , where Z is the ionization center, is described by the equation

$$IP(X_1, Y_j) = a_0 + a_1 X_1' + a_2 Y_j' + \alpha X_1' Y_j' \quad (1)$$

where  $a_0$  - is the IP value for the standard substituents  $X_0$  and  $Y_0$ ,

$a_1$ ,  $a_2$ , and  $\alpha$  are constants

whereas

$$X_1' = IP(X_1, Y_0) - IP(X_0, Y_0) \quad (2)$$

and,

$$Y_j = IP(X_0, Y_j) - IP(X_0, Y_0) \quad (3)$$

By definition, besides the theoretically expected value of the intercept  $a_0 = IP(X_0, Y_0)$ , the mathematical expectations of the regression coefficient  $a_1$  and  $a_2$  are also a priori fixed, i.e.  $a_1 = a_2 = 1$ . That reduces the possibility of discrimination in the case of additive interaction of the statistically significant (but unjustified) cross term due to the shifts of the  $a_0$ ,  $a_1$ , and  $a_2$  values from the theoretical values either because of the non-orthogonality of the used substituent parameters  $X_1'$  and  $Y_j'$  or by some other reasons.

On condition that  $Y_j' = \text{const}$  Eqn.(1) reduces to the equation of the straight line:

$$IP(X_1, Y_j) = a_0' + a_1' X_1' , \quad (4)$$

$$\text{where } a_0' = a_0 + a_2 Y_j' \quad (5)$$

$$\text{and} \quad a_1' = a_1 + \alpha X_j' \quad (6)$$

On the other hand,  $X_1' = \text{const}$  another simple linear relationship holds:

$$IP(X_1, Y_j) = a_0'' + a_2'' Y_j' \quad (7)$$

$$\text{where} \quad a_0'' = a_0 + a_1 X_1' \quad (8)$$

$$\text{and} \quad a_2'' = a_2 + \alpha X_1' \quad (9)$$

Relationships (6) and (9) can be used for the definition and calculation of the so called isoparametric values<sup>5</sup>,  $\hat{X}_1$  and  $\hat{Y}_j$ , of the substituent parameters  $X_1'$  and  $Y_j'$  :

$$\hat{X}_1 = \hat{Y}_j = -1/\alpha \quad (10)$$

In other words, at these values of substituent parameters  $X_1'$  and/or  $Y_j'$  the inversion of the dependence of the response function  $IP(X_1, Y_j)$  on the structure of one substituent takes place while the nature of the other substituent changes.

In the case of the larger number of influencing factors (e.g., substituents) their non-additive influence is characterized by the equations which are rather analogous to Eqn.1. So, in the case of three substituents the full response function consists besides three single terms containing only the characteristics of one substituent also of three pair-wise cross terms containing the products of substituent constants and one triple cross term - the product of internal parameters of all three substituents.

In the present work, the statistical treatment of the experimental data deals mostly with the ionization potentials of the compounds  $X_1ZY_j$  in which only two substituents are attached to the ionization center. Accordingly the least squares analysis of these data is performed in terms of Eqn.(1).

The data bank on IP-s of amines  $X_1Y_jZ_kN$  and substituted ethylenes  $X_1X_2C=CX_3X_4$  is also rather extensive. However, due



to the statistically insufficiently representative set of these compounds it is rather difficult to choose the standard compounds for the calculations of the sufficiently balanced sets of substituent internal parameters for the analysis of the influence of substituent effects in the general case of the simultaneous influence of three or even four substituents. Therefore, in the case of the latter series the statistical analysis of the substituent effects was performed for two variable substituents ( $X_1 Y_j C=CH_2$ ) only, whereas the series of substituted amines  $X_1 Y_j Z_k N$  was described in terms of the simplified equation.

$$IP(X_1, Y_j, Z_k) = a_0 + a_1 X_1^i + a_2 Y_j^i + a_2 Z_k^i + \alpha X_1^i Y_j^i$$

which includes only one pair-wise cross term and no triple cross term<sup>2</sup>.

As a rule, for the comparison, alongside with the statistical treatment of the data in terms of Eqn.(1) the hypothesis about the additive influence of the substituent effects was also checked (in these cases the cross term was not included into Eqn.(1), i.e.  $\alpha=0$ ).

Most of the IP values used in the statistical treatment are taken from the Appendix to our earlier paper.<sup>1</sup>

Both alkyl and electronegative substituents were involved.

The statistical data processing was performed according to the method of least squares using the program written by Prof. V.A. Palm. The major features of the program are described in Ref. 6.

The inclusion of the substituent scales and that of the cross term was performed according to the Fisher's test (at the 95 per cent level). The inclusion of the data points in its turn was done using the Student's t-test (95 per cent level).

<sup>2</sup> From the three possible pair-wise products of parameters  $X_1^i$ ,  $Y_j^i$ , and  $Z_k^i$  only one was statistically independent.

Table 1  
The Results of the Statistical Treatment of the Ionization Potentials in  
Terms of Eqn. (1).<sup>a</sup>

Series		a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	α	n	R	s
1	2	3	4	5	6	7	8	9
1.1	X <sub>1</sub> OY <sub>j</sub> <sup>b</sup>	10.94 (0.11)	0.943 (0.024)	0.907 (0.022)	-	51 (13)	0.989	0.10
1.2	"	10.93 (0.07)	0.986 (0.016)	0.939 (0.015)	0.252 (0.031)	51 (12)	0.995	0.07
1.3 <sup>c</sup>	"	10.94 (0.04)	1.004 (0.009)	0.970 (0.009)	0.309 (0.019)	48 (9)	0.999	0.04
2.1	X <sub>1</sub> SY <sub>j</sub> <sup>d</sup>	9.41 (0.09)	0.798 (0.022)	0.943 (0.025)	-	48 (16)	0.989	0.09
2.2	"	9.42 (0.06)	0.933 (0.022)	0.998 (0.017)	0.391 (0.046)	47 (16)	0.994	0.06
2.3 <sup>e</sup>	"	9.43 (0.04)	0.933 (0.015)	1.005 (0.013)	0.479 (0.037)	43 (12)	0.997	0.04
3.1	X <sub>1</sub> Y <sub>j</sub> C=CH <sub>2</sub> <sup>f</sup>	9.87 (0.13)	0.988 (0.079)	0.850 (0.096)	-	19 (3)	0.961	0.13
3.2 <sup>g</sup>	"	9.88 (0.08)	0.964 (0.049)	0.884 (0.065)	-	17 (1)	0.982	0.08
3.3	"	9.88 (0.13)	0.996 (0.085)	0.860 (0.104)	0.078 (0.256)	19 (2)	0.959	0.13

Table 1 continued

1	2	3	4	5	6	7	8	9
3.4 <sup>g</sup>	$X_1 Y_j C=CH_2$	9.88 (0.08)	0.982 (0.054)	0.917 (0.076)	-0.150 (0.176)	17	0.982	0.08
4.1	$X_1 C=CY_j^h$	10.37 (0.06)	0.898 (0.036)	1.009 (0.030)	-	23 (3)	0.988	0.06
4.2	"	10.37 (0.01)	1.002 (0.009)	1.001 (0.007)	0.396 (0.020)	23 (2)	0.999	0.014
5.1 <sup>i</sup>	$X_i COY_j^j$	10.20 (0.02)	0.984 (0.012)	0.980 (0.013)	-	33 (8)	0.998	0.03
5.2 <sup>k</sup>	"	10.20 (0.04)	0.956 (0.015)	0.951 (0.017)	-0.123 (0.032)	34 (8)	0.997	0.04
5.3	$X_1 CONX_2 X_3^1$	10.05 (0.22)	0.500 (0.218)	0.930 (0.123)	-	15 (3)	0.794	0.22
5.4 <sup>m</sup>	"	9.98 (0.07)	0.831 (0.071)	1.015 (0.036)	-	13 (1)	0.964	0.06
5.5	"	10.02 (0.21)	0.718 (0.254)	0.805 (0.144)	0.823 (0.952)	15 (2)	0.813	0.21
5.6 <sup>m</sup>	"	9.97 (0.07)	0.839 (0.086)	1.007 (0.051)	0.043 (0.198)	13 (0)	0.982	0.07
5.7	$X_1 COOY_2^n$	10.79 (0.05)	0.960 (0.082)	1.032 (0.123)	-0.081 (0.276)	38 (14)	0.938	0.22
5.8	$X_i COY_j^{j,0}$	10.21 (0.25)	0.847 (0.040)	0.891 (0.041)	-	103 (53)	0.916	0.25
5.9 <sup>p</sup>	"	10.20 (0.03)	0.982 (0.006)	0.999 (0.006)	-	68 (17)	0.999	0.03



Table 1 continued

1	2	3	4	5	6	7	8	9
5.10	$X_1COY_j$	10.20 (0.26)	0.858 (0.068)	0.872 (0.047)	0.066 (0.068)	103 (52)	0.916	0.25
5.11 <sup>r</sup>	"	10.20 (0.02)	0.990 (0.014)	1.004 (0.006)	0.116 (0.014)	70 (18)	0.999	0.02
5.1	$X_1Y_jZ_kN^s$	8.73 (0.15)	1.039 (0.112)	0.976 (0.096)	1.284 <sup>t,u</sup> (0.300)	19 (1)	0.946	0.15
6.2	"	8.68 (0.17)	1.029 (0.110)	1.063 (0.118)	0.920 <sup>t,v</sup> (0.420)	19 (1)	0.948	0.15
6.3	"	8.73 (0.07)	0.920 (0.046)	0.988 (0.048)	1.136 <sup>t,w</sup> (0.168)	17 (1)	0.990	0.06

Footnotes:

a - In columns 3-6 in the parenthesis under the regression coefficients  $a_0, a_1, a_2$ , and  $a$  are given their error limits; the dash in column 6 means that the cross-term was not included into the Eqn.(1); n - the number of points, in the same column, under its values in the parenthesis is given the number of the degrees of freedom  $f = n$  minus the number of regression coefficients minus the number of data points used for the derivation of the substituent parameters; R - multiple regression coefficient; s - standard deviation (in eV).

b - Reference compound - methanol ( $X_0=Me, Y_0=H$ ;  $IP(X_0, Y_0)=10.94$  eV).

- c - As compared with series 1.1 and 1.2 the points for  $\text{Ph}_2\text{O}$ ,  $\text{ICH}_2\text{CH}_2\text{OMe}$  and  $\text{PhOCH}=\text{CH}_2$  were excluded.
- d - Reference compound -  $\text{MeSH}$  ( $X_0=\text{Me}$ ,  $Y_0=\text{H}$ ;  $\text{IP}(X_0, Y_0) = 9.44 \text{ eV}$ ).
- e - As compared with series 2.2 the points for  $2\text{-BuSEt}$ ,  $\text{EtSCH}=\text{CH}_2$ ,  $\text{PhSCH}_2\text{SiMe}_3$ , were excluded.
- f - Reference compound -  $\text{MeCH}=\text{CH}_2$  ( $\text{IP}(X_0, Y_0) = 9.88 \text{ eV}$ ).
- g - As compared with series 3.1 and 3.3 the points for  $\text{Me}(\text{Pr})\text{C}=\text{CH}_2$  and  $\text{Et}_2\text{C}=\text{CH}_2$  were excluded.
- h - Reference compound  $\text{MeC}\equiv\text{CH}$ ;  $\text{IP}(X_0, Y_0) = 10.37 \text{ eV}$ .
- i - Aldehydes and ketones only are included; the points for  $\text{MeCOPr}$ ,  $t\text{-BuCHO}$ ,  $i\text{-BuCHO}$ ,  $\text{CF}_3\text{COCCl}_3$ ,  $t\text{-Bu}_2\text{CO}$ ,  $i\text{-PrCO}(t\text{-Bu})$ ,  $\text{CF}_3\text{COCF}_3$ ,  $(\text{ClCH}_2)_2\text{CO}$ , and  $\text{Cl}_2\text{CHCOME}$  does not fit that correlation.
- j - Reference compound - acetaldehyde;  $\text{IP}(X_0, Y_0)=10.20 \text{ eV}$ .
- k - The points for  $\text{MeCOPr}$ ,  $t\text{-BuCHO}$ ,  $i\text{-BuCHO}$ ,  $\text{CF}_3\text{COCCl}_3$ ,  $t\text{-Bu}_2\text{CO}$ ,  $i\text{-PrCO}(t\text{-Bu})$ ,  $(\text{ClCH}_2)_2\text{CO}$  and  $\text{Cl}_2\text{CHCOME}$  does not fit that correlation.
- l - Reference compound -  $\text{MeCONH}_2$ ;  $\text{IP}(X_0, Y_0)=9.96 \text{ eV}$ ; only the points for amides were included.
- m - As compared with the series 5.3 and 5.5 the points for  $(\text{Me}_2\text{N})_2\text{CO}$  and  $\text{Me}_2\text{NCONHMe}$  were excluded.
- n - Reference compound - acetic acid;  $\text{IP}(X_0, Y_0)=10.84 \text{ eV}$ ; only the points for carboxylic acids and their esters were included.

- o - The simultaneous formal correlation of data for aldehydes, ketones, amides, esters, carboxylic acids and their halogen anhydrides.
- p - As compared with series 5.8 the points for  $\text{ClCH}_2\text{COCl}$ ,  $\text{F}_2\text{CO}$ ,  $(\text{Me}_2\text{N})_2\text{CO}$ ,  $\text{CCl}_3\text{COCl}$ ,  $\text{i-PrCONEt}_2$ ,  $\text{H}_2\text{C=CHCOOMe}$ ,  $\text{MeNHCONMe}_2$ ,  $\text{HC=CCOOH}$ ,  $\text{Ph}_2\text{CO}$ ,  $\text{i-BuCHO}$ ,  $\text{Me}_2\text{NCONH}_2$ ,  $\text{i-PrCOOMe}$ ,  $\text{H}_2\text{NCONHMe}$ ,  $\text{CF}_3\text{COOH}$ ,  $\text{Cl}_2\text{CHCOCl}$ ,  $\text{CF}_3\text{COCCL}_3$ ,  $\text{t-BuCOPh}$ ,  $(\text{H}_2\text{N})_2\text{CO}$ ,  $\text{ClCH}_2\text{COOH}$ ,  $(\text{H}_2\text{C=CH})_2\text{CO}$ ,  $\text{CF}_3\text{COCF}_3$ ,  $\text{Cl}_2\text{CHCOMe}$ ,  $\text{i-PrCOOH}$ ,  $\text{PhCOCH}_2\text{Cl}$ ,  $\text{H}_2\text{C=CHCOOH}$ ,  $\text{EtCOOH}$ ,  $(\text{ClCH}_2)_2\text{CO}$ ,  $\text{CF}_3\text{CONH}_2$ ,  $\text{MeCOOH}$ ,  $\text{i-BuCOOH}$ ,  $\text{CCl}_3\text{COMe}$ ,  $\text{CF}_3\text{COOEt}$ ,  $\text{PrCOOH}$ ,  $\text{BuCOOH}$ ,  $\text{i-PrCO(t-Bu)}$  were excluded.
- r - As compared with series 5.8 and 5.10 the points for  $\text{ClCH}_2\text{COCl}$ ,  $(\text{Me}_2\text{N})_2\text{CO}$ ,  $\text{i-PrCONEt}_2$ ,  $\text{F}_2\text{CO}$ ,  $\text{H}_2\text{C=CHCOOMe}$ ,  $\text{MeNHCONMe}_2$ ,  $\text{Ph}_2\text{CO}$ ,  $\text{HC=CCOOH}$ ,  $\text{Me}_2\text{NCONH}_2$ ,  $\text{i-BuCHO}$ ,  $\text{MeNHCONH}_2$ ,  $\text{CCl}_3\text{COCl}$ ,  $\text{Cl}_2\text{CHCOCl}$ ,  $\text{CF}_3\text{COCCL}_3$ ,  $\text{t-BuCOPh}$ ,  $\text{i-PrCOOMe}$ ,  $\text{CF}_3\text{COOH}$ ,  $(\text{H}_2\text{N})_2\text{CO}$ ,  $(\text{H}_2\text{C=CH})_2\text{CO}$ ,  $\text{ClCH}_2\text{COOH}$ ,  $\text{Cl}_2\text{CHCOMe}$ ,  $(\text{CF}_3)_2\text{CO}$ ,  $\text{CF}_3\text{COOEt}$ ,  $\text{t-Bu}_2\text{CO}$ ,  $\text{i-PrCOOH}$ ,  $\text{H}_2\text{C=CHCONH}_2$ ,  $\text{PhCOCH}_2\text{Cl}$ ,  $\text{PrCOOMe}$ ,  $(\text{ClCH}_2)_2\text{CO}$ ,  $\text{CF}_3\text{CONH}_2$ ,  $\text{H}_2\text{C=CHCOOH}$ ,  $\text{PrCOOEt}$ ,  $\text{EtCOOH}$  were excluded.
- s - Reference compound  $\text{Et(Me)NH}$ ,  $\text{IP}(X_0, Y_0, Z_0) = 8.73 \text{ eV}$ .
- t - Regression coefficient  $a_3$  at  $Z_k$ .
- u - The cross terms were not included into the correlation equation.
- v - Only one pair-wise product cross term was statistically independent; the corresponding regression coefficient  $\alpha = 0.790 \pm 0.650$ .
- w - Only one pair-wise product cross term was statistically independent; the corresponding regression coefficient  $\alpha = 0.802 \pm 0.263$ . As compared with series 6.3 the points for  $\text{NH}_3$  and  $\text{Me}_2\text{NOMe}$  were excluded.



The results of the least squares analysis of the use of the internal substituent parameters for the correlation of IP-s in terms of Eqn.(1) are given in Table 1.

### Discussion

According to the statistical characteristics and the range of variation of IP-s included into correlation equations from Table 1 one has, from the purely mathematical, formal viewpoint, to acknowledge that in most cases (even while using the additive scheme) the internal substituent parameters lead to at least satisfactory description of the dependence of IP-s of the compounds of many classes on their structure (standard deviations range from 0.04 to 0.25 eV).

At the same time, Table 1 also shows that especially in terms of the additive scheme the above-mentioned theoretical expectations about the values of the intercept  $a_0$  and regression coefficients  $a_1$  and  $a_2$  are frequently far from being fulfilled (i.e.  $a_0 \neq \text{IP}(X_0, Y_0)$  and  $a_1 \neq a_2 \neq 1$ ; see series 1.1, 2.1, 3.1, 3.2, 4.1, 5.1, 5.3, 5.4, 5.8). In the framework of the additive approach the latter conditions might tell either about the really non-additive substituent effects or about the non-orthogonality of the internal substituent parameters, or about both of these matters simultaneously. The latter approach assumes that in their turn, the theoretically expected values of regression coefficients  $a_0$ ,  $a_1$ , and  $a_2$  evidence at the "reasonable (i.e., comparable with the experimental error) standard deviation of the correlation and sufficient number of the degrees of freedom about the additive homogenous or quasihomogenous influence of the given set of substituents on the response function, i.e. in the present case - IP- of various aliphatic compounds.

Naturally the results of the use of the non-additive model (1) for the correlation of the additive influence of the substituent effects should coincide with those in the framework of the additive approach while using the Eq.(1) without the cross-term.

One can see from Table 1 that within the error limits

the substituent effects are additive for disubstituted ethylenes  $X_1Y_2C=CH_2$  (series 3.1 - 3.4) and for carboxylic acids and their esters (series 5.7).

Rather weak but still statistically significant is the non-additive influence of two substituents in aldehydes and ketones (series 5.11, the maximum deviation from additivity does not exceed 0.05 eV), in amides (series 5.3-5.6, the maximum deviation from the additivity is for  $HCONEt_2$  0.07 eV).

Somewhat more important are the non-additivity effects in disubstituted acetylenes (series 4.2, the maximum deviation from the additivity ( $FC=CSiMe_3$ ) is 0.28 eV), in ethers and alcohols (the deviation for the  $t-Bu_2O$  is 0.44 eV), and in the sulfides and mercaptanes ( $Ph_2S$  deviates by 0.45 eV).

Most probably, the substituent effects in amines  $X_1Y_2Z_kN$  are also non-additive (series 6.1-6.3). So for  $MeONH_2$  the non-additivity effect amounts up to 0.42 eV. .

The attempt of the simultaneous correlation of the data for various classes of carbonyl containing compounds  $X_1COY_2$  (series 5.8-5.11) shows that at least in terms of the internal substituent parameters aldehydes and ketones are not compatitive with the amides, halogen anhydrides, carboxylic acids and their esters, i.e. with the carbonyl compounds which have the lone electron pair on the atom which is adjacent to the CO-group.<sup>52</sup> At the same time it could be mentioned that the sign of the regression coefficient  $\alpha$  is negative only for the series of aldehydes and ketones (5.2). One, however, has also to keep in mind that in the case of the latter series the conditions  $a_1=a_2=1.0$  are probably not yet closely enough fulfilled and therefore the simple additive correlation 5.1 with  $\alpha=0$  and with even lower standard deviation  $s$  seems more preferable.

In the rest of cases (see Table 1)  $\alpha$  is positive which means that the mutually perturbing influence of two substituents  $X_1$  and  $Y_2$  results in the relative increase of the

<sup>52</sup> The analogous separation of the various classes of carbonyl compounds was noticed on the basis of the analysis of the dependences of their ionization potentials on their proton affinities and core level 1s0 bonding energies of the carbonyl oxygen atom.

IP of the compounds,  $\bar{X}_1\bar{X}_j$ , as compared with the corresponding values calculated on the basis of the additive scheme assuming  $a_1=a_2=1$  and  $\alpha=0$ . The comparison of the calculated on the basis of Table 1 isoparametric values  $-a_1/\alpha = -a_2/\alpha = \hat{X}_1' = \hat{X}_j'$  with the real concrete values of the experimentally determined internal substituent parameters  $X_1'$  and  $Y_j'$  shows that not in a single above-considered case the isoparametric phenomenon can be realized in practice.

In other words, the inversion of the direction of the substituent effects on the energetics of the gas phase transfer of the neutral molecule into the cation-radical does not take place in reality.

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ISOPARAMETRIC EFFECTS AND IONIZATION POTENTIALS  
OF 1,4-DISUBSTITUTED BENZENES


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It was established that the influence of the structural factors on the ionization potentials (IP) of 1,4-disubstituted benzenes  $X_1C_6H_4Y_j$  is non-additive and is described in terms of Eqns.(4) and (9) which formally quantitatively characterize the dependence of IP on the structure of  $X_1$  and  $Y_j$ .

At the present time several factors are known the influence of which on the physical, physico-chemical and chemical properties of organic compounds is non-additive.<sup>1-15</sup>

The isoparametrical effect<sup>16</sup> is the result of such non-additive interactions.

In this paper the analysis of substituent effects on IP-s of  $\pi$ -orbitals of  $b_1$  type of symmetry of 1,4-disubstituted benzenes  $X_1$ -- $Y_j$  has been performed.

It means that one of the simplest ways to study the mutually dependent substituent effects is through the use of the so called internal operational scales<sup>7</sup>  $X'_1$  and  $Y'_j$  of substituents,  $X_1$  and  $Y_j$ :

$$IP(X_1, Y_j) = a_0 + a_1 X'_1 + a_2 Y'_j + \alpha X'_1 Y'_j, \quad (1)$$

where  $a_0$  is the IP value for the standard substituents  $X_0$  and  $Y_0$

$$X'_1 = IP(X_1, Y_0) - IP(X_0, Y_0) \quad (2)$$

$$\text{and } Y_j' = IP(X_0, Y_j) - IP(X_0, Y_0) \quad (3)$$

Naturally characteristics of substituents defined by Eqns.(2) and (3) should be, preferentially, applicable for the correlations of IP values because in some sense they account for the substituent effects more adequately than the wide-spread general-purpose scales of the substituent constants.<sup>16,18</sup> On the other hand, the use of the formalism of the polylinearity principle in the form of Eqn.(1) is also very convenient from the purely mathematical viewpoint because for all regression coefficients ( $a_0, a_1$  and  $a_2$ ) but  $\alpha$  their mathematically expected values are known in advance.<sup>7,16</sup>

Indeed, for the coefficients of Eqn.(1) the theoretical value of  $a_0$   $IP(X_0, Y_0)$  is determined by its definition and the expected values of  $a_1$  and  $a_2$  are determined by the simple relationship  $a_1 = a_2 = 1$ . On condition that these requirements are fulfilled it is evidently much simpler to evaluate also the statistical significance of the really unbiased regression coefficient  $\alpha$  which is included into the cross term of the right-hand side of Eqn.(1).

All IP values for 1,4-disubstituted benzenes  $X_1C_6H_4Y_j$  used in the present work were taken from various literature sources.

The  $IP(H, Cl) = 9.10$  eV was used as reference. The internal substituent constants  $X_1'$  (11 values) and  $Y_j'$  (23 values) were calculated according to Eqns.(2) and (3).

The final statistical least square analysis<sup>17</sup> of the experimental data in terms of Eqn.(1) leads to the following relationship<sup>\*</sup>:

---

<sup>\*</sup> Here and in the following text the statistical errors of the regression coefficients are given in parenthesis whereas  $s$  is the standard deviation,  $n$  - the number of points and  $r$  - the correlation coefficient.

$$\text{IP}(X_1, Y_j) = 9.07(0.01) + 1.10(0.02)X_1' + 1.02(0.02)Y_j' + 0.48(0.03)X_1'Y_j' \quad (4)$$

$r = 0.995$ ;  $s = 0.06$  eV and  $n = 55$

which with the excellent precision reproduces the dependence of the experimental IP values of the 1,4-disubstituted benzenes on their structure. The cross term is without no doubt ( $\rho = 0.48 \pm 0.03$ ) statistically significant. Nevertheless, the isoparametric point  $\hat{X}_1' = \hat{Y}_j' = -1/\rho = -2.08$  is not realizable in the experiment for both substituents,  $X_1$  and  $Y_j$ .

It should be mentioned that in the literature<sup>16,18</sup> for the quantitative study of the non-additive influence of the substituent effects on the various physico-chemical characteristics one usually uses in Eqns. of type (1) the Hammett-Taft substituent constants ( $\sigma$ ,  $\sigma^{\pm}$ ,  $\sigma^-$ ,  $\sigma^0$ ,  $\sigma_R^{\pm}$ ,  $\sigma^+$ ,  $\sigma_R^0$ , etc.) instead of the internal substituent parameters. At the same time it is essential that in the case of homogeneous or quasi-homogeneous influence both approaches should lead, in principle, to the comparable results.


For the sake of obviousness and simplicity of the approach (but, unfortunately, to some detriment of its strictness) the present analysis of the non-additive substituent effects on the IP-s of  $\pi$ -orbitals of  $b_1$  symmetry of the 1,4-substituted benzenes in terms of the so called external scales of substituent constants has been made using the simplest "practical" scale<sup>16,18</sup> of Hammett  $\sigma$ -constants (or  $\sigma^-$  and  $\sigma^+$ )<sup>††</sup>

One can see from Table 1 that the experimental data on

<sup>†</sup> Corresponds to IP = 6.99 eV.

<sup>††</sup> It is self-evident that the more strict approach should use instead of the composite non-homogeneous  $\sigma$ ,  $\sigma^-$  and  $\sigma^+$  the combinations from the inductive ( $\sigma^0$ ,  $\sigma_I$ , etc.) and resonance ( $\sigma_R^{\pm}$  or  $\sigma_R^0$ ) constants.



IP-s of  $b_1$  type of symmetry for the compounds  $X_1$ -- $Y_j$  for the fixed  $Y_j$  are described by the simple equations of the following type (compare also with Ref. 19):

$$IP = (IP)_0 + \rho \sigma_{X_1} \quad (5)$$

where  $\sigma_{X_1}$  is the substituent constant for the  $X_1$  group,  $(IP)_0$  is the IP value for  $X_1=H$  and  $\rho$  - is the constant characteristic for the series of compounds with fixed  $Y_j$ .

Table 1

The Results of Regression Analysis of IP of 1,4-Di-substituted Benzenes in Terms of Eqn.(5)<sup>a</sup>

$Y_j$	$(IP)_0$	$\rho$	r	s	n
1. H	8.91(0.01)	1.32(0.06)	0.981	0.14	20
2. Me	8.56(0.01)	1.18(0.09)	0.968	0.17	14
3. F	8.98(0.01)	1.04(0.27)	0.914	0.20	5
4. Cl	8.92(0.01)	1.31(0.11)	0.958	0.19	14
5. Br	8.75(0.07)	1.26(0.16)	0.938	0.22	11
6. MeO	8.17(0.01)	1.02(0.09)	0.957	0.15	13
7. EtO	8.34(0.09)	1.01(0.17)	0.933	0.23	7
8. $NH_2$	7.99(0.01)	0.73(0.11)	0.908	0.15	12
9. $NMe_2$	7.44(0.07)	0.65(0.13)	0.854	0.17	11
10. $NO_2$	9.17(0.01)	1.26(0.22)	0.946	0.24	6
11. $CF_3$	9.52(0.23)	1.54(0.72)	0.835	0.28	4
12. NO	8.81(0.03)	1.22(0.14)	0.993	0.11	3
13. OH	8.50(0.01)	0.94(0.17)	0.947	0.16	7

a - The errors of regression coefficients are given in parenthesis, r - correlation coefficient, s - standard deviation (in eV), n - the number of points.

Table 1 clearly reveals that the sensitivity  $\rho$  of the given series of compounds towards the variation of the substituent  $X_1$  is rather different for the various reaction series (for  $Y_j = NMe_2$  the  $\rho$  value is 0.65 whereas for  $Y_j = NO_2$  it is already 1.55) which evidences about the non-additive effect of

$X_1$  and  $Y_j$  on IP values of the above-mentioned compounds. In other words, the intensity of the influence of  $X_1$  on IP values depends on the nature of  $Y_j$  and vice versa. This situation is described by the following equation:

$$\rho = 1.16(0.01) + 0.59(0.04)\sigma_{Y_j} \quad (6)$$

where  $r = 0.983$ ;  $s = 0.06$  eV and  $n = 12$  and visualized in Fig. 1.

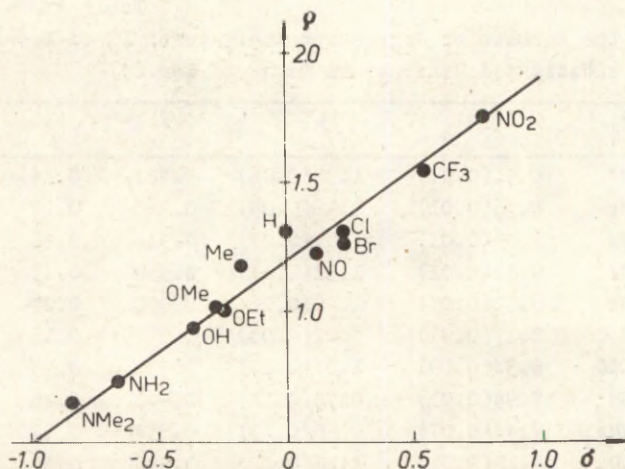


Fig. 1. The dependence of the sensitivity  $\rho$  of ionization potentials of 1,4-substituted benzenes  $X_1C_6H_4Y_j$  towards the change of  $X_1$ -group (at  $Y_j = \text{const}$ ) on the variation of the substituent constant ( $\sigma$ ) of another substituent  $Y_j$ .

On the other hand, the rather satisfactory linear relationship (see Fig. 2) holds also between the values of the slope ( $\rho$ ) and intercept ( $(IP)_0$ ) of Eqn.(5).

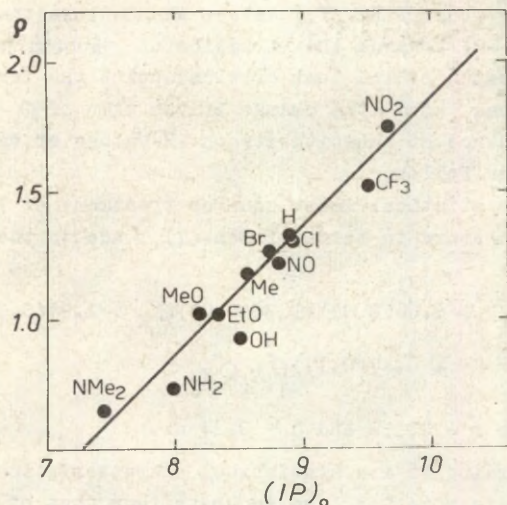


Fig. 2. The relationship between regression coefficients of Eqn.(5)- $\rho$  and  $(IP)_0$  values - for the series of 1,4-disubstituted benzenes  $X_iC_6H_4Y_j$

It follows from the above-said that in the case of using the external substituent constants for the description of the non-additive influence of two substituents  $X_i$  and  $Y_j$  the equation which is formally analogous to Eqn.(1) holds:

$$IP(X_i, Y_j) = a_0' + a_1' \sigma_{X_i} + a_2' \sigma_{Y_j} + \alpha' \sigma_{X_i} \sigma_{Y_j}, \quad (7)$$

where  $a_0'$ ,  $a_1'$ ,  $a_2'$ , and  $\alpha'$  are constants.

On condition that  $\sigma_{Y_j} = \text{const}$  Eqn.(7) transforms into relationship (8):



$$IP(X_1, Y_j) = (a_0' + a_2' \sigma_{Y_j}) + (a_1' + \alpha' \sigma_{Y_j}) \sigma_{X_1}, \quad (8)$$

which for  $(a_0' + a_2' \sigma_{Y_j}) = (IP)_0$  and

$a_1' + \alpha' \sigma_{Y_j} = \rho$  is identical to Eqn.(5).

One can see, that at a certain critical condition  $\hat{\sigma}_{Y_j} = -a_1'/\alpha'$  the  $IP(X_1, Y_j)$  values should lose the sensitivity ( $\rho = 0$ ) towards the variation of substituent  $X_1$ . In the region behind that critical point the inversion of the general trend (the change of the sign of  $\rho$ -value) of the influence of substituents on IP-values of these compounds can follow.

The statistical least squares treatment of 73 IP values from literature in terms of Eqn.(7) leads to the following equation:

$$IP(X_1, Y_j) = 8.66(0.03) + 1.36(0.09) \sigma_{X_1} + 1.24(0.06) \sigma_{Y_j} + 0.47(0.17) \sigma_{X_1} \sigma_{Y_j}, \quad (9)$$

where  $r = 0.958$  and  $s = 0.24$  eV.

According to its statistical characteristics the latter equation is somewhat less accurate than that of Eqn.(4). This could be connected either with the purely practical preferences of the inner substituent scales (vide supra) or with the potential shortcomings of the used sets of external substituent  $\sigma$ -constants.

However, these circumstances do not concern the major qualitative consequences of the present work. So, according to the isoparametric value ( $\hat{\sigma}_{Y_j} = -2.9$  and  $\hat{IP} = 5.1$  eV) of the  $\sigma$ -constants calculated from Eqn.9 it is evident that the above-made (on the basis of Eq.(4)) conclusion about the impossibility of the experimental realization of the isoparametric point on the example of the IP of 1,4-disubstituted benzenes still holds. On the other hand, without any doubt Eqn.(9) confirms also the inference about the non-additive influence of the substituents in the case of these compounds.

It is interesting to notify that despite the rather close relationship<sup>20</sup> between the IP of valence and inner shell electrons the analysis of data from Ref. 21 leads to the preliminary tentative conclusion that in the case of the latter quantities the similar non-additivity for 1,4-disubstituted benzenes does not take place.

On the other hand, the data treatment made in this work also shows that in the case of IP-s of the orbitals of another type of symmetry- $a_2$ - the influence of the substituents  $X_1$  and  $Y_1$  on the corresponding IP-s of 1,4-disubstituted benzenes is practically additive.

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РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.

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