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органических соединений

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CORRELATION ANALYSIS - PROSPECT[Ⓜ]

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In this account some fundamental problems of correlation analysis are presented and discussed on selected examples. The treatment should reveal, at least in some cases, which procedures are promising and which problems must be still regarded as unsolved. Special attention has been given to some typical errors and to less familiar approaches.

The first question to be dealt with concerns the scope of correlation analysis. In the broad sense this term means systematic mathematical comparison of experimental data to reveal the relationships and their possible physical meaning. Fig. 1 is an example of this conception in which two sets of original experimental results are plotted against each other. The obtained information is not only the fact that a linear relationship exists, but also its slope and the deviations of some points which are connected with the term validity range. More often plots of an experimental quantity vs some parameters (e.g. reactivity or solvent parameters) are encountered but even these parameters are essentially experimental quantities, whether directly esti-

[Ⓜ] Presented at the Second EUCHEM Conference on Correlation Analysis in Organic Chemistry, held at the University of Hull, England, in July 1982.

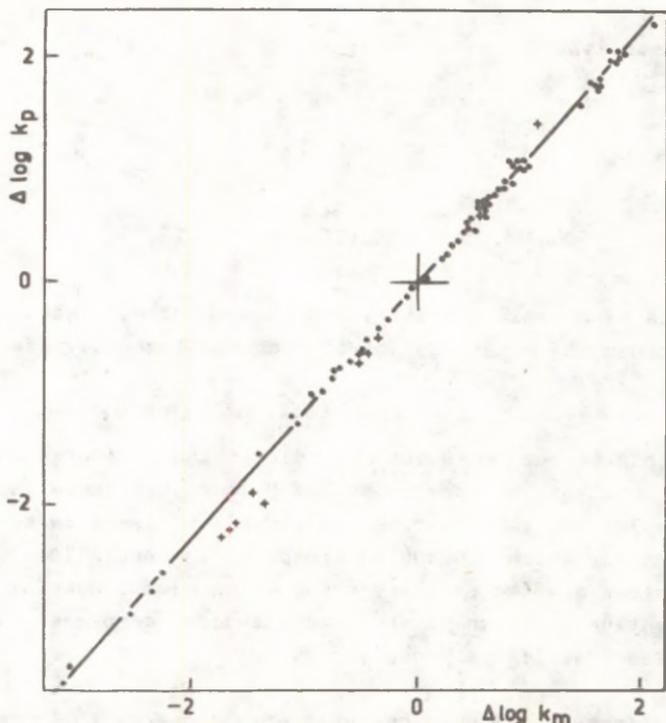
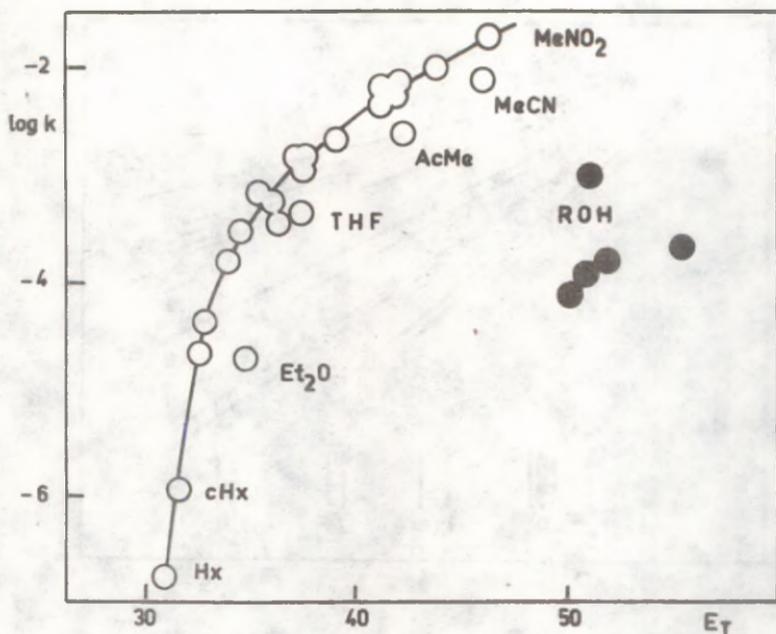


Fig. 1 Plot of $\log k$ of para-derivatives vs meta-derivatives in diverse reactions (ref. 1); + substituents COX, • substituents NO_2 , CN, SO_2X , CF_3 .

mated or statistically averaged. The original restriction to linear relationships (Linear Free Energy Relationships) is evidently too narrow since it promotes linearity to a kind of natural law. The correlation in Fig. 2 is not less telling for the reason that it is not linear: the different behaviour of the main classes is well evidenced and some specific deviations are apparent.

More complex correlations cannot be pictured as a simple plot. For instance a pattern like in Fig. 3 arises when new experimental data are correlated between themselves without reference to some previously known parameters. A still more complex pattern cannot be represented in two dimensions and turns gradually from the methods of classical



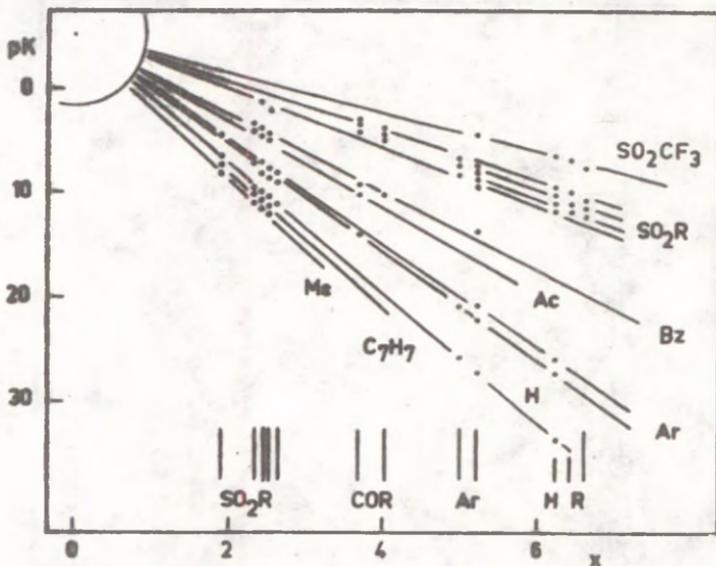


Fig. 3 Correlation of pK values of N-acids, R^1NHR^2 (ref. 4); acids with the common substituent R^1 are placed on the same ordinate, with the common substituent R^2 on the same full straight line.

were once established by a correlation de novo based on a more or less large set of data (σ_I valid within the series of aliphatic and polycyclic acids, σ_p within the series of para-substituted benzene derivatives). There are, however, some parameters defined merely from theoretical grounds, so that their applicability in their pure form is not essential (AN as solvent parameter⁸ or even σ_R if determined from infrared intensities⁹).

Among the less common types of parameters some physico-chemical quantities are being used which do not require a particular model compound and are defined on the very substrate; they are sometimes referred to as "non-empirical". Note e.g. the difference between relative permittivity determined only on the given solvent and E_T which requires a specially defined solute as a model³. Still further

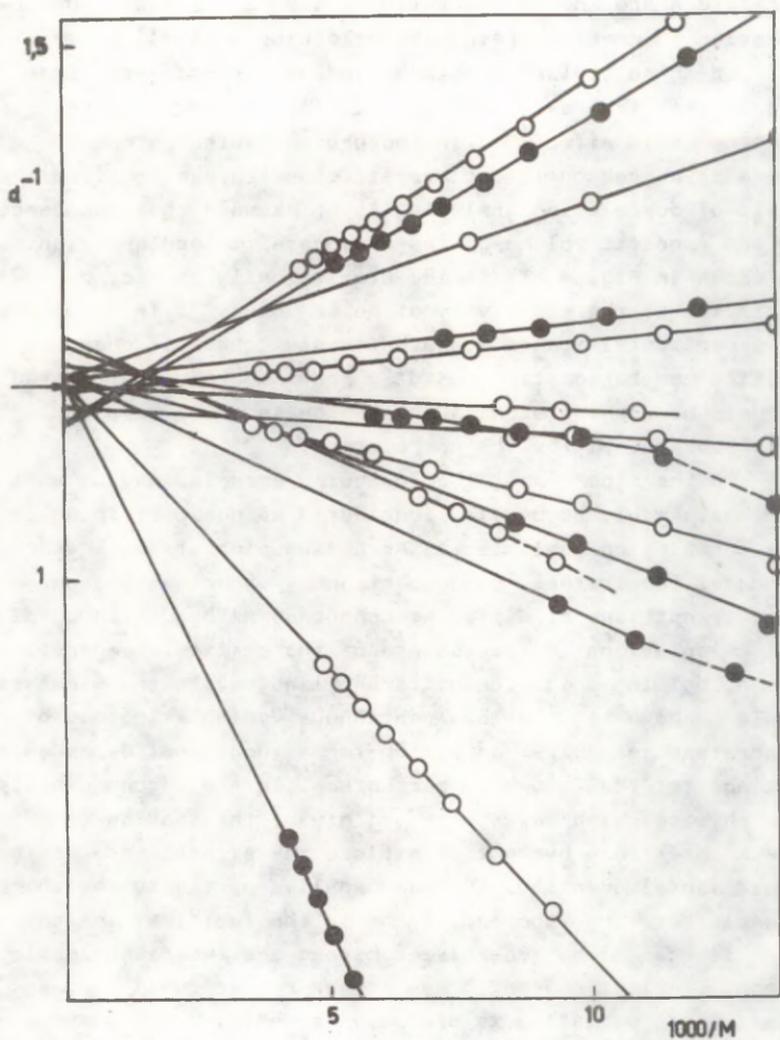


Fig. 4 Dependence of the specific volume in several homologous series on the reciprocal molecular weight - statistically correct representation of the approximate additivity of molar volume (ref. 11). The average intercept of all straight lines corresponds to the specific volume of polyethylene and determines the increment of the methylene group; the slope of each line determines the increment of the respective functional group.

parameters are known so exactly that an experimental determination is needless (e.g. the molecular weight), or are defined in molecular dimensions and better estimated from models than from experiments (the distance r accounting for the field effect¹⁰). In the present author's opinion there is no reason to exclude all these parameters from the field of correlation analysis. As an example the dependence of the specific volume on the reciprocal molecular weight is shown in Fig. 4. It is the statistically correct representation of the additivity of molar volume¹¹. In the place of experimental quantities even quantum chemical characteristics can be sometimes used¹², provided they are treated as data of unknown significance which is to be revealed only subsequently by the correlation.

On the other hand, the following examples may be quoted which would be usually considered as not pertaining to the correlation analysis: a) Arrhenius plot of $\log k$ vs reciprocal temperature, b) comparison of experimental spectral transitions of different compounds with quantum chemical calculations, c) dependence of the critical temperature on the boiling point for different liquids. In the first example we have to do with a continuous variable instead of discrete objects; we can search for a functional dependence but not for the values of parameters. In the second example the physical meaning is a priori given, the task is to check the theory but not to explore the significance of the experimental quantity. The same applies partly to the third example but more important might be the fact that the correlation cannot be generalized beyond one two-dimensional graph. The last reasoning may appear rather subtle and an exact differentiation is probably impossible. The purpose of this discussion was not to draw a boundary line but to point out less familiar procedures.

Let us proceed to the next question: which kinds of correlations are possible or allowed. It is certainly not forbidden to seek for relationships between quantities quite different in character. However, any empirical correla-

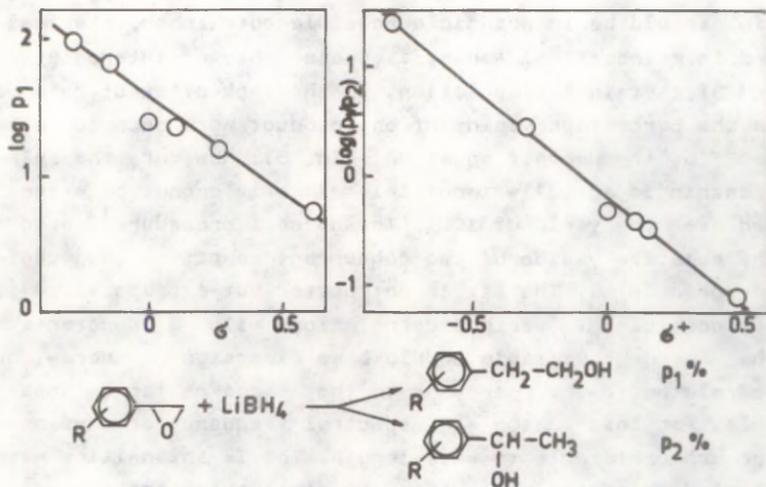


Fig. 5 A Hammett plot lacking physical meaning where \log 's of percentage yields are plotted (left-hand line, according to ref.13), and a correct plot using \log 's of relative yields (right-hand line, ref.14).

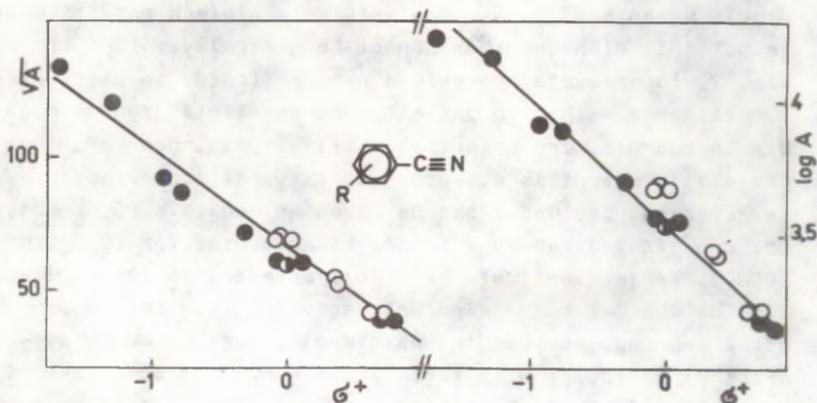


Fig. 6 Hammett plots of the infrared intensities of the $\text{C}\equiv\text{N}$ stretching in substituted benzonitriles (data from ref. 15), left-hand line plotting square root of A, right-hand line plotting $\log A$; \circ meta substituents, \bullet para substituents.

tion should be in principle possible both in the physical and in mathematical sense, i.e., also able of interpolation and of certain extrapolation. In the lack of exact rate data the percentage yields of one product were once correlated¹³ by the Hammett equation (Fig. 5). However, the relationship is actually impossible since it cannot be extended over the yield of 100%. The correct procedure¹⁴ used the relative yields of two concurrent reactions (Wegscheider principle). The fit is not better but extrapolation is now possible. In various correlations with δ constants the dependent variable should have dimension of energy, or be related to the energy or to the charge as far as possible. For this reason e.g. spectral frequency or wave-number are preferable to wave-length. The IR intensities were plotted as square roots (Fig. 6) since these are proportional to the change of dipole moment and hence to the fractional charge¹⁵. The correlation, however, cannot be extended below zero. Alternatively, the plot¹⁶ of $\log A$ is mathematically acceptable but physically meaningless. This contradiction has not been solved to date. Correlations of dipole moments with δ constants were claimed many times (e.g.,^{17,18}) although they cannot be generally valid¹⁹. Fig. 7, for example, reveals a general trend; in particular substituents with high positive δ constants produce high dipole moments. The principal difficulty is, however, that the dipole moment is a vector quantity. If its direction is reversed, its value can be taken as negative ($C_6H_5CH_3$), but non-axial directions cannot be accounted for (C_6H_5O , $COCH_3$). Projection¹⁷ of the dipole moment into the direction of the C-X bond helps only sometimes and has no physical meaning. Further inconsistencies are caused by symmetrical molecules with zero dipole moment irrespective of any value of δ (substituent $N=NC_6H_5$), and by complex substituents with an insulated polar group (reduced δ constants and high dipole moments in the case of CH_2CN and $C_6H_4NO_2$). Such correlations should be avoided even when they appear to work within a restricted range.

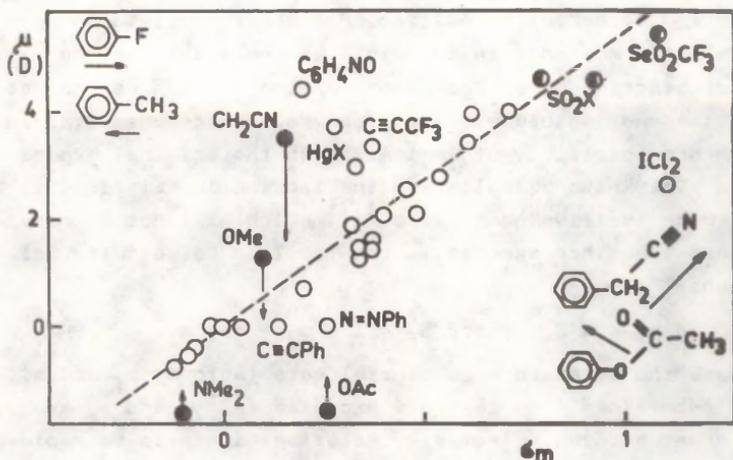


Fig. 7 Approximate correlation of dipole moments of benzene mono derivatives with constants σ_p (better fit than with σ_m), which does not respect the vector character and cannot be generally valid (see the formulae); \circ symmetrical, \bullet unsymmetrical, \bullet approximately symmetrical substituents.

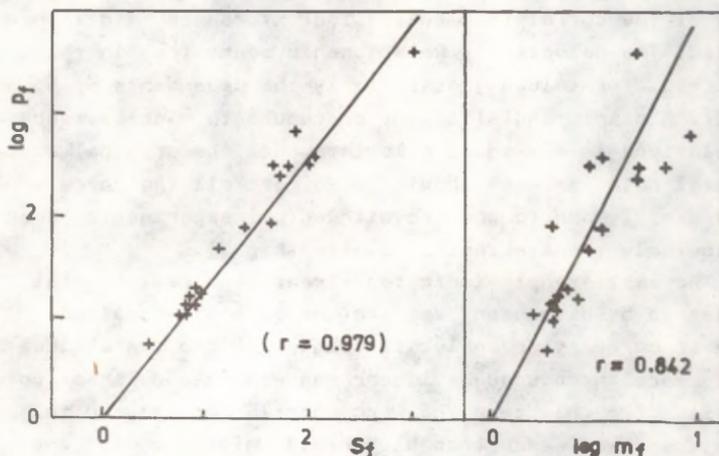


Fig. 8 The Selectivity Relationship (ref. 22) applied only to the reactions when para and meta rate constants have been determined in separate experiments. On the left the traditional, statistically incorrect plot, on the right the correct plot with a much worse fit.

A serious danger is connected with correlations of derived and dependent quantities. Parameters derived in one correlation must not in principle be input into another one as starting data. The error arising in this way may be sometimes negligible but sometimes results can be obtained which are completely at variance with the original experiments. The known examples are the isokinetic relationship²⁰ and molar additive quantities^{11,21} which will not be repeated here. Another example is the familiar Selectivity Relationship²²:

$$\log p_f = a S_f, \text{ where } S_f = \log p_f - \log m_f.$$

In case the para and meta partial rate factors, p_f and m_f , were determined from separate experiments, S_f and p_f are dependent and the Selectivity Relationship is to be replaced by the equation with independent variables:

$$\log p_f = \frac{a}{1-a} \log m_f$$

Fig. 8 reveals that this equation is fulfilled with a significantly lower accuracy than the above one; in view of the value of the correlation coefficient it can be said to be invalid. The Selectivity Relationship means thus in this case (i.e. for toluene) essentially the dependence of p_f on itself. A simple and efficient procedure to disclose such correlations is always to calculate back the original experimental data, as they should be to meet all the correlations exactly and to compare with actual experiments (see particularly the isokinetic relationship²⁰).

The last example indicated already the next general problem to be discussed: application of statistical methods in correlation analysis. Originally two statistical models were introduced²³: linear regression and linear correlation. (In this term the word correlation is used in another, narrower sense than hitherto.) Unfortunately, they were mixed together while neither is perfectly fulfilled in most chemical applications. More satisfactory from the

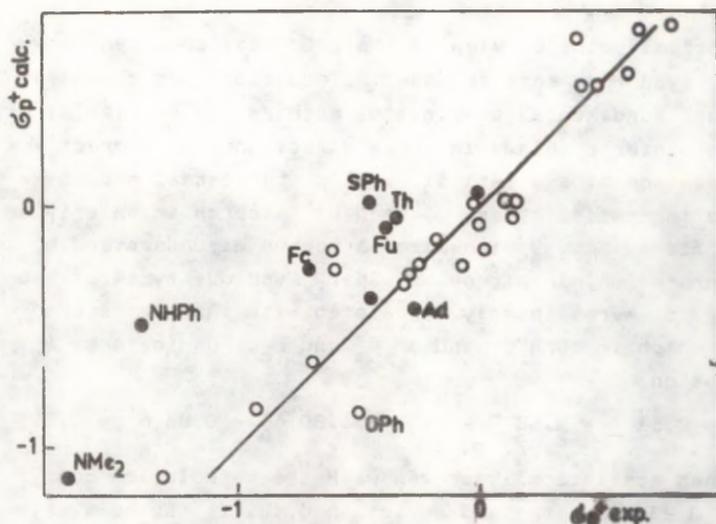


Fig. 9 Test of the relationship (ref. 25) between constants σ_p^+ , σ_p , and σ_m by plotting σ_p^{+exp} vs σ_p^{+calc} ; \circ original set of substituents (ref. 25), \bullet new substituents added.

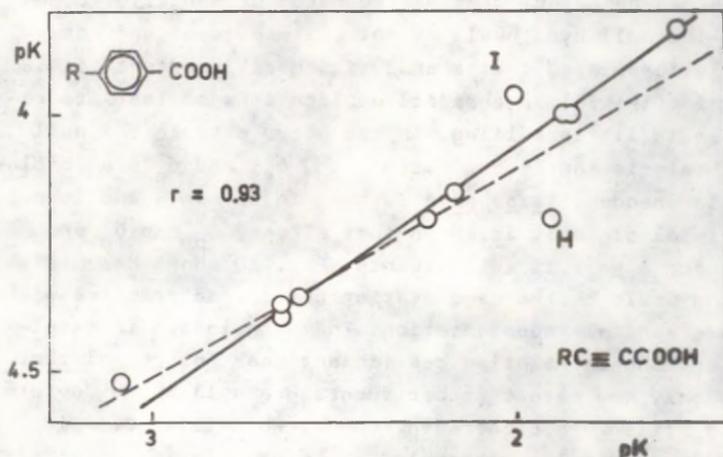


Fig. 10 Irregular pattern of a correlation with significant deviations of some substituents (H, I) which are not reflected in the statistical figures (pK 's of substituted propionic acids, according to ref. 26); broken line for all points, full line except H, I.

theoretical point of view is the principal component model²⁴, even when some fundamental equations are the same. Although fundamental statistical methods are available, one can encounter problems in three directions: a) correct interpretation of statistical results, b) special models required in special cases, c) need of research in underlying conceptions. Fig. 9 visualizes a common misunderstanding in interpretation. In a popular paper²⁵ various types of constants σ were linearly correlated with the parameters \underline{R} and \underline{F} which in turn depend on σ_m and σ_p . For instance the regression

$$\sigma_p^+ = 0.51 \underline{F} + 1.58 \underline{R} - 0.07 = 1.80 \sigma_p - 0.83 \sigma_m - 0.07$$

has been statistically proven with the correlation coefficient 0.939 and standard deviation 0.18. It is, however, completely wrong to infer²⁵ that the constants σ_p^+ are no longer necessary and can be replaced by a linear combination of \underline{R} and \underline{F} . The heart of the matter is in the term statistical significance. It means that a given null hypothesis can be rejected with a required probability. Sometimes the null hypothesis is not quite evident and not clearly formulated in the analysis. More important, it is often too trivial in chemical applications so that its rejection is little telling. In the above example the null hypothesis is that the constants σ_p , σ_m , and σ_p^+ are completely independent (*i.e.* have nothing in common), and is quite trivial since it is known that already σ_p and σ_p^+ are equal for a half of substituents. Fig. 10 shows how misleading could be the mere statistical characteristics without a graphical representation. The correlation is excellent, but the correlation coefficient does not reveal that it is only two points (substituents H and I) which deviate from a still much closer dependence. While this example was discussed fully correctly²⁶, the example in Fig. 11 is a clear mistake. When instead of absolute values of $\log k$ the relative values of $\log(k/k^0)$ are input into a regression, the results are not changed but the number of points

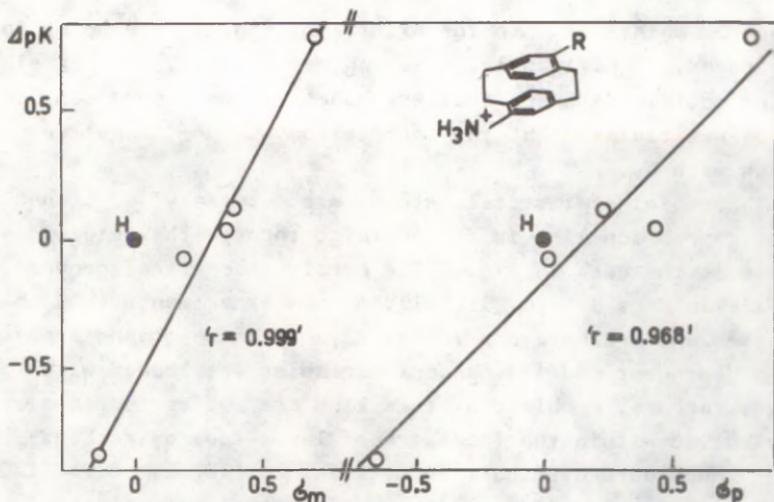


Fig. 11 Hammett correlations with statistical calculations erroneously omitting the point for hydrogen (pK of substituted aminocyclophanes, ref. 30); the values of correlation coefficients are too high.

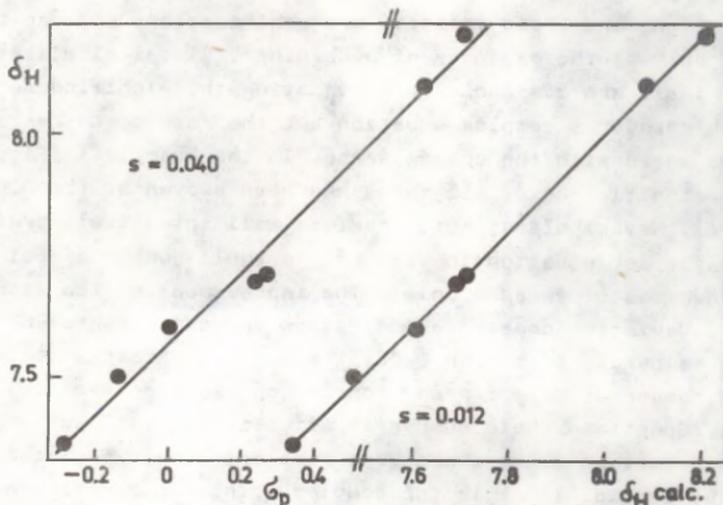


Fig. 12 Example of a correlation of the same data (δ_H of substituted propargyl benzenesulphonates, ref. 31) with one parameter ($\delta_H = 0.743 \sigma_p + 7.570$, on the left) and with three parameters ($\delta_H = 0.486 \sigma_o + 0.246 \sigma_R^+ + 0.456 \sigma_R^- + 7.607$, on the right).

must be maintained. In the example of Fig. 11 the point for hydrogen, significantly deviating, was omitted. The correlation coefficients are thus erroneous and an absurd conclusion was claimed that the correlation with δ'_m is better than with δ_p .

Special statistical methods are necessary, e.g. when the regression line is forced to go through the origin. This is the case in Fig. 8 for merely theoretical grounds, while in Figs 1 or 17 it follows from experiments (the abscissa and ordinate are identical). In these graphs also the dependent and independent variables are loaded with equal errors. Problems of this kind are not serious and can be solved within the framework of least-squares method.

Much more difficult and still uncompletely solved is the problem of validity range vs the complexity of the equation. Generally, when the accuracy of a correlation is not quite satisfactory, one can either apply a more sophisticated equation (with more terms), or restrict the validity range. The three requirements of high accuracy, simple equation, and broad validity are contradictory and can be met only at the expenses of each other. Classical statistical tests are available for evaluating the significance of each term of a complex equation but the results do not always agree with the common sense. In the example in Fig. 12 the significance of all terms has been proven at the 0.05 level. Nevertheless, most chemists will intuitively prefer the simpler equation in view of the small number of points (3 degrees of freedom only). The improvement of the standard deviation does not count since the experimental error can be hardly less than 0.02. The enormous importance of the number of data for any conclusion was stressed many times. Sometimes their number is effectively still smaller since certain objects are very similar, almost indistinguishable. In Fig. 12 it is the doubled point for substituents Cl and Br the deviation of which actually necessitated the two additional terms. Common statistical tests cannot account for these details. In the case of larger data sets

the adequate number of terms may be efficiently estimated by the method of cross-validation²⁷. On the other hand, the proper range of validity is still estimated merely by chemical intuition. With the increasing range the precision drops, i.e., the standard deviation \underline{s} increases, from a certain point more steeply. At the same time the range of all values (expressed by the standard deviation \underline{s}_0 from the average) increases, too, but from a certain point probably less steeply. Under these assumptions one can expect that the ratio $\Psi = \underline{s}/\underline{s}_0$ exhibits a minimum corresponding to an optimum validity range²⁸. Fig. 13 shows some experimental evidence obtained to date; the main problem is a systematic enlargement of the data set according to a chemical principle.

The statistic²¹ Ψ is related to another fundamental problem: how to evaluate in general the agreement between experiment and (empirical or non-empirical) theory. While the standard deviation \underline{s} tells us whether the precision is good in relation to the experimental error (or to a given practical standard), Ψ allows to compare different kinds of correlations - which is "better". It was advanced for large data sets and its distribution in small samples was not investigated²¹. More attention has been given to the special case of linear regression (see²⁹) where Ψ gives (on another scale) essentially the same information as the correlation coefficient \underline{r} . For instance, a regression with zero slope is to be rejected as such (according to $\underline{r} = 0$ or $\Psi = 1$) but is acceptable as a part of a broader system (according to \underline{s}), i.e., it does not violate the Hammett equation as a general law. The reliability of both \underline{r} and Ψ strongly depends on sample size. To account for this effect, t-test or F-test can be used (see i.e.^{24,32}), the formulae being almost identical. Nevertheless, the results from small samples are always less telling whichever characteristic might be used. Much discussion^{29,33} has been devoted to the question whether \underline{s}_0 is to be measured from the average or rather from zero. It is not so important for

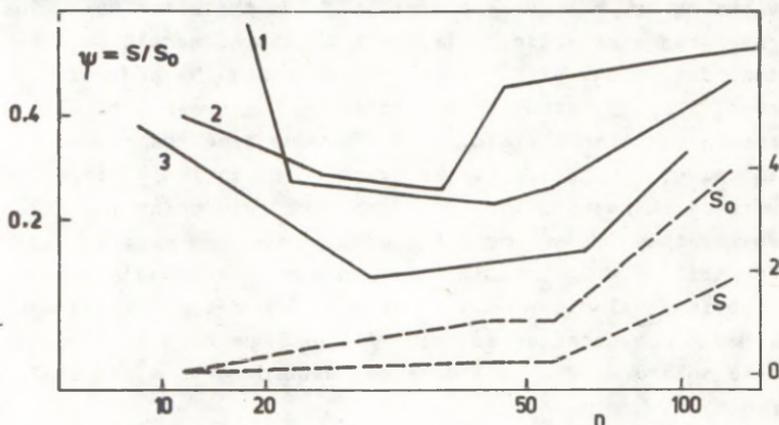


Fig. 13 Precision of a correlation equation as a function of the validity range (= number of data); full lines - statistic ψ for three aliphatic series, broken lines - standard deviations s and s_0 for the series 1 (ref. 28).

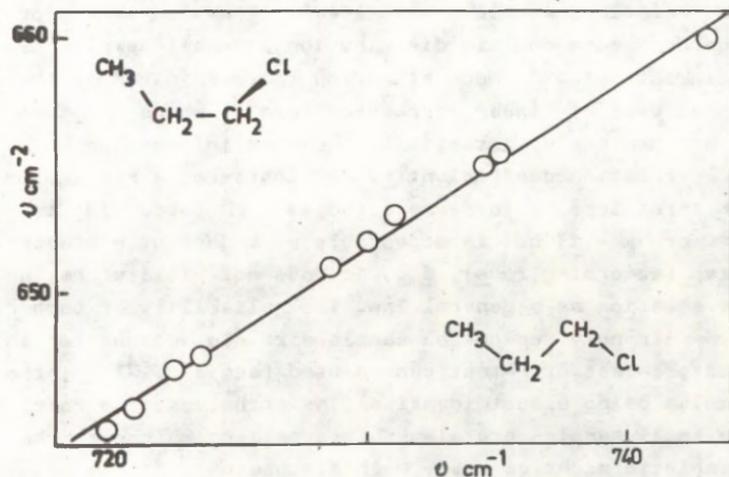


Fig. 14 A correlation caused by great similarity of the two systems intercorrelated: C-Cl vibration frequencies of ap-BuCl and sc-BuCl in various solvents (data from ref. 35).

quantities like relative rate constants but serious error may arise for quantities with the average very far from zero (wave numbers, refractive index) or with an arbitrary zero (half-wave potentials). The zero reference and a modified formula should be probably appropriate for calculating ψ in the case of extensive quantities (enthalpies, spectral intensities), but the theory has not yet been developed.

Further task of primary importance is the interpretation of the results in chemical terms; without it the correlation analysis would become a play with numbers. Two approaches are currently in use. The first one exploits parameters determined in advance in such a way that they serve as measure of a certain concept (inductive effect, solvent basicity). A successful correlation is then considered a proof that the pertinent effect is operative. In terms of the data matrix one can state that the data are different in character, some of them being considered as primary by definition. In most applications, however, the primary parameters are known, the task being only to apply them to new experimental results. In the second approach a correlation de novo is carried out and the abstract parameters are obtained which lack any physical meaning. At this stage, questions may be answered concerning the number of independent factors, separating of objects into classes etc. Subsequently, the abstract parameters may be modified by rotation, in order to be related to some prefixed scale, so that the same final results may be reached as in the first approach. Recently it was argued³⁴ - essentially in favour of the second approach - that a correlation evidences always only local similarity and does not prove any fundamental law of chemistry. This is essentially true if the term similarity is defined with more precision. The correlation of IR frequencies shown in Fig. 14 expresses certainly only the great similarity of the two molecules, the measured physical quantity being the same. No conclusion about interactions with the solvent can be drawn; these may be rather diverse only if they are similar for the two molecules. On the contrary,

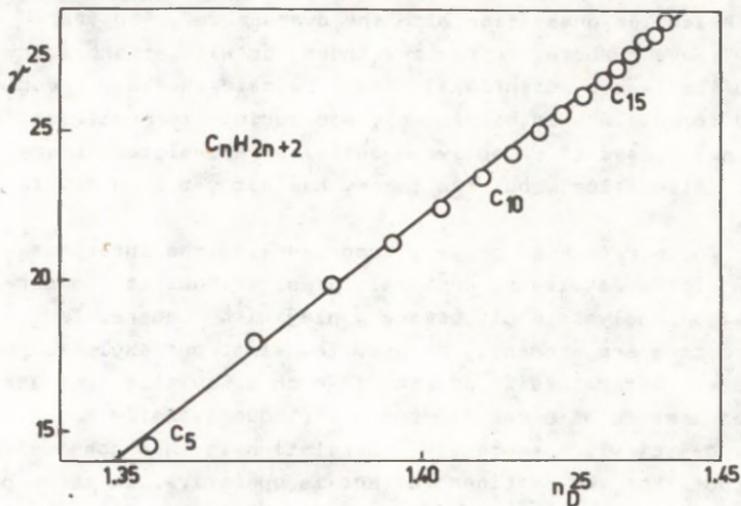


Fig. 15 A correlation caused by the similarity within the series of objects: surface tension vs refractive index in the series of normal paraffins.

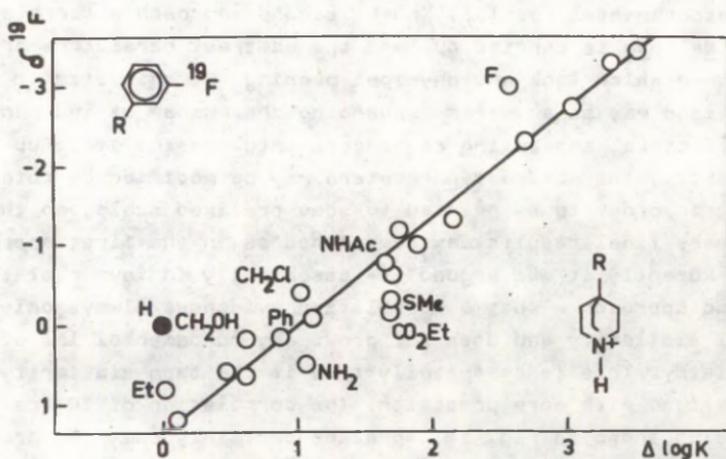


Fig. 16 A correlation caused by the similarity in the mechanism of substituent effects: ^{19}F -NMR shifts in meta-substituted benzenes vs pK of 4-substituted quinuclidines (data from ref. 36, 37).

the correlation in Fig. 15 involves a series of very similar compounds but the physical properties compared are fundamentally different. The correlation does not tell anything about the surface tension, refractive index or their relationship, it only confirms the great structural and physico-chemical similarity within the series of paraffins. The correlation in Fig. 16, even when not very close, reveals some similarity which cannot concern the molecules involved nor the physical quantities, the only explanation being the similarity in the mechanism of the substituent effect. Thus in a particular case even a "fundamental law" can be checked.

When interpreting individual correlations the present author strongly advocates the principle of Occam's razor, it means to prefer the simplest explanation unless there are strong counter-arguments. The correlation^{1,38} in Fig. 17 infers that the substituents involved act by a common mechanism in the meta and para position, the effect being stronger in the para position (see also³⁹). How this effect is named, is not essential. Some authors found this explanation unacceptable and preferred the assumption that there are two mechanisms but virtually proportional for all the substituents of so diverse structure^{33, 40-42}. This is at least at variance with the named principle.

One can now attempt to define which correlations are "good" or, say, of value. Certainly it is not important whether a perfect linear plot was obtained but whether some conclusions can be drawn. Of importance may be correlations with predetermined parameters (Figs 5,6,19), with non-classical quantities (Fig. 4), as well as de novo - simple (Figs 1,14-17) or more complex (Figs 3,4), further non-linear plots (Fig. 3) or plots with a big scatter (Fig. 18); but they must not be at variance with physical and mathematical principles and must contain a sufficient amount of information. The last condition means not only a sufficient number of data - allowing even to find the deviations - but also good covering of the data space and sufficient experi-

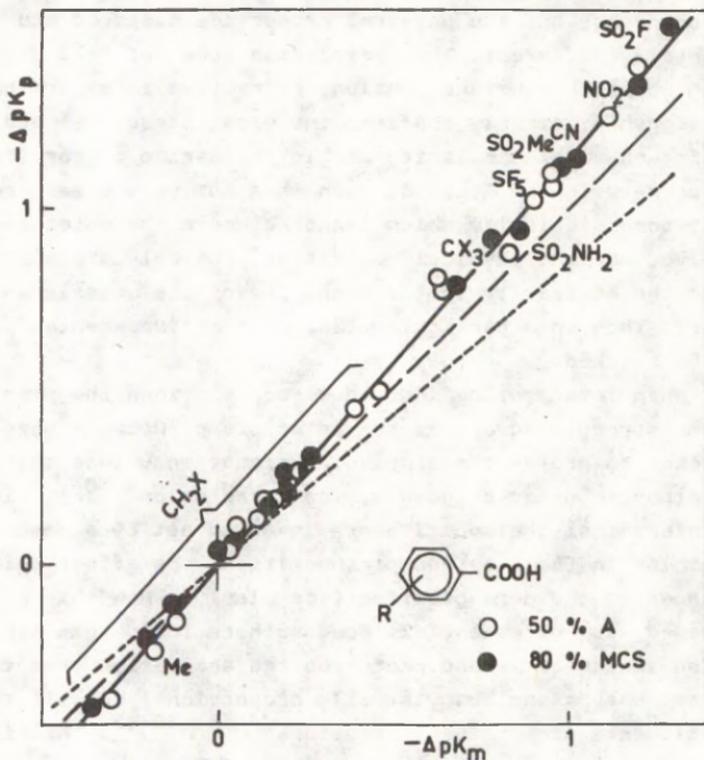


Fig. 17 Correlation of pK values of para- vs meta-substituted benzoic acids in two solvents (only substituents without a lone electron pair in α -position, ref. 1) and possible interpretations: full line - regression, broken lines - theoretically assumed slopes.

mental accuracy with respect to the extent of values. All the conditions are fulfilled in Fig. 1, except possibly that the choice of substituents is not broad enough. Opposite examples, where conclusions were drawn from small data sets, irregularly covered, or from rough correlations are numerous.

Finally, let us add some comments to the relation of classical correlation analysis to chemometrics, or better

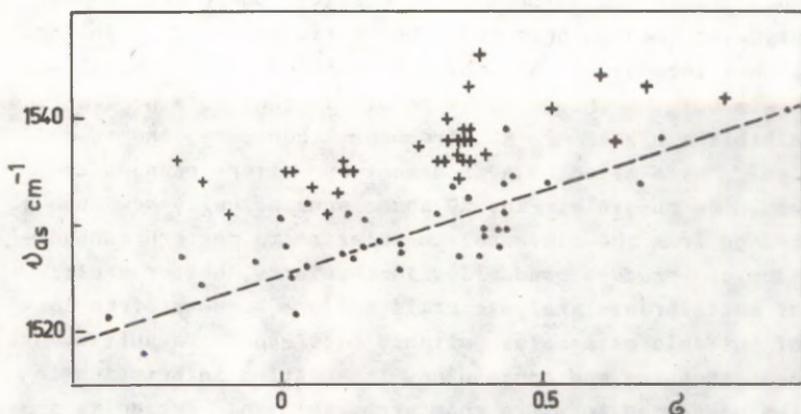


Fig. 18 Correlation with a big scatter and with separation into classes. Hammett plot of the NO₂ antisymmetrical stretching frequency in substituted nitrobenzenes; ● para derivatives, + meta derivatives, ref. 43.

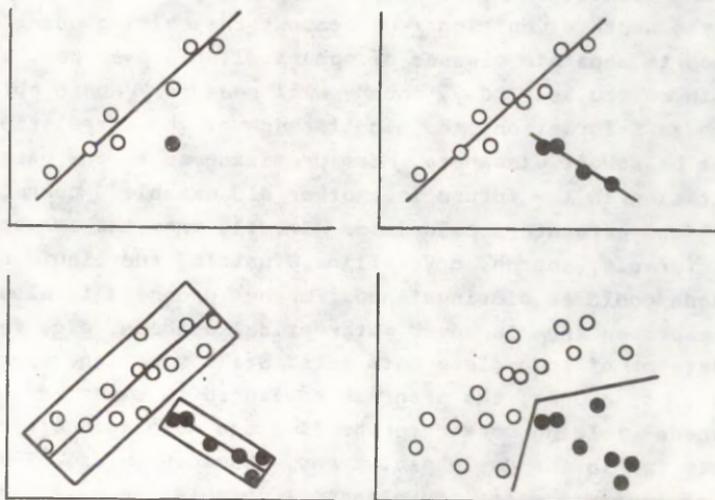


Fig. 19 Schematic representation of a gradual transition from classical correlation analysis to chemometrics: a plot with one deviating point, splitting into two lines, definition of classes within the SIMCA model, separation of classes by a piecewise linear boundary.

to multivariate analysis. The difference is merely in methods (more sophisticated mathematics, computers, number of data) than in principle. For instance the plot in Fig. 18 was intended within the framework of the classical analysis but the only evident result is that meta derivatives exhibit a higher $\nu_{as} \text{NO}_2$ frequency than para, the so-called⁴³ "meta-effect". A treatment by pattern recognition would be possible, Fig. 19 shows schematically how such a change from the classical correlation to pattern recognition can proceed gradually. In chemistry, better exploiting of multivariate analysis still suffers somewhat from lack of suitable data sets. Suitable data should be sufficiently comprehensive and contain any interesting information in the undecoded form. In chemistry, this information is sometimes too hidden if present at all (melting points, chromatography), or on the contrary quite evident and not needing any analysis (X-ray). Maybe that the NMR-shifts stay in the middle between these two possibilities and could be a promising quantity in this respect. In an old example⁴⁴ a plot of the heats of melting ΔH_m against the melting point allowed to separate classes of spherical, plate-shaped, and chain molecules. Today, nobody will measure ΔH_m to obtain such an information; the significance of the correlation must be sought elsewhere. More promising as to the possible imitation in the future is another old example⁴⁵ correlating two parameters calculated directly from the structural formula; amorph, crystalline, fusible, and liquid compounds could be distinguished. Further progress is also to be expected from improved mathematical methods, e.g. for treatment of incomplete data sets. Still more important appears; of course, the progress envisaged in experimental methods yielding more comprehensive and more accurate results (pK in the gas phase, X-ray, thermodynamics). This is of importance for the classical correlation analysis as well as for multivariate analysis.

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PHOTOELECTRON SPECTRA OF MOLECULES

6. Substituted Pyridines

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The assignment of the position of the lone electron pair band of the nitrogen atom of the substituted pyridines was made on the basis of the empirically found relationships. The linearities of the unit slope between the IP of the lone electron pair of the pyridine's nitrogen atom and its core level 1-s electron ionization levels were used. The $IP(n_N)$ values determined this way depend linearly on the gas phase proton affinities and on the complex-formation shifts of the stretching frequencies of the phenol's OH group in CCl_4 solution.

Despite the use of various experimental techniques and modern quantum chemical methods the electronic structure of the pyridine molecule and its derivatives has been the matter of the continuous discussions for the several decades.

The complexity of the interpretation of PES of pyridine stems on the fact that it has rather closely spaced bands of the different origin (the π -orbitals of the aromatic ring from one hand, and of the nitrogens lone pair from the other). The situation is even more complicated because the band which corresponds to the nitrogens lone pair is much wider than those which are characteristic for the typical compounds with the localized lone pairs (e.g. halides¹ except the fluorides).

The broadening of n_N band is usually ascribed to the partial inclusion of the orbital of the lone electron pair of the nitrogen atom in the σ -electron system (due to the symmetry constraints this orbital cannot participate in the aromatic π -system)².

As far as n - and π -systems are independent it is difficult to find the crucial method which would indicate unambiguously which of the two bands (n or π) corresponds to lower energy. The standard technique which makes use of the analysis of the vibrational structure band is also unapplicable because the substitution of CH bond in the benzene for the isoelectronic atom of nitrogen simultaneously reduces the symmetry of the molecule, removes the vibrational degeneracy. Therefore, the fine structure of the band gets too much complicated for the analysis.

The review on the earlier studies of the PES of pyridines is given in Ref. 3 where perfluoro-effect was used for the interpretation of their spectra. In the PES of perfluorinated pyridines the σ -bands exercise a significant shift (by several eV) as compared with the initial compound whereas the shift of π -bands is much more modest. This circumstance is used for the assignment of the order of different bands in the nonfluorinated derivative. For example, on the basis of the fact that the 1st PES band shifts on perfluorination of pyridine by 2.41 eV towards higher energies the inference was drawn that the MO order in this case should be $a_1(n)$, $a_2(\pi)$, $b_1(\pi)$.

However, the quantum chemical calculations with the use of the Koopman's theorem lead to the different results. Our semiempirical CNDO/2 calculations, as well as the ab initio works (by Kimura (4-31G basis)⁴ and others⁵ predict the MO order for pyridine as $a_2(\pi)$, $b_1(\pi)$, $a_1(n)$. Up to now we are unaware of any calculations of the pyridine molecule using the approach beyond the limits of the Koopmans' theorem.

PES of the derivatives of pyridine was studied widely but there is no unanimity in their interpretation by the different authors. The analysis of PES of alkyl pyridines

is accompanied with the same problems^{4,6,7} as the assignment of the spectrum of the parent compound. The high resolution PES of fluorinated pyridines were analysed⁸ on the assumption that in fluorobenzenes the inductive perturbation by fluoro-substitution is of the 1st order and, therefore, causes the additive shift of the band of the nitrogen atom in the PES.^{*} The PES of chloro-,^{2,7,10} amino- and cyano-,¹¹ hydroxy- and methoxypyridines¹² were also studied.

The rather general and accurate linearity is observed between the ionization energies of valence shell and core or intermediate level electrons of the ionization center for various kinds of compounds.

The preferential and dominant localization of the lone electron pair on the ionization center serves evidently as one of the major preconditions for the observance of the relationships of that kind. The latter were recently used by the present authors for the assignment of PES bands of alcohols¹³, ethers¹⁴, nitriles¹⁵, amines¹⁶, and halides¹. As a rule, the slope of these linearities between valence and core level IP-s is within its error limits indistinguishable from unity. In other words, the sensitivity of these properties of inner and valence shell electrons towards the substituent effects is roughly the same.

As regards the monosubstituted pyridines then one can also observe the similar linear relationship between $IP(n_N)$ of the valence electron shell of the nitrogen atom from one hand, and the bonding energies of the 1s electrons of the same atom, from the other hand. It turns out that ortho-, meta-, and para- substituted derivatives lie on the three separate and parallel lines.

The regression analysis of the data (the binding energies of 1s electrons of the nitrogen atom were taken from Ref.17; the ESCA band of the lowest energy is always assigned to the nitrogen atom of the pyridine ring) from Table 1 leads

^{*} PES of perfluoropyridine was studied in Ref. 9.

to the following equations:

a) 4- X- pyridines

$$IP(n_N) = -387.27(15.95) + 0.980(0.039) E_B(1sN) \quad (1)$$

$$r = 0.996; s = 0.05 \text{ eV}; n = 7$$

b) 3-X- pyridines

$$IP(n_N) = -321.34(55.29) + 0.817(0.136) E_B(1sN) \quad (2)$$

$$r = 0.961; s = 0.1 \text{ eV}; n = 5$$

c) 2-X-pyridines

$$IP(n_N) = -360.35(47.42) + 0.914(0.117) E_B(1sN), \quad (3)$$

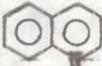
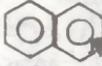
$$r = 0.961; s = 0.12 \text{ eV}; n = 7$$

where r is the correlation coefficient, s - standard deviation, n - the number of points, the error limits of the regression coefficients are shown in the parenthesis.

All IP values given in Table 1 are taken from the published PES. However, their interpretation is something different from that given in the original papers. The assignment of the bands by the present method is unambiguous on condition that the $E_B(1sN)$ values are fully reliable and the MO-s of the nitrogen valence shell electrons are not too extensively delocalized. The above-given relationships refer only to the mono-substituted pyridines and don't tell about the order of the MO-s of the parent compound itself.

Table 1

The $IP(n_N)$ Values of Pyridines and Some Other Aromatic Nitrogen Compounds Determined from PES on the Basis of Eqns. 1-4. The Orbital-Orbital Interactions are Taken Into Account.

No	Substituents	$IP(n_N)$	No	Substituents	$IP(n_N)$
1.	H	9.66	17.	Cl_5	11.38
2.	2-Me	9.5	18.	2-OH	10.08
3.	4-Me	9.5	19.	3-OH	9.71
4.	2,5-Me ₂	8.80	20.	2-OMe	9.82
5.	3,4-Me ₂	9.15	21.	4-OMe	9.3
6.	2,6-Me ₂	9.30	22.	2-CN	10.65
7.	3,5-Me ₂	9.52	23.	3-CN	10.30
8.	2,4,6-Me ₃	9.20	24.	4-CN	10.44
9.	4-t-Bu	9.45	25.	2-NH ₂	9.57
10.	2-F	10.37	26.	3-NH ₂	9.47
11.	3-F	10.09	27.	4-NH ₂	9.20
12.	F ₅	12.0	28.	4-NMe ₂	8.82
13.	2-Cl	10.3			
14.	3-Cl	9.85	29.		9.50
15.	4-Cl	10.0			
16.	3,5-Cl ₂	10.26	30.		9.16
			31.		10.3
			32.		10.48
			33.	4-CHO	10.12

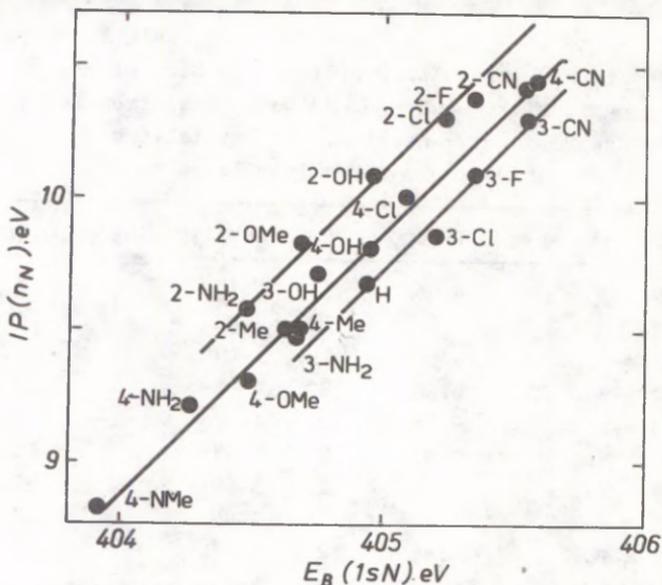


Fig. 1. The dependence of $IP(n_N)$ of the nitrogen lone pair for 2-, 3- and 4-substituted pyridines on the corresponding binding energies $E_B(1sN)$ of its electrons.

Fig. 1 visualizes the straight lines which correspond to Eqns. (1) - (3). 2- and 3- methyl derivatives deserve some additional comments. So, in Ref. 6 the 1st PES band of these compounds is (by the analogy with pyridine itself) assumed to consist from two overlapping bands the second of which (9.5 eV^b for 2- and 4- substituted derivatives) is believed to have the n-character. K. Kimura^a, however, does not accept the idea of two bands. Keeping in mind the above-reported Eqns. (1) - (3) one, probably, has to support the first hypothesis.

In several cases^{1,13-16} the linearity between IP-s of the lone electron pairs of the bases and complex-formation shifts of the stretching frequencies of the phenol's OH-group in CCl_4 solution were observed. The same seems to be true also for the pyridines (Fig.2). Within their experimental uncertainties these two qualities fit the single

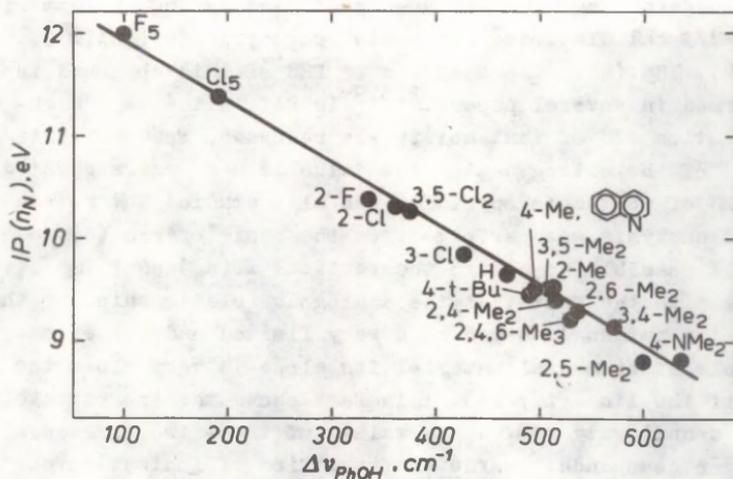


Fig. 2. The dependence of $IP(n_N)$ of the substituted pyridines on the corresponding hydrogen bond shifts of the stretching frequencies of phenol's OH band in CCl_4 solution

linearity for 2-, 3- and 4-substituted pyridines which can be described by Eqn.(4):

$$IP(n_N) = 12.50(0.07) - 0.0061(0.0013) \Delta \nu_{PhOH} \quad (4)$$

$$r = 0.994 \quad s = 0.09 \text{ eV} \quad n = 21$$

The similar linearity is observed also between the proton affinities of pyridines and their $\Delta \nu_{PhOH}$ parameters determined in CCl_4 solution. It evidences about the similar behavior of the gas phase basicity and liquid phase hydrogen bond acceptor strength of this class of bases.

The relationship (4) between $IP(n_N)$ and $\Delta \nu_{PhOH}$ values allows one to make some assignments of the lone electron pair bands in PES in these cases when the corresponding ESCA data on 1s electron binding energies are not available.

The $IP(n_N)$ values determined using Eqn.(4) are also included into Table 1. So, the use of Δv_{PhOH} value 486 cm^{-1} for $3\text{-MeC}_5\text{H}_4\text{N}$ ¹⁸ leads to $IP(n_N)$ value equal to 9.6 eV. Eqn.(4) also confirms the order of MO-s predicted by the semiempirical HAM/3 calculations⁹ for pentafluoropyridine ($3a_2(\pi)$, $5b_1(\pi)$, $18a_1(n)$). The analysis of PES of this compound is performed in several papers.^{2,3,9} In Ref. 9 the very high-resolution PES of that moiety was recorded. For the vertical $IP(n_N)$ of the nitrogen atom the value 12.0 eV was suggested. The PES of pentachloropyridine was also studied but no detailed analysis was performed. On the basis of Eqn.(4) we find it possible to assign the vertical $IP(n_N)$ as 11.88 eV.

Despite the fact that the analogous relationship for the aliphatic amines is based on a very limited and rather unreliable experimental material its slope is very close to that of the linearity (4). This fact shows the approximately equal sensitivity of Δv_{PhOH} values of these two classes of nitrogen compounds towards the variation of ionization potentials. At the same time the straight line for the pyridines is shifted approximately by 1.5 eV upwards on the IP axis from the analogous line for the aliphatic amines (see also Ref. 16).

The plots of IP-s of the oxygen lone pairs vs. the Δv_{PhOH} parameters for the alcohols and ether form parallel lines whereas the point for H_2O does not fit any of them.^{13,14} Another situation holds for the substituted pyridines where the parent compound obeys the general common relationship (4) for its derivatives.

It was recently shown¹⁹ that there is an approximate correlation between gas phase basicity of pyridines and 1s electron binding energies for the basicity center (see also²⁰).

On the other hand, the results of the ab initio (STO-3G basis) calculations²¹ show that the predicted MO energies of the lone pairs for 21 substituted pyridines are closely correlated with their experimental proton affinity values; the relationships for 3- and 4-substituted derivatives are statistically indistinguishable.

As it was argued earlier^{19,20} the linearity between experimental values of PA and IP is expected on the condition that the center of photoionization coincides with the center of protonization of the same base.

The most extensive compilation of PA values of substituted pyridines is given in the recent book²². However, the results of the various authors and at different times differ as much as by 1.5 kcal/mol. In the present work the PA data from Refs. 23-26 was used. All the values were standardized relative to the fixed PA value of the ammonia (207 kcal/mol; see also Ref. 20).

The statistical treatment of these data by the least squares method results in the separate linear relationships for 2-,3-4-derivatives (see Fig.3):

a) 3,5-substituted Py

$$\text{PA} = -15.18(1.50)\text{IP}(n_{\text{N}}) + 368.0(14.6) \quad (5)$$

$r = 0.981; s = 1.4 \text{ kcal/mol}, n = 6$

b) 2,6-substituted Py

$$\text{PA} = -16.14(1.32)\text{IP}(n_{\text{N}}) + 380.5(13.1) \quad (6)$$

$r = 0.984; s = 1.5 \text{ kcal/mol}, n = 7$

c) 4-substituted Py

$$\text{PA} = -15.50(0.25)\text{IP}(n_{\text{N}}) + 374.1(2.5) \quad (7)$$

$r = 0.999; s = 0.4 \text{ kcal/mol}, n = 9$

The unsubstituted pyridine most probably fits Eqn.(5) for the meta substituted pyridines the best.

One can see (Figs.1 and 3) that some scatter of the points for the methyl-pyridines is observed. Evidently, some problems of separation of overlapping bands (vide supra) still remain. Some controversy while using Eqn.(4) and (5) for the assignment of $\text{IP}(n_{\text{N}})$ arises also for the 3,5-dimethyl pyridine. From its PES⁷ the energies of its two first bands were determined as 9.25 and 9.52 eV whereas the authors of the original paper interpret the 2nd band as corresponding to the ionization of the nitrogen's lone pair..

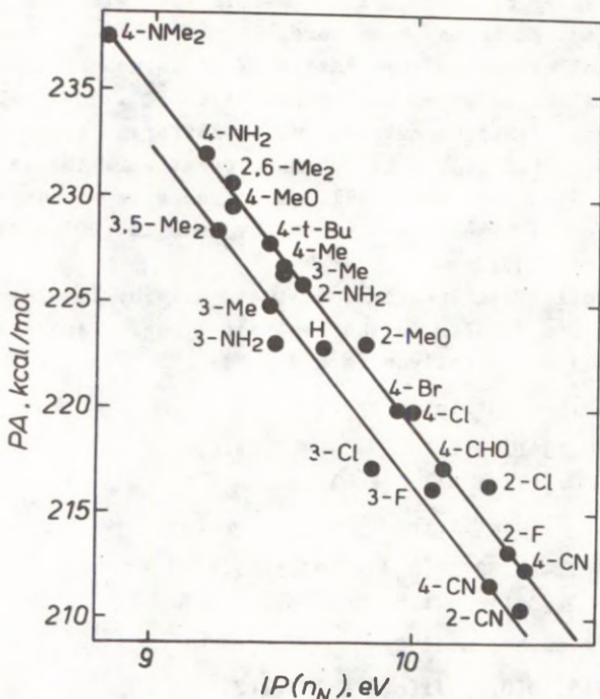


Fig. 3. The dependence of proton affinities of pyridines on the lone pair ionization potentials of the protonization center.

This value fits Eqn.(4) better than the IP which corresponds to the first band. However, Eqn.(5), while using $PA=228.3 \text{ kcal/mol}^{23}$ for $3,5-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N}$ predicts for the $IP(n_N)$ another value (9.25) which coincides with the energy of the 1st band in PES. Taking into account the statistical reliability limits of Eqn.(5) and the experimental errors of the experimental PA values one has to draw an **inference** that the second band in the PES of this compound cannot represent the ionization of the nitrogen's lone pair. Therefore, we have to assume that the ΔV_{PhOH}

value of this base should be somewhat lower as compared with the value (511 cm^{-1}) used by us in the present work. For the unambiguous interpretation of the PES of this compound it would be highly desirable to measure the binding energies of the $1s$ electrons of the nitrogen atom of the given compound. For 2,6-dimethylpyridine the $PA=230.8 \text{ kcal/mol}$ ²³ better fits the relationship (6) than the alternate value 229.1 kcal/mol suggested in Ref.22. In its turn for the $4\text{-H}_2\text{NC}_5\text{H}_4\text{N}$ the preferable by Eqn.(7) PA value is 232 kcal/mol .

Analogously to the above-considered relationship (3) (see also Fig. 1) the point for 2-CN-pyridine does not fit Eqn.(6) which assumes a somewhat lower $IP(n_N)$ value for this compound.

It seems that the use of the complex approach to the analysis of PES with the inclusion of the various information on the electronic structure of the compounds often allows to make the unambiguous choice between the alternative interpretations of PES bands.

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CHEMICAL SHIFTS OF HYDROXYLIC PROTONS
IN BINARY MIXTURES OF ALIPHATIC ALCOHOLS
WITH APROTIC SOLVENTS

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The chemical shifts of the hydroxylic protons of aliphatic alcohols in their mixtures with some aprotic solvents (DMSO, acetone, triethylamine, tetrahydrofuran, pyridine, dimethylformamide) have been measured.

It was found that in all cases (except some mixtures of alcohols with pyridine) the chemical shift of the hydroxylic proton $\delta_{1\text{HO}}$ of MeOH, EtOH, 1-PrOH and t-BuOH varies monotonously with the composition of the binary mixture increasing (downfield shift) with the increase of the concentration of the alcohol in the mixture.

In the system pyridine-alcohol and in some mixtures of aprotic solvents with nonassociated alcohols which include strongly electronegative substituents (e.g., $(\text{CF}_3)_3\text{COH}$) the reversed trend is observed.

It was shown that at the significant dilution ($M_{\text{ROH}}=0.1$) of alcohols ROH with the aprotic solvent the $\delta_{1\text{HO}}$ - values depend linearly on the σ^{H} -constants of the radical R'. The sensitivity towards these substituent effects changes slightly with the nature of the aprotic component of the mixture.

The influence of the nature and composition of the binary mixtures of aliphatic alcohols with apolar or dipolar aprotic solvents on the rate constants of various chemical reactions was repeatedly studied in this laboratory¹⁻⁷ as well as by several other investigators.⁸⁻¹³

The solvatochromic effects of the mixed solvents of that type on the absorption maximums of some indicators of the solvent gross polarity (E_T , Z , etc.) were also studied.¹⁴⁻¹⁵ Also a thorough investigation of some solute-independent properties of the above-mentioned binary mixtures has been made by several workers. The studies of the dielectric constants and refractive indexes, activation energies of viscous flow and heats of mixing of the binary mixtures of apolar and dipolar aprotic solvents with alcohols were made.¹⁶⁻²⁰ In some papers the chemical shifts of the alcohol's hydroxylic proton as some gross quantity which characterizes the solvent-solvent interactions in binary mixtures of the alcohols with the apolar or dipolar aprotic solvents were measured. So, for example, the mixtures of methanol with CCl_4 ^{21,22}, DMSO with methanol²³, cyclohexanol²⁴, $t\text{-BuOH}$ ²⁵, $t\text{-Bu}_2\text{CHOH}$ ²⁵ and MeEt_2COH ²⁵ were studied.

In Ref. 26 the measurement of the chemical shifts of the alcohol's hydroxylic proton in the relatively dilute solution in the DMSO was suggested for the analytical purposes. It was also found²⁵ that the direction of the change of δ_{HO} values in the mixtures with DMSO with dilution depends on the nature of the alcohol.

Relatively less attention has gotten the study of the variation of the electron accepting properties of the alcohols radical R on the δ_{HO} values. The investigation of the dependence of the latter on the donor strength of the aprotic component, as well as on the significant variation of the ratios of the donor and acceptor components needs also additional attention. Some of these problems were also studied in the present work. So, in order to determine some empirical gross characteristic of the "activity" of the hydroxylic hydrogen atom of alcohols in their binary mix-

tures with the aprotic solvents, and to study its dependence on the composition and the chemical nature of the components the $\delta_{1\text{HO}}$ values were measured for the mixtures of several aliphatic alcohols ($0.1 \leq N_{\text{ROH}} \leq 1.0$) with DMSO, acetone, Et_3N , pyridine, dimethylformamide. Further, the influence of the electronic structure of the alcohol's radical R on $\delta_{1\text{HO}}$ -parameters was also studied in the relatively dilute ($N_{\text{ROH}} = 0.1$) solutions of ROH in the aprotic component. The alkyl, as well as electronegative substituents were included.

Experimental.

Aprotic solvents (DMSO, Me_2CO , $\text{C}_5\text{H}_5\text{N}$, THF, DMF, Et_3N) were purified and dried by the standard techniques.^{27,28} Aliphatic alcohols (R=Me, Et, Pr, i-Pr, n-Bu, t-Bu, i-Bu, n-Pe, cyclo-Hex, n-Hex, n-Hept, n-Oct, n-Non, n-Dec) were also purified using standard procedures. $\text{CCl}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CH}_2\text{OH}$, $(\text{CF}_3)_3\text{COH}$, PhCH_2OH , Ph_2CHOH , Ph_3COH were used without further purification. $\text{HC}\equiv\text{CCH}_2\text{OH}$ was purified by distillation.

The proton NMR spectra of the systems studied were measured at the room temperature on the TESLA BS 487 B spectrometer at 80 MHz. TMS was used as the internal reference. The analysis of the more complex spectra was performed using the EC-1022 computer. In the case of anhydrous ("absolute") alcohols the splitting of the OH proton's signal into the multiplet takes place. For methanol, the latter consists of 4 lines (1:2:2:1). The signal from OH-group of the all other primary alcohols has triplet structure (1:2:1), secondary alcohols have doublet (1:1) and tertiary ones - singlet.

In the case of the splitting the $\delta_{1\text{HO}}$ -parameters were determined as the weighted and averaged values from the chemical shifts (frequencies) of the various lines of the multiplet taking into account their degeneracy (statistical weight).

For the mixtures of four alcohols (MeOH, EtOH, i-PrOH and t-BuOH) with DMSO, Me_2CO , Et_3N and pyridine the dependence of the hydroxylic proton chemical shift on the composition of the mixture was studied over the maximum range

of variation of the components. ($0.1 \leq N_{ROH} \leq 1.0$). The same is true also for the mixtures of DMF with methanol and t-BuOH. For the other alcohols the corresponding δ_{iHO} values were determined at the fixed $N_{ROH}=0.1$. The results of the measurements are given in Tables 1 and 2 and visualized in Figs. 1-6.

Table 1.
Chemical Shifts (in Hz) of Hydroxylic Proton of Alcohols in Their Mixtures with Aprotic Solvents.
Internal Reference - TMS, Working Frequency - 80 MHz.

N_{ROH}	DMSO				Me_2CO			
	MeOH	EtOH	1-PrOH	t-BuOH	MeOH	EtOH	1-PrOH	t-BuOH
1	2	3	4	5	6	7	8	9
0.1	327 ^a	349 ^a	348 ^a	333 ^a	277	287	285	281
0.2	327	349	348	333	291	300	296	287
0.3	327	349	348	333	309	318	318	293
0.4	327	349	348	333	325	336	337	300
0.5	330	-	-	-	333	357	348	309
0.6	333	354	353	338	340	374	362	322
0.7	-	-	-	-	353	385	376	335
0.8	358	381	378	352	368	398	389	352
0.9	-	-	-	-	381	413	406	364
1.0	396	428	422	378	396	428	422	378

(Continues)

N_{ROH}	DMF		Et_3N				$C_5H_5N^b$		
	MeOH	t-BuOH	MeOH	EtOH	1-PrOH	t-BuOH	MeOH	1-PrOH	t-BuOH
1	2	3	4	5	6	7	8	9	10
0.1	330	336	283	351	340	298	437	459	438
0.2	332	338	318	376	369	327	447	457	432
0.3	336	339	341	382	384	336	444	453	427
0.4	342	341	362	400	391	347	441	449	421
0.5	350	345	381	407	399	353	436	445	418
0.6	356	350	396	415	407	360	429	439	413

Table 1 continued

1	2	3	4	5	6	7	8	9	10
0.7	-	-	400	420	413	365	425	436	408
0.8	370	364	403	424	419	373	421	430	402
0.9	-	-	400	426	420	376	412	426	394
1.0	396	378	396	428	422	378	396	422	378

a - See also Ref. 26

b - The significant broadening of the OH-proton signal takes place for EtOH-C₅H₅N system.

Table 2.

Chemical Shifts of the Proton of the Alcohols' Hydroxylic Group in the Dilute ($N_{ROH}=0.1$) solution of ROH in the Aprotic Solvents. TMS Served as the Internal Reference, Spectra were Recorded at 80 MHz.

R		δ_{1HC}				
		Me ₂ SO	M ₂ CO	Et ₃ N	THF	C ₅ H ₅ N
1	2	3	4	5	6	7
1.	H	270 ^a	-	-		-
2.	CH ₃	327 ^b	277	283		437
3.	C ₂ H ₅	349 ^b	287	351		459
4.	C ₃ H ₇	353	288	354		464
5.	(CH ₃) ₂ CH	348 ^b	285	340		459
6.	C ₄ H ₉	348.2	287	341		457
7.	(CH ₃) ₂ CHCH ₂	352	288	351		462
8.	(CH ₃) ₃ C	333 ^b	281	298		438
9.	C ₅ H ₁₁	356.7	286	334		456
10.	C ₆ H ₅ CH ₂	412 ^b	356	462	367	
11.	(C ₆ H ₅) ₂ CH	462	387	502	394	
12.	(C ₆ H ₅) ₃ C	517	428	542	438	
13.	HC=CCH ₂	415	332	443	350	
14.	CF ₃ CH ₂	484	434	523	412	
15.	CCl ₃ CH ₂	546	464	592	472	
16.	(CF ₃) ₃ C	833	742	819	737	
17.	C ₆ H ₅	740 ^a	-	-	-	

Table 2 continued

1	2	3	4	5	6	7
18.	C_6H_{13}	345.6				
19.	C_7H_{15}	345				
20.	C_8H_{17}	344				
21.	C_9H_{19}	343.6				
22.	$C_{10}H_{21}$	343.2				

Discussion

In the case of mixtures of THF with alkylsubstituted alcohols we were not able to measure the chemical shifts of the hydroxylic proton because of the resonance of the latter is observed in the same region as the protons of the THF ring. On the same reasons it was impossible to measure δ_{HO^-} values for the binary mixtures of the pyridine with alcohols containing electronegative substituents.

In several cases the interaction between alcohol and aprotic component is responsible for some qualitative change in the spectrum of the pure alcohol. So, for the DMSO-ethanol system at the excess of dipolar aprotic solvent an additional doublet appears in the NMR spectrum of the ethanol's $-CH_2-$ group protons.

The NMR spectrum of the methanol's protons belongs to A_3X group and consists of 6 lines. However, in the diluted ($N_{ROH}=0.05$) acetone solutions it changes into the A_3B -type spectrum, and, starting with $N_{ROH} \approx 0.03$ consists of the single line.

Our measurements once more confirm the fact²⁵ that the chemical shifts of the hydroxylic proton of the sterically not hindered aliphatic (alkyl-substituted) alcohols while diluted with the aprotic component, display usually the upfield solvent shifts. (see Fig. 1 - 6, the behavior of

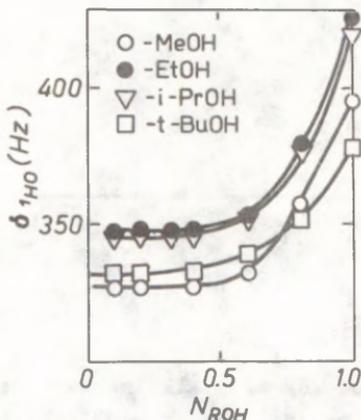


Fig.1. The dependence of the proton chemical shifts δ_{1HO} of the OH-group of aliphatic alcohols in their mixtures with DMSO on the mole fraction of ROH.

Py-alcohol is exceptional). On the contrary, our study shows that alcohols which possess strongly electronegative groups behave in the mixtures with DMSO similar to the sterically highly hindered aliphatic alcohols ($t\text{-Bu}_2\text{CHOH}$)²⁵, i.e. the downfield shift of δ_{1HO} is observed on dilution of the

alcohol with DMSO. One might think that such "anomalous" behavior of the electronegatively substituted alcohols is due to their very low auto-association. This conclusion is also supported by the IR data²⁹ which support the hypothesis that, e.g., the neat $(\text{CF}_3)_3\text{COH}$ is practically not associated.

Several differences exist in behavior of δ_{1HO} values on the concentration and nature of the components for the various binary mixtures. So, one can see (Fig.1) that for the binary mixtures of DMSO with alcohols at $N_{ROH} \leq 0.4-0.5$ the δ_{1HO} -values are practically independent of the further dilution of alcohol with DMSO²⁸. The similar behavior is also known³⁰ that in the diluted aqueous solutions of DMSO ($0.002 \leq N_{H_2O} \leq 0.1$) the δ_{1HO} values are independent of the concentration of H_2O . The same parameter does not vary too much also in the aqueous solutions of Me_2CO , MeCN , THF , etc.

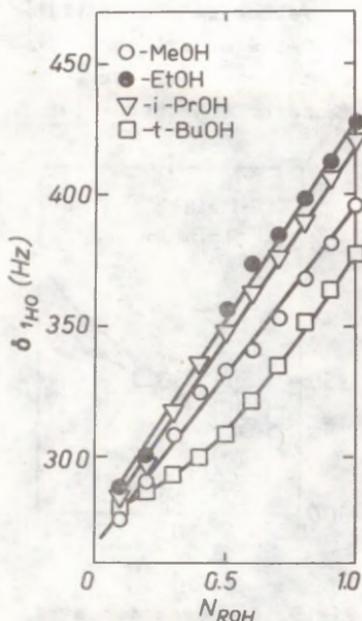


Fig. 2. The dependence of the proton chemical shifts $\delta_{1\text{H}\text{O}}$ of the OH-group of aliphatic alcohols in their mixtures with acetone on the mole fraction of ROH.

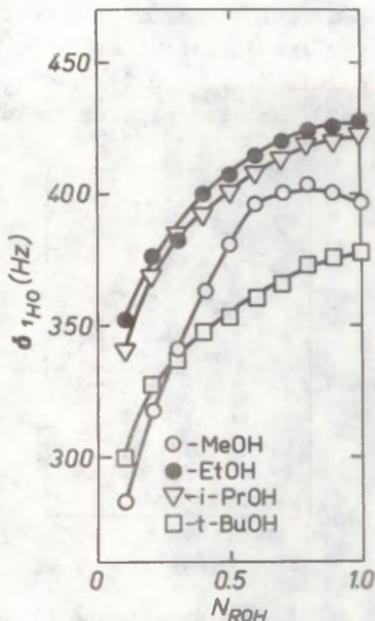


Fig. 3. The dependence of the proton chemical shifts $\delta_{1\text{H}\text{O}}$ of the OH-group of aliphatic alcohols in their mixtures with triethylamine on the mole fraction of ROH.

characteristic also for the mixture of DMP with alcohols (Fig. 5).

The study of the deviations $\Delta\delta_{1\text{H}\text{O}}$ of the chemical shifts of the hydroxylic protons in binary mixtures from their mole fractional additivity show (Fig. 6) that for the system DMSO-ROH the maximum values of that parameter occur at $N_{\text{ROH}} \approx 0.6 - 0.7$, i.e. in the system where there are two molecules of alcohol per one molecule of DMSO. The largest absolute values of $\Delta\delta_{1\text{H}\text{O}}$ in this system belong to EtOH, where

t-BuOH displays the lowest deviations from the additivity.

Somewhat anomalous order of $\delta_{1\text{HO}}$ values is characteristic for the different alcohols ROH of the normal chain in the dilute ($N_{\text{ROH}} = 0.1$) solutions of DMSO. One can see (Fig. 7) that the plot of the dependence of this parameter

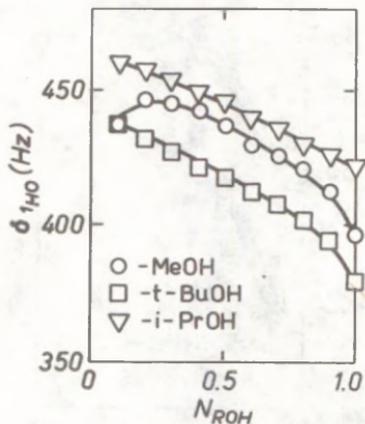


Fig. 4. The dependence of the proton chemical shifts $\delta_{1\text{HO}}$ of the OH-group of aliphatic alcohols in their mixtures with pyridine on the mole fraction of ROH.

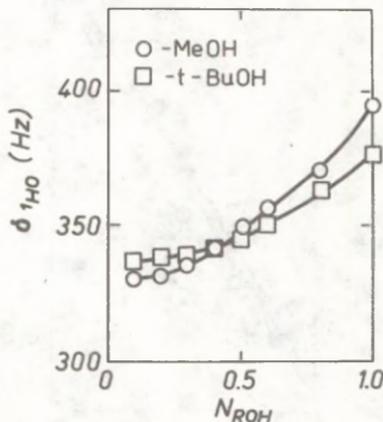


Fig. 5. The dependence of the proton chemical shifts $\delta_{1\text{HO}}$ of the OH-group of aliphatic alcohols in their mixtures with DMP on the mole fraction of ROH

on the number of carbon atoms in R has an extremum (maximum) at $n = 3-4$. In other words, the chemical shifts $\delta_{1\text{HO}}$ of the hydroxylic proton of MeOH and EtOH are lower than the same parameter for PrOH and BuOH. Further increase of n results in some decrease of its value. The anomalously low (see Fig. 2-5 and Table 1) chemical shifts $\delta_{1\text{HO}}$ for MeOH (and sometimes EtOH) as compared with the higher $\delta_{1\text{HO}}$ alcohols (i-PrOH, t-BuOH) are also characteristic for the other binary systems studied.

The variations of $\delta_{1\text{HO}}$ - values for the mixtures of $\text{Et}_3\text{N-ROH}$ (at $N_{\text{ROH}} \geq 0.6$), pyridine-EtOH and pyridine 1-PrOH (at $N_{\text{ROH}} \leq 0.5$) are rather modest. At the same time, the pyridine-alcohol mixtures possess the highest absolute values of $\delta_{1\text{HO}}$ while the downfield dilution effect is

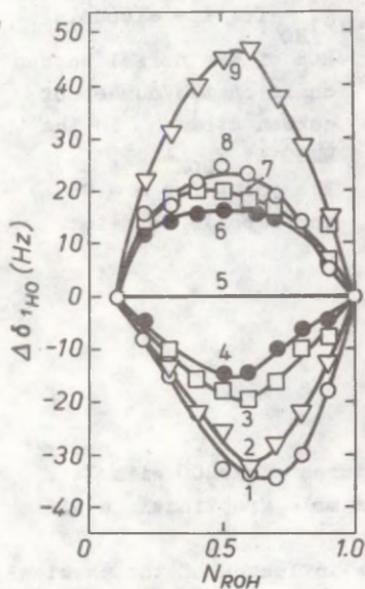


Fig. b. The dependence of the deviations $\Delta\delta_{1\text{HO}}$ of the proton chemical shifts of the OH-group of aliphatic alcohols from additivity on the alcohols mole fraction N_{ROH} for the following binary mixtures:

- 1-DMSO-EtOH, 2-DMSO-MeOH;
- 3-t-BuOH-DMSO,
- 4-1-PrOH-Me₂CO; 5-Me₂CO-EtOH, Me₂CO-MeOH, 1-PrOH-Me₂CO, 1-PrOH-Py ($\Delta\delta_{1\text{HO}} \approx 0$);
- 6-Py-MeOH;
- 7-t-BuOH-Et₃N;
- 8-Et₃N-EtOH; 9-Et₃N-MeOH.

observed[■].

The acetone-alcohol mixtures do not have the areas where the $\delta_{1\text{HO}}$ values practically do not depend on N_{ROH} . At the

[■] This anomaly is probably due to the complicating influence of the magnetic anisotropy of the pyridine molecules on the resonance frequency of the hydroxylic proton.

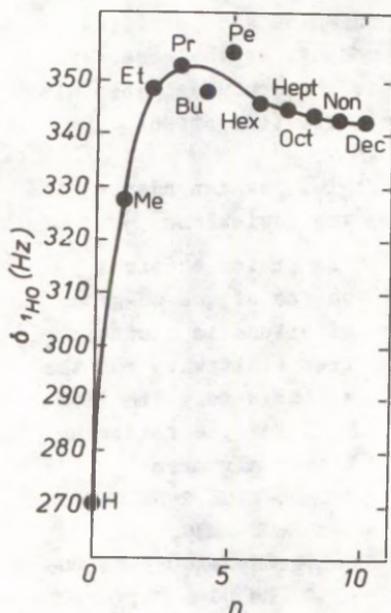


Fig. 7. The dependence of δ_{HO}^1 for the alcohols ROH of the normal carbon chain on the number of carbon atoms n in the DMSO at $N_{\text{ROH}}=0.1$. The point for $n = 0$ corresponds to water.

same time the behavior of the mixtures of Me_2CO with EtOH and *i*-PrOH is characterized by the mole fractional additivity.

It is interesting to study the influence of the chemical nature and concentration of the alcohol as well as aprotic component on the plots of deviations ($\Delta\delta_{\text{HO}}^1$) from the additivity of the measured hydroxylic proton chemical shifts vs. the composition of various binary mixtures.

One can see from Fig. 6 that both the absolute value and the sign of the deviations $\Delta\delta_{\text{HO}}^1$ change from one system to another. The positive values of $\Delta\delta_{\text{HO}}^1$ are characteristic to all systems except DMSO-ROH, DMP-ROH, and *t*-BuOH-aceton. The approximate additivity ($\Delta\delta_{\text{HO}}^1 \approx 0$) holds for the mixtures of acetone with MeOH, EtOH and *i*-PrOH and for the mixture of pyridine with *i*-PrOH.

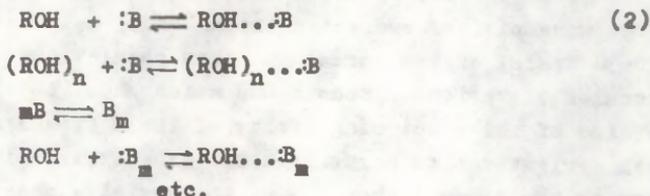
Unlike to the systems of DMSO-ROH and DMP-ROH the maximum values of $\Delta\delta_{\text{HO}}^1$ for the mixtures of amines (Py and

Et_3N) appear at the approximately equimolar ratios of the components. The same is true also for the system $t\text{-BuOH-Me}_2\text{CO}$.

It seems probable that in the case of the binary mixtures studied the chemical shift of the hydroxylic proton is the complex gross parameter which mostly carries the information about two competing processes - autoassociation of the alcohol molecules according to the scheme



and complex formation (heteroassociation) of the monomeric molecules or polymeric aggregates of the alcohols with the aprotic (basic) component B which also can be in the form of monomeric molecules or their aggregates:



On the basis of the data from the present work and literature sources²⁵ it seems that the autoassociation of the aliphatic alkyl-substituted alcohols leads to the downfield shift of the resonance of the hydroxylic proton whereas interactions between alcohol and base are responsible for the opposite trend. However, we should acknowledge that the available information on the behavior of $\delta_{i\text{HO}}$ in the binary mixtures of alcohols with aprotic components is not sufficient for the building of a physical model which would quantitatively account for the dependence of $\delta_{i\text{HO}}$ values on the nature and concentration of the components of the binary mixture.

It seems to be of some value to study the dependence of $\delta_{i\text{HO}}$ values on the structure of the alcohol molecule at the fixed conditions (the same basic component, fixed and as low as possible concentration of the alcohol, etc.). These prerequisites are to some extent met in the case of data

displayed in Table 2. where $\delta_{1\text{HO}}$ values refer to the relatively dilute ($M_{\text{ROH}}=0.1$) solutions of several ROH in DMSO.

The results of the statistical least squares treatment of these data in terms of the simple single parameter Tarr equation

$$\delta_{1\text{HO}} = a + b\sigma_{\text{H}}^{\text{R}}, \quad (3)$$

where a and b are constants, and $\sigma_{\text{H}}^{\text{R}}$ is the inductive constant of the alcohols radical R. are reported in Table 3.

One can see that in all cases, the increase of the electronegativity of the substituent R (more positive $\sigma_{\text{H}}^{\text{R}}$ values) results in the increase of the $\delta_{1\text{HO}}$ values (downfield shift).

In favor of that interpretation evidence also the results of the nonempirical quantum chemical model calculations³¹ (STO-3G basis) or the normal Mulliken populations in the molecules of various alcohols ROH which show that the increase of the electronegativity of the R (transfer from alkyl derivatives to perfluoroalkyl substituted alcohols) leads to the gradual increase of the positive charge on the hydrogen atom (q_{H}) of the hydroxyl group and to the decrease of the shielding of that proton (see Fig. 8).

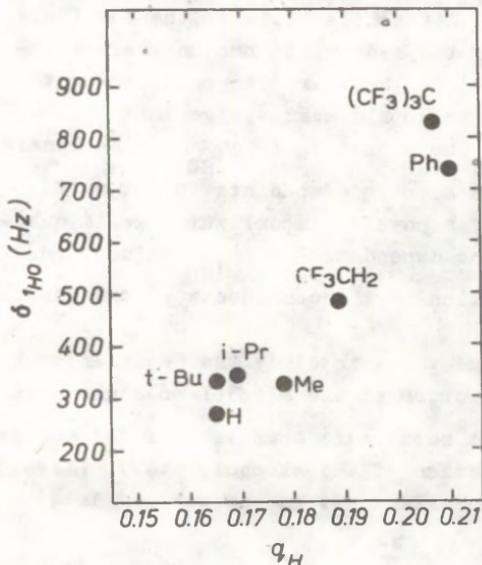


Fig.8. The plot of chemical shifts of the hydroxylic proton of alcohols in DMSO ($M_{\text{ROH}}=0.1$) vs. the formal positive charge q_{H} on the hydrogen atom of the OH-group (STO-3G basis, q_{H} is given in the charges of the electron).

The comparison of $\delta_{1\text{HO}}$ values with the STO-3G Mulliken charge q_{H} of the hydrogen atom of the alcohols OH group in the monohydrates³¹ $\text{ROH}\dots\text{CH}_2$ leads to the same conclusion. In the latter case, due to the coordination between the electrophile (ROH) and lone electron pair donor ($:\text{CH}_2$) the positive charge q_{H} on the alcohols OH hydrogen atom increases for all alcohols considered (charge transfer) and the general parallel trend for q_{H} and $\delta_{1\text{HO}}$ still holds.

The influence of the nature of the aprotic component of the binary mixture is manifested by the relatively modest change of the values of the ordinate a and slope b of Eqn.(3) (see Table 3).

The inclusion of the polarizability term³¹ into Eqn.(3) by the use of Eqn.(4)

$$\delta_{1\text{HO}} = a' + b'\sigma_{\text{R}}^{\text{M}} + c\Delta\text{R} \quad , \quad (4)$$

where a' , b' and c are constants, and

$$\Delta\text{R} = \text{MR}_{\text{D}(\text{R})} - \text{MR}_{\text{D}(\text{Me})}$$

improves the correlations moderately (see Table 3). Formally, the higher polarizability of the substituent R increases ($c > 0$) the chemical shift $\delta_{1\text{HO}}$ (downfield shift). The point for MeOH always does not fit the correlations (3) and (4). In some cases more or less deviates the point for $\text{CF}_3\text{CH}_2\text{OH}$ (in DMSO, THF) and sometimes also $\text{CCl}_2\text{CH}_2\text{OH}$ (DMSO, acetone). Water ($\text{R}_1\text{-H}$) deviates very substantially from Eqn.(3) and (4) manifesting about some sort of the effect³¹ of the hydrogen atom connected immediately to the reaction center.

Naturally, in the present case the success of the correlations in terms of Eqns.(3) and (4) depends significantly on the shift of the position of the solvation equilibria (1) and (2). Only on condition of high dilution for any R_1 practically all monomeric alcohol molecules are in the form of heteroassociates $\text{R}_1\text{-O-H}\dots\text{B}_j$ (where $j = \text{const}$) with lone pair donors B_j , Eqns.(3) and (4) should account for the substituent effects of R_1 on some properties of the hydroxy-

Table 3

Results^M of Statistical Analysis of Data on Chemical Shifts of Hydroxylic Proton in Diluted Solutions of Alcohols ROH ($N_{ROH} = 0.1$) in Aprotic Solvents. The Numbering of Substituents is Taken From Table 2.

Medium	a(a°)	b(b°)	c	R	s	s%	n	Substituents	
1	2	3	4	5	6	7	8	9	10
1. Me ₂ SO	376.5	176.9	-	0.999	8.0	1.6	11	3 - 11, 15, 16	
	(8.1)	(3.0)							
	372.1	176.5	0.274	0.997	7.1	1.4	12	3 - 12, 15, 16	
	(7.6)	(2.7)	(0.114)						
	320.8	-	2.72	0.971	15.1	7.9	11	2 - 12	
	(15.8)		(0.22)						
2. Me ₂ CO	312.3	165.5	-	0.999	7.3	1.6	12	3 - 12, 15, 16	
	(7.3)	(2.7)							
	308.4	163.2	0.135	0.993	10.2	2.2	13	3 - 12, 14 - 16	
	(10.8)	(3.8)	(0.154)						
3. Et ₃ N	380.9	182.3	-	0.981	29.9	5.7	13	3 - 12, 14 - 16	
	(30.1)	(10.8)							
	262.4	178.7	0.958	0.971	24.1	4.6	13	3 - 12, 14 - 16	
	(25.4)	(8.7)	(0.363)						

Table 3 continued

1	2	3	4	5	6	7	8	9	10
		355.7 (13.7)	174.9 (4.9)	0.972 (0.197)	0.992	13.0	1.9	11	3-9, 11, 12, 14, 16
4.	THF	326.8 (4.9)	158.1 (2.3)	-	0.990	4.3	1.2	5	10 - 12, 15, 16
		328.2 (7.4)	157.8 (3.1)	-0.028 (0.119)	0.998	5.2	1.4	5	10 - 12, 15, 16

55

$n - \sigma^M$ constants from Ref. 35 were used. Molecular refractivities are from Ref. 36.

In columns 3-5 the error limits of the regression coefficients are given in parenthesis; s - is the standard error, $s\% = (s/\Delta\sigma_{\max})100$, where $\Delta\sigma_{\max}$ is the maximum range of variation of $\sigma_{1_{HO}}$ values; r - correlation coefficient,

n - the number of points. The dash in columns 4 and 5 means that the corresponding term was not included into Eqn.(4).

lic proton in these associates^{II}. One might expect that in the present case the acidity of alcohols R_1OH in the given aprotic solvent pK_a will follow closely the property of the molecule R_1OH which determines the intensity of the hydrogen bond in heteroassociates $R_1OH \cdots B_1$ for the fixed B_1 and other conditions.

Indeed, the comparison of δ_{1HO} values for the R_1OH in DMSO solution with the corresponding pK_a values³²⁻³⁴ or these alcohols in the same medium reveals quite a satisfactory linearity between these two quantities (Fig.9).

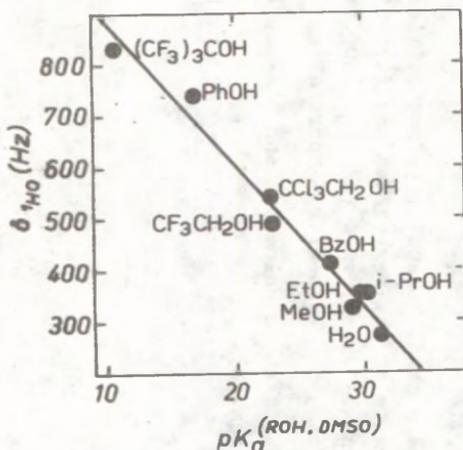


Fig.9. The dependence of δ_{1HO} values for the alcohols R_1OH in DMSO ($M_{ROH}=0.1$) on their pK_a values in the same aprotic solvent.

Remarkably, the points for MeOH and water also fit the same straight line with the "normally" behaving alcohols R_1OH .

^{III} The shifts of the solvation equilibria (1) and (2) for some alcohols or aprotic components B_1 should, however, result in the inhomogeneous simultaneous influence of several factors on δ_{1HO} - parameters. The latter situation can be described by Eqns.(3) and (4) only in some special cases.

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SUBSTITUENT EFFECT IN THE REACTION
OF DIPHENYLSULFONE DERIVATIVE FORMATION
FROM DIPHENYL SUBSTITUTES

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The reaction kinetics of 4,4-diaminodiphenyl sulfonation has been studied spectrophotometrically. It was established that the reaction is of general second order: the first as to the sulfidized substrate and the first as to the sulfidizing agent.

The substituent effect on the sulfonation reaction of disubstituted diphenyl derivatives was studied. On the basis of the data about the substituent effect it is shown that the cyclization stage serves as the rate-determining one in the formation of disubstituted diphenylsulfone derivatives.

The method of chemical modeling was used to show that in the sulfonation reaction of 4,4-diaminodiphenyl the formation of 2,7-diaminodiphenylsulfone takes place by means of benzidine-2-sulfonic acid.

Recently the researchers have become interested in 2,7-diaminodiphenylenesulfone which is used in the synthesis of aromatic polyamides. The latter have a set of valuable technical properties¹. It can be obtained in the reaction of 4,4-diaminodiphenyl sulfonation².

In order to optimize the process of obtaining 2,7-diaminodiphenylenesulfone we have studied the reaction kinetics of

4,4-diaminodiphenyl sulfonation spectrophotometrically. The method is based on the quantitative determination of the forming finished product. The study of absorption spectra of the initial 4,4-diaminodiphenyl and the forming 2,7-diaminodiphenylenesulfone showed that in the range $\lambda = 410$ nm only 2,7-diaminodiphenylenesulfone absorbs. Consequently, the reaction rate can be monitored by increasing in time the intensity of reaction solution absorption in this point of the spectrum.

The course of the process was studied by the method of taking samples as well as by determining the density of reaction solutions on a spectrophotometer SF-16.

The molar coefficient of extinction which is necessary for calculating the concentration of the forming 2,7-diaminodiphenylenesulfone was determined by means of special calibrating tests. Its mean value at $\lambda = 410$ nm was 2003 ± 150 l. mol⁻¹. cm⁻¹.

The sulfonation kinetics was studied in the presence of excessive oleum which means that the reaction was conducted under pseudomolecular conditions.

The rate constants were calculated according to the formula for first order reactions³. The calculated rate constants are presented in Table 1.

The stability of rate constants in time (Table 1) confirms the first order of the reaction as to 4,4-diaminodiphenyl.

The first order rate constants were calculated also by the differential method⁴ from the slope of the straight line in the coordinates $\log C - \tau$ (Fig. 1).

The rate constants which were determined by the graphic method practically coincide with the mean constant values calculated according to the formula for first order reactions (Table 1).

To check the influence of the concentration of initial reacting substances on the rate constant of first order reactions we studied the kinetics of the process at various concentrations of 4,4-diaminodiphenyl (Table 2) and oleum (Fig. 2).

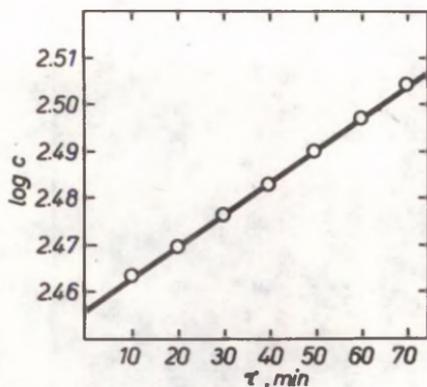


Fig. 1. Semilogarithmic anamorphosis of the kinetic curve of the reaction of 4,4'-diaminodiphenyl sulfonation.

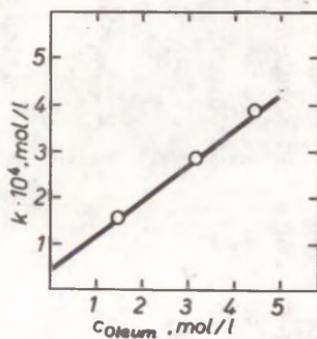


Fig. 2. Dependence of k on oleum concentration for the reaction of 4,4'-diaminodiphenyl sulfonation at 20.0 C.

Table 1
Rate Constants of 4,4'-diaminodiphenyl Sulfonation at Various Temperatures

$t^{\circ}\text{C}$	τ , min	C, mol/l	$k \cdot 10^3$ min^{-1}	$t^{\circ}\text{C}$	τ , min	C, mol/l	$k \cdot 10^3$ min^{-1}	$t^{\circ}\text{C}$	τ , min	C, mol/l	$k \cdot 10^3$ min^{-1}	$t^{\circ}\text{C}$	τ , min	C, mol/l	$k \cdot 10^3$ min^{-1}
20	8	0.03484	0,152	40	10	0,0328	6,48	60	5	0,0337	7.47	80	5	0.0309	24.43
20	15	0.03481	0.156	40	15	0.0324	5.14	60	10	0.0306	8.76	80	10	0.0210	51.22
20	25	0.03480	0.160	40	20	0.0318	4.97	60	15	0.0279	11.63	80	15	0.0120	69.81
20	30	0.03473	0.162	40	25	0.0312	4.53	60	20	0.0238	14.39	80	20	0.0103	63.78
20	40	0.03466	0.165	40	35	0.0306	4.38	60	25	0.0226	14.65	80	25	0.0079	59.47
20	50	0.03457	0.168	40	40	0.0299	4.50	60	30	0.0202	15.71	80	30	0.0061	58.43
20	60	0.03451	0.167	40	45	0.0294	4.38	60	35	0.0161	14.32	80	35	0.0049	56.34
20	70	0.03446	0.168	40	50	0.0287	4.42	60	40	0.0114	19.52	80	40	0.0026	65.48
20	80	0.03438	0.169	40	55	0.0284	4.14	60	45	0.0096	-	80	-	-	-
20	90	0.03416	0.170	40	60	0.0278	3.81	60	50	0.0072	-	80	-	-	-
$k_m = 0.000164 \pm$ $\pm 0.16^{\#}$ $k_{\text{graph}} = 0.000166$				$k_m = 0.004674 \pm$ ± 0.12 $k_{\text{graph}} = 0.004641$				$k_m = 0.015046$ ± 1.2 $k_{\text{graph}} = 0.0154$				$k_m = 0.06064 \pm$ ± 0.8 $k_{\text{graph}} = 0.06231$			

* - The mean square deviation is given

Table 2
Rate Constants of the Sulfonation Reaction
at Various Initial Concentrations of 4,4'-diamino-
diphenyl

C, mol/l	0.00354	0.0503	0.0708
$k \cdot 10^4, \text{min}^{-1}$	1.22 ± 0.2	1.19 ± 0.4	1.27 ± 0.2

It can be seen from Table that at various initial concentrations of the initial 4,4'-diaminodiphenyl at the given temperature the value of the rate constant remains almost stable which reinforces the validity of the conclusion that the given reaction is of first order as to 4,4'-diaminodiphenyl.

The rate constants calculated at sulfidizing various concentrations with oleum depend linearly on the concentration of the sulfonating agent (Fig. 2). This fact indicates that the studied reaction is of first order relative to the latter component.

To confirm the obtained data about the kinetic regularities of the course of the reaction the calculations were carried out by means of Van't Hoff's graphical methods in addition to applying the following equation:

$$\log V = \log k + n \log C$$

The calculated values of concentration and time orders of the reaction as to 4,4'-diaminodiphenyl are correspondingly equal to 1.16 and 1.10.

Consequently, the data obtained by the integral and differential methods of reaction order determination practically coincide.

The general order of reactions was determined by the Ostwald-Noyes method using Ostwald's separation (Table 3).

The calculation formula:

$$\pi = I + \frac{\log (\tau_2 / \tau_1)}{\log (C_1^0 / C_2^0)},$$

where C_1 and C_2 are the initial concentrations of 4,4'-diaminodiphenyl in two parallel tests; τ_1 and τ_2 are the preceding time of the reactions in two parallel tests up to one and the same degree of transformation.

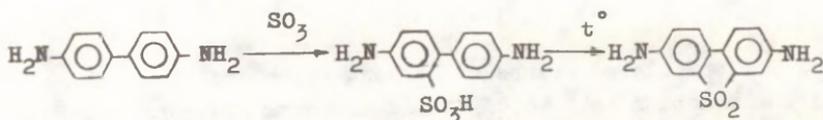
Table 3

Determination of the General Order of the Reaction of 4,4'-diaminodiphenyl Sulfonation by the Ostwald-Noyes Method

No	C_1 mol/l	C_2 mol/l	1 min	2 min	\bar{n}
1	0.0503	0.0708	35	25	1.98
2	0.0503	0.0708	28	20	1.89

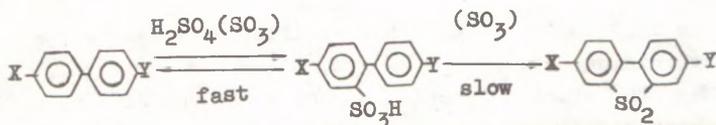
Thus, the results of the studies carried out show that the process of benzidine sulfonation appears to be a second-order reaction (Table 3) - the first as to the sulfidized substrate and the first as to the sulfidizing agent.

It is a well-known fact that the formation of diphenylsulfone - a side product of benzene sulfonation - proceeds in two stages⁵. Therefore, it can be assumed that the process of obtaining 2,7-diaminodiphenylenesulfone takes place by means of forming benzidine-2-sulfonic acid:



However, it is not possible to separate the intermediate product from the reaction mixture. Our kinetic data do not allow us to draw the final conclusion as to the mechanism of the reaction studied.

To do this, we have studied the substituent effect in the reaction of disubstituted diphenylsulfone derivative formation from the corresponding diphenyl derivatives.



- I X = Y = NH₂; II X = Y = NO₂; III X = NO₂, Y = NH₂;
 IV X = COOH; V X = COOH, Y = NO₂; VI X = COOH, Y = NH₂.

The results of the studies (Table 4) show that as to activity the studied compounds occupy the following positions in the row: I > VI > V > III > II > IV.

Table 4

Sulfonation of Disubstituted Diphenyl Derivatives.
 The Weight Ratio of Substrate: Sulfonating Agent
 (oleum 2.5%). The Temperature of the Reaction
 100°C.

Sulfonated diphenyl derivatives	Yield of the substituted diphenylsulfone in% from theor.
I 4,4'-diaminodiphenyl [⊗]	90.0
II 4,4'-dinitrodiphenyl ^{⊗⊗}	32.5
III 4-amino-4'-nitrophenyl	38.0
IV 4,4'-dicarboxydiphenyl ^{⊗⊗⊗}	31.0
V 4-nitro-4'-carboxydiphenyl	60.0
VI 4-amino-4'-carboxydiphenyl	65.0

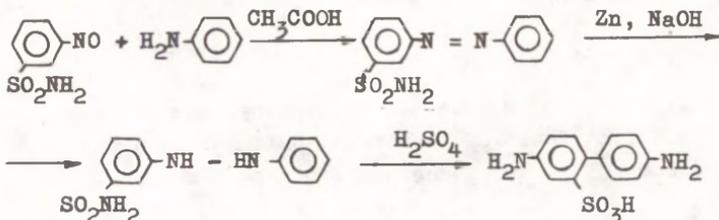
The maximum yield is reached: [⊗] at 70 - 80°C (95%)
^{⊗⊗} at 140 - 150°C (60%)
^{⊗⊗⊗} at 190 - 200°C (96%)

Consequently, benzidine appears to be most reactive, the next in the row are diphenyl derivatives of carboxylic acid. Since sulfonation is the first stage of the process it is clear that the nuclei with less acceptor substituents (-COOH) should undergo sulfonation more easily. At the same time the process of sulfone formation facilitates in the presence of the strongest acceptor group (-NH₂).

This fact indicates that the cyclization stage is the rate-determining one.

Thus, the studied reaction kinetics of benzidine sulfonation characterizes the cyclization rate of benzidine-2-sulfonic acid. The first order as to the sulfidizing agent makes it possible to assume that the reaction proceeds only in its presence.

To confirm this, we carried out the purposeful synthesis of benzidine-2-sulfonic acid:



The obtained target product transformed under the conditions presented in Table 4 into 2,7-diaminodiphenylenesulfone. At the same time in sulfuric acid the formation of the thiopheneoxide cycle does not take place.

Experimental

Kinetic Measurements

The kinetic measurements were carried out under the pseudomonomolecular conditions (50-time excess of the sulfonating agent) by the method of taking samples and their spectrophotometric analysis.

The prepared and back-titrated oleum⁶ was poured into a three-necked flask which was supplied with a mixer, a contact thermometer as well as with a thermometer for temperature control. The suspension of 4,4'-diaminodiphenyl was loaded into oleum while mixing.

At given time intervals 2 ml of the reacting volume was separated and poured onto ice in a 100 ml flask.

To precipitate 2,7-diaminodiphenylenesulfone sulfate an excess of water was added. The residue was solved in dimethylacetamide and the volume of the solution was increased up

to 100ml. The optical density of the obtained solution was recorded on a spectrophotometer.

The values of the rate constants which are presented in Tables are the mean ones out of three parallel measurements. The precision of kinetic measurements was assessed by the method of mathematical statistics, the confidence level being 0.95. At this the variation coefficient at calculating the values of rate constants didn't exceed 5%.

Synthesis of Substituted Diphenylenesulfones

In the studies reactants I-III were used, their physical constants corresponded to literature values. Compounds IV-VI were obtained according to known methods.

Sulfonation was carried out by adding diphenyl substitutes in 2.5% oleum which was pre-heated up to 100°C. The latter was in ratio substrate:sulfidizing agent 1:10 according to weight. In an hour the contents were poured out on ice. The separation of reaction products for I-III was carried out by adding sodium hydroxide to the mixture of aqueous solution until the reaction was weakly alkaline. The contents were filtered, washed with water until the reaction was neutral, dried and analyzed (Table 5).

Synthesis of Benzidine-2-Sulfonic Acid

m-Nitrosobenzenesulfamide was synthesized from m-nitrobenzenesulfamide by reducing it to m-hydroxylaminobenzene-sulfamide and then oxidizing it with ferric chloride¹³. The nitrosoaminocondensation of m-nitrosobenzinesulfamide and aniline was carried out in ethanol¹⁴. The analysis of m-nitrosobenzenesulfamide and azobenzene-3-sulfamide was carried out by the polarographic method on a polarograph PL-7 (thermostated cell) in dimethylformamide solutions against the background of a universal buffer solution (pH 4.0-4.1) at the ratio of DMFA:buffer solution % in vol. 80:20 on the dropping mercurous electrode. The reference electrode was bottom mercury. The potentials of half-waves were the following: m-nitrosobenzenesulfamide (-0.56 B), azobenzene-3-sulfa-

mide (-0.72 B) and (-0.94 B). Sodium hydrobenzene-3-sulfonate was not separated from the reaction solution but after the zincates had been separated it was subjected to regrouping. Benzidine-2-sulfonic acid was analyzed by potentiometric titration. At diazotization sodium nitrate served as the titrant in acid medium with lithium chloride as the catalyzer (jump of the potential in the range +430-600mB). The content of the basic substance was 98.9%. The found %: C 54.61; H 4.59; S 12.18; $C_{12}H_{12}O_3SN_2$. The calculated %: C 54.54; H 4.54; S 12.12.

Table 5

Results of the Analysis of Initial Substituted Diphenyls and Final Diphenylenesulfones

No	Diphenyl derivatives			Diphenylenesulfone derivatives	
	Melting t. C	Acid number	Melting t. C	Acid number	
				Found	Calculated
I	127-128 ⁷	-	325-327 ²	-	-
II	236-237 ⁸	-	278-279 ¹²	-	-
III	199-200 ⁹	-	291-292 ¹¹	-	-
IV	does not melt ¹⁰	462.0	325-327	367.8	368.4
V	334-336 ¹¹	230.0	325-327	182.9	183.6
VD	239-245 ¹¹	262.0	325-327	202.1	203.6

⁷Found %: C 52.28; H 2.96; S 11.65; $C_{12}H_8N_2O_4S$

Calculated %: C 52.17; H 2.89; S 11.59;

~~11~~Found %: C 55.31; H 2.71; S 10.59; $C_{14}H_8O_6S$

Calculated %: C 55.26; H 2.63; S 10.52;

~~11~~Found %: C 51.21; H 2.32; S 10.53; $C_{13}H_7O_6NS$

Calculated %: C 51.14; H 2.29; S 10.49;

~~11~~Found %: C 56.78; H 3.31; S 11.69; $C_{13}H_9O_4NS$

Calculated %: C 56.72; H 3.27; S 11.63;

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STUDY OF S_N1 REACTIONS USING TRIPHENYLVERDAZYL.
 VII[†]. Ph_2CHBr IONIZATION KINETICS IN PROPYLENE CARBONATE

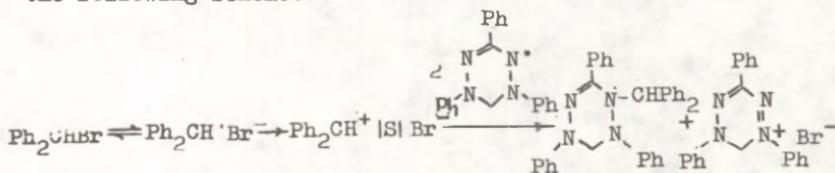
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The paper deals with Ph_2CHBr monomolecular heterolysis in propylene carbonate, $v = k[\text{Ph}_2\text{CHBr}]$, $k_{25^\circ} = 4.61 \cdot 10^{-6} \text{ s}^{-1}$, $\Delta H^\ddagger = 71.6 \text{ kJ/mole}$, $\Delta S^\ddagger = -103.0 \text{ J/mole} \cdot ^\circ\text{C}$. Bromide additions have no effect on the reaction rate, no usual salt effect or mass action salt effect are observed. Special salt effect is observed in the presence of LiClO_4 , Et_4NJ additions decrease the reaction rate. At the rate-determining step of Ph_2CHBr heterolysis the formation of a solvent-separated ion pair is supposed.

In continuation of our studies of the solvent effect on Ph_2CHBr monomolecular heterolysis, kinetic experiments were run in propylene carbonate, a strongly polar aprotic solvent ($\epsilon = 70$). As earlier the experiments were conducted in the presence of triphenylverdazyl (Vd^*) as an internal indicator. It was reported previously, that Ph_2CHBr heterolysis in aprotic solvents (MeCN , PhNO_2 , PhCN , Me_2CO , dichloroethane) in the presence of Vd^* proceeds according to the following scheme:



[†] See Ref. I for VI.

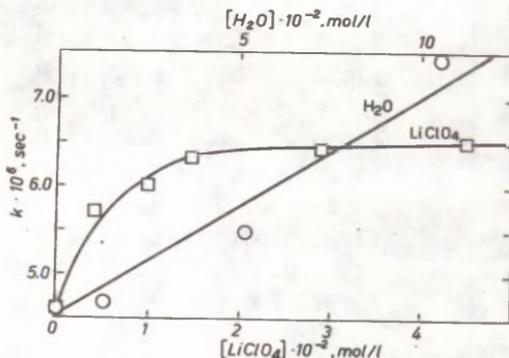
It is supposed¹ that at the rate-determining step the intimate ion pair of the substrate is converted into the solvent-separated one which further rapidly reacts with Vd^+ giving the tetrazine and the verdazylum salt (Vd^+Br^-).

Conditions and results of kinetic experiments are shown in Table 1.

The reaction rate, determined spectrophotometrically against Vd^+ consumption and Vd^+Br^- formation is satisfactorily described by the first order kinetic equation.

$$-d[Vd^+]/2dt = d[Vd^+Br^-]/dt = k[Ph_2CHBr]$$

The values of constants, calculated against Vd^+ and Vd^+Br^- concentrations (columns 6 and 7, Table 1) are in good agreement. Similar to the other solvents the reaction rate does not depend on the Vd^+ concentration (Exp.6-8). Consequently, the verdazyl enters the reaction after its rate-determining step. Vd^+ is supposed³ to be the solvent-separated ion pair indicator. The intermediate formation of the solvent-separated ion pair is also supported by the linear increase of the reaction rate in the presence of small quantities of water³ (Exp.12-15, Figure) as well as the availability of the special salt effect of $LiClO_4$ (Exp.16-20, Figure).



The effect of $LiClO_4$ and water additions on Ph_2CHBr heterolysis rate in propylene carbonate at 25°C.

Table 1
 Ph_2CHBr Heterolysis Kinetics in Propylene Carbonate
 in the Presence of Vd^*

Exp. No	$[\text{Vd}] \cdot 10^4$ mole/l	$[\text{Ph}_2\text{CHBr}] \cdot 10^3$ mole/l	Temperature, $^\circ\text{C}$	Additions, mole/l	$10^6 \cdot k, \text{s}^{-1}$		
					$\text{Vd}^{*1)}$	$\text{Vd}^{*2)}$	Average
1	1.57	4.43	14.5	-	1.77	1.76	1.76 ± 0.02
2	1.57	5.01			1.78	1.72	
3	1.13	4.66	19.5	-	3.06	3.06	3.03 ± 0.03
4	1.13	3.54			3.00	3.01	
5	1.76	1.81	25.0	-	4.59	4.45	4.61 ± 0.07
6	1.76	1.97			4.60	4.69	
7	1.32	3.50			4.68	4.76	
8	0.803	1.73			4.55	4.59	
9	1.05	2.00	29.5	-	8.51	8.23	8.37 ± 0.09
10	1.05	1.03			8.33	8.42	
11	1.05	1.73	32.0	-	10.6	9.95	10.3 ± 0.30
12	1.45	2.12	25.0	$\text{H}_2\text{O}, 0.0127$	4.68	4.68	4.68 ± 0.01
13	1.45	2.15		$\text{H}_2\text{O}, 0.0516$	5.45	5.51	5.48 ± 0.03
14	1.42	1.76		$\text{H}_2\text{O}, 0.105$	7.47	7.39	7.43 ± 0.04
15	1.42	1.24		$\text{H}_2\text{O}, 0.150$	8.41	8.41	8.41 ± 0.01
16	1.29	1.62		$\text{LiClO}_4, 0.00401$	5.86	5.56	5.71 ± 0.15
17	1.16	1.80		$\text{LiClO}_4, 0.00980$	6.14	5.88	6.01 ± 0.13
18	0.978	1.68		$\text{LiClO}_4, 0.0146$	6.40	6.25	6.32 ± 0.08
19	1.29	1.56		$\text{LiClO}_4, 0.0291$	6.43	6.38	6.41 ± 0.03
20	1.51	1.66		$\text{LiClO}_4, 0.0449$	6.62	6.37	6.50 ± 0.13
21	1.36	2.86		$\text{Et}_4\text{NBr}, 0.000581$	4.72	4.68	4.70 ± 0.02
22	1.32	3.58		$\text{Et}_4\text{NBr}, 0.00110$	4.72	4.74	4.73 ± 0.01
23	1.36	3.10		$\text{LiBr}, 0.00109$	4.48	4.40	4.44 ± 0.04
24	1.05	3.49		$\text{LiBr}, 0.00106$	4.74	4.47	4.60 ± 0.14
25	1.42	3.75		$\text{Et}_4\text{NI}, 0.000408$	3.88	3.88	3.88 ± 0.01
26	1.55	5.43		$\text{Et}_4\text{NI}, 0.000704$	3.31	3.36	3.34 ± 0.03
27	1.55	5.27	$\text{Et}_4\text{NI}, 0.00109$	3.36	3.28	3.32 ± 0.04	

*1) Average of two-three determinations.

According to our interpretation of the above effect^{1,3} ClO_4^- anion nucleophilically catalyses the conversion of the intimate ion pair into the solvent-separated one. Observed saturation curve shows the equilibrium formation of $\text{ClO}_4^- \cdot \text{S} | \text{Ph}_2\text{CH}^+\text{Br}^-$ anion triplet, which is more readily converted into the solvent-separated ion pair than the intimate ion pair itself. The extrapolation of the second part of the curve for the zero salt concentration gives the maximum special salt effect value $k_{\text{S}}^0 = 6.40 \cdot 10^{-6} \text{ s}^{-1}$ which, due to the fact that the usual salt effect is missing (the second part of the curve is parallel to the abscissa-axis) equals the maximum rate constant value at the LiClO_4 concentrations used. This value is 1.4 times greater than the rate constant values without LiClO_4 additions, i.e. the conversion of $\text{ClO}_4^- \cdot \text{S} | \text{Ph}_2\text{CH}^+\text{Br}^-$ triplet into the solvent-separated ion pair occurs 1.4 times faster than that of $\text{Ph}_2\text{CH}^+\text{Br}^-$. Bromide additions have no effect on the reaction rate (Exp. 21-24). Bearing in mind that the usual salt effect is missing under our conditions one may conclude that there is no mass action salt effect (the fact that no depression is observed on the reaction rate curve in the presence of the salt with a common ion has nothing to do with the compensation of the usual salt effect and mass action salt effect). Therefore, no carbocation is formed during Ph_2CHBr heterolysis in propylene carbonate.

The linear reaction rate which increases with the addition of small quantities of water (Exp. 12-15, Figure) seems likely to be determined by the electrophilic promotion of the intimate ion pair conversion into the solvent-separated one³ as a result of the formation of H-complex $\text{Ph}_2\text{CH}^+\text{Br}^- \cdots \text{H}_2\text{O}$.

Thus, Ph_2CHBr heterolysis rate in propylene carbonate, as in other aprotic solvents¹ is limited by the formation of the solvent-separated ion pair which reacts with Vd^+ rapidly and quantitatively.

In contrast to the bromides Et_4NI additions drop the reaction rate (Exp. 25-27). There appears a negative salt effect, which according to Ref.^{1,3} is determined by the reaction of the contact ion pair with the salt anion- $\text{S}_{\text{N}}2$ -ion pair reaction⁴ occurs to be competing with the conversion process of the intimate ion pair into the solvent separated one.

The mechanism of Ph₂CHBr heterolysis in propylene carbonate as well as the effects of salt and water on this process may be shown as follows:

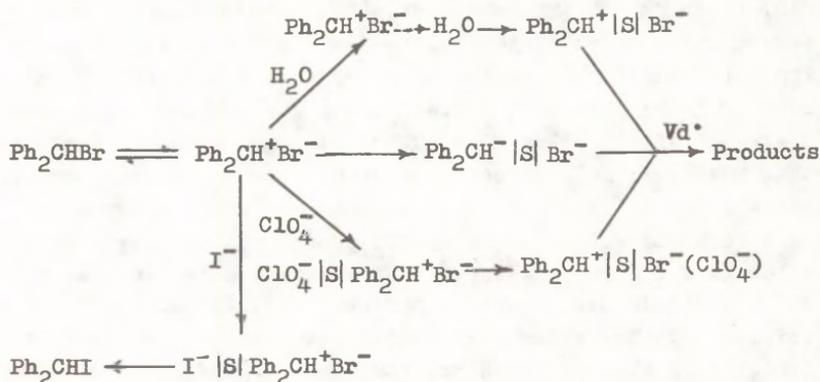


Table 2 shows the kinetic parameters of Ph₂CHBr heterolysis in propylene carbonate in comparison with similar data for t-BuBr.

Table 2
Kinetic Parameters of Ph₂CHBr and t-BuBr heterolysis in propylene carbonate at 25°C

Substrate	$-\lg k \text{ (s}^{-1}\text{)}$	ΔH^\ddagger kJ/mole	ΔS^\ddagger J/mole °C
Ph ₂ CHBr	5.33*	71.6*	-103.0*
t-BuBr	5.50**	84.6**	-66.6**

* Calculated using the data from Table 1.

** As reported in Ref.5.

Similar to other aprotic solvents, in propylene carbonate the t-BuBr and Ph₂CHBr heterolysis rates are close to each other. The formation of the intimate ion pair is rate-determining in the first case³ whereas in the second one the rate is determined by the solvent-separated ion pair. Comparison of ΔH^\ddagger and ΔS^\ddagger is in agreement with the above conclusion. During the transition from t-BuBr to Ph₂CHBr both ΔH^\ddagger

and ΔS^\ddagger markedly decrease. The decrease of the first value is connected with the growing stability of the forming carbocation, whereas that of the second one is due to the additional coordination of the solvent molecule in the transition state resulting from the formation of the solvent-separated ion pair.

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REACTIVITY OF AROMATIC AND HETEROCYCLIC
HYDRAZINE DERIVATIVES

I. REACTION KINETICS OF ACYLATING CHLORO-
SUBSTITUTED HYDRAZIDES OF AROMATIC CAR-
BOXYLIC ACID HYDRAZIDES WITH BENZOYL
CHLORIDE IN CHLOROPFORM

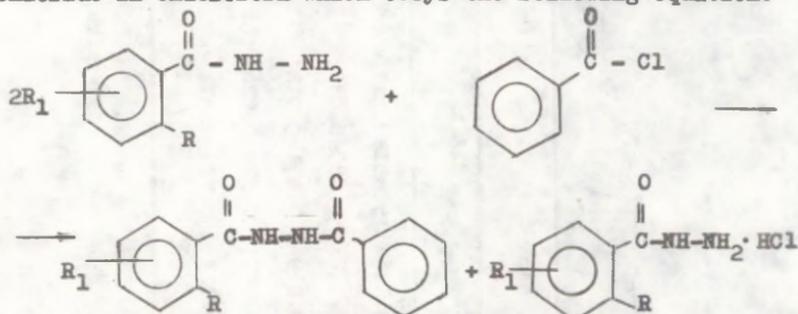
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The reaction kinetics of acylating five chlorine-substituted aromatic carboxylic acid hydrazides with benzoyl chloride in chloroform has been studied in the temperature range 288-328K. It was shown that the process can be described by the second order kinetic equation for irreversible reactions. Rate constants, energies, enthalpies, entropies and free activation energies were calculated. The influence of the nature and position of substituents in the hydrazide molecule on the reactivity of the hydrazide group in the acylation reaction was studied.

The hydrazides of aromatic carboxylic acids and their derivatives are widely used as physiologically active preparations. They have anticancer^{1,2}, antiviral³, antispasmodic⁴⁻⁶ as well as anticephalic properties. Therefore, the study of the reactivity of these compounds is not only of theoretical but also of considerable practical interest. In order to find optimum synthesis conditions for the deriva-

tives of chlorine-substituted aromatic carboxylic acid hydrazides which have a great future with respect to biology as well as to the comparative estimation of their reactivity, we have studied the substituent effect of various electronic nature in the molecule of arylhydrazide on the reactivity of the hydrazide group. To solve this problem, we have chosen the reaction of acylating hydrazides with benzoyl chloride in chloroform which obeys the following equation:



Changes in the concentration of hydrazides in time were determined by nitritometric potentiometric titration⁸. The choice of benzoyl chloride as the acylating reagent was caused by its high reactivity as well as by the absence of the autocatalytic effect in the reactions of the given type⁹.

The reaction of acylating arylhydrazides with benzoyl chloride is irreversible and is described by the second order kinetic equation which is confirmed by the stability of rate constants (Table 1) calculated according to the equation:

$$k = \frac{1}{2\beta t} \cdot \left(\frac{1}{a-x} - \frac{1}{a} \right)$$

where k is the rate constant ($l \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$);

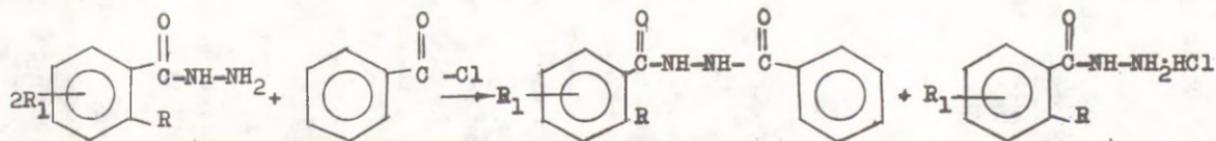
a - the initial concentration of benzoyl chloride (M);

x - the concentration of benzoyl chloride (M) at the moment of time t (sec);

β - the concentration which takes into account the change in the concentration of reagents when chloroform extends thermally from 29 K up to the tem-

Table 1

Kinetic Parameters of Reactions


 $k \text{ l. mol}^{-1} \cdot \text{sec}^{-1}$

R	R ₁	288°K	298°K	308°K	318°K	328°K
H	H	-	2.506±0.093	4.006±0.126	5.551±0.111	7.186±0.083
Cl	H	0.312±0.008	0.463±0.034	0.675±0.010	0.999±0.039	1.481±0.063
Cl	4-Cl	0.256±0.005	0.402±0.027	0.645±0.019	0.891±0.018	1.250±0.070
Cl	4-NO ₂	-	0.230±0.019	0.352±0.040	0.528±0.026	0.766±0.027
Cl	5-SO ₂ NH ₂	-	0.330±0.015	0.500±0.014	0.727±0.031	1.037±0.049

perature of the experiment.

The reaction studied obeys the Arrhenius equation in the temperature range (288-328K) which is evidenced by the linear dependence between the logarithms of rate constants and the values for reversed temperatures. This made it possible to calculate the activation energy E (kcal/mol) and the pre-exponential factor A according to the Arrhenius equation and the thermodynamic parameters of activation (enthalpy ΔH^\ddagger (kcal/mol), entropy ΔS^\ddagger (e.u.), free activation energy ΔG^\ddagger (kcal/mol) according to Eyring¹⁰ (Table 2).

The values for acylation rate constants depend on the nature and position of substituents in the molecule of arylhydrazide. The introduction of electron-acceptor substituents (especially the NO_2 group) to the structure of the latter leads to a considerable decrease in the reactivity of the hydrazide group. At this the rate constants of the given reaction decrease symbatically with an increase in the electronegative substituent (with an increase in $\bar{\sigma}$ - the Hammett constant) (Table 1). It is interesting to note that the appearance of a chlorine atom in the molecule of hydrazide in the o position leads to a more abrupt decrease in the rate of the acylation reaction (5.4 times) than the introduction of another chlorine atom in the π position (1.15 times). This might be due to the ortho-effect of the substituent¹¹.

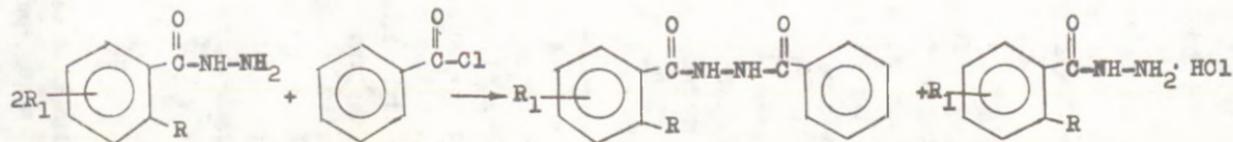
Similar regularities are observed also in the changes of energies, enthalpies as well as free activation energies depending on the nature and position of the substituents (Table 2). However, the thermodynamic activation parameters are less sensitive to the structural changes in the molecule of arylhydrazide. The activation entropies for all the studied hydrazides are close to one another which confirms the unite mechanism of acylating the studied hydrazides with acid chloride¹².

Experimental

The hydrazides of aromatic carboxylic acid were synthesized according to known methods^{9,13} and were purified

Table 2

Thermodynamic Parameters of Activating the Reaction

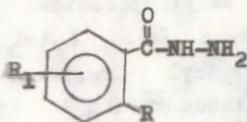


R	R ₁	ΔH^\ddagger kcal/mol	$-\Delta S^\ddagger$ e.u.	ΔG^\ddagger kcal/mol (298 K)	E _A kcal/mol	ln A
H	H	6.52 ± 0.18	34.8 ± 0.6	16.9	6.79 ± 0.17	12.43 ± 0.27
Cl	H	7.25 ± 0.05	35.8 ± 0.8	17.9	7.27 ± 0.31	11.53 ± 0.60
Cl	4-Cl	6.99 ± 0.08	36.9 ± 0.3	17.6	7.49 ± 0.30	11.72 ± 0.05
Cl	4-NO ₂	7.44 ± 0.18	36.6 ± 0.9	18.3	7.81 ± 0.08	11.70 ± 0.13
Cl	5-SO ₂ NH ₂	7.20 ± 0.16	36.6 ± 0.3	18.1	7.38 ± 0.13	11.36 ± 0.20

by multiple recrystallization up to the permanent melting temperature (Table 3). Benzoyl chloride and chloroform were purified according to references 14 and 15 and were checked densitometrically and chromatographically. The kinetic measurements were carried out according to the methods described in ref. 9.

Table 3

Substituted Hydrazides of Aromatic Carboxylic Acids



R :	R ₁ :	^o C melting T :	Found % N :	Brutto- formula :	Calculated % N :
H	H	112 - 115	20.46	C ₇ H ₈ N ₂ O	20.57
Cl	H	117 - 118	16.58	C ₇ H ₇ ClN ₂ O	16.42
Cl	4-Cl	167 - 168	13.72	C ₇ H ₆ Cl ₂ N ₂ O	13.66
Cl	4-NO ₂	149 - 150	19.63	C ₇ H ₆ ClN ₂ O ₃	19.49
Cl	5-SO ₂ NH ₂	181 - 183	17.00	C ₇ H ₈ ClN ₂ O ₃ S	16.83

Arylhydrazides were determined by titrating them potentiometrically with a 0.01M solution of sodium nitrate with platinum ETPL-01M and chlorosilver EVL-IMI electrodes in the presence of potassium bromide as the catalyser and the mediator : 0.001M solutions K₄[Fe(CN)₆] and K₃[Fe(CN)₆].

Kinetic studies were carried out at 288, 298, 308, 318, 328 K. When determining the rate constants the experiment was repeated three times and it included 6 - 8 measurements. The precision of the obtained values was assessed by the method of mathematical statistics (the confidence level being 0.95)¹⁶. The thermodynamic activation parameters were

calculated according to the well-known least-squares method¹⁰. The precision of the calculated kinetic parameters was characterized by the value of the least-squares deviation.

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KINETIC STUDY OF BENZOATE HYDROLYSIS.
XVI. ALKALINE HYDROLYSIS OF m- AND p-SUBSTITUTED
BENZOATES IN CONCENTRATED AQUEOUS n-Bu₄NBr AND
Et₄NBr SALT SOLUTIONS.

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The kinetics of alkaline hydrolysis of six substituted phenyl benzoates C₆H₅COOC₆H₄-X (X=4-NO₂, 3-NO₂, 3-Cl, 4-F, 3-NH₂, H) as dependent on the additions of salts n-Bu₄NBr and Et₄NBr has been studied in water at 50°C.

In the presence of both salts negative salt effects were detected, their values increasing with a decrease in the σ° value for the corresponding substituted phenyls. In the presence of both salts, n-Bu₄NBr as well as Et₄NBr, the ρ° value was found to increase in comparison with water.

When passing from water to 2.25 molar n-Bu₄NBr solution the ρ° value was found to increase by 0.90 units. The analogous value for Et₄NBr is equal to 0.67 units of ρ° .

Steigman and Sussman^{1,2} have published the pK_a values for a series of substituted benzoic acids, phenols and amines in 7.75 molal aqueous tetra-n-butylammonium bromide solution.

It was found^{3,4} in the case of both aromatic carboxylic acids and phenols that the ρ° value increases nearly by 1.0 unit when passing from water to 7.75 molal n-Bu₄NBr solution. At the same time it can be concluded from the kinetic data on the alkaline hydrolysis of substituted phenyl benzoates and phenyl tosylates that the additions of salts, NaCl as well as NaClO₄, lower the ρ° value by comparison with the ρ° value for water⁵⁻⁷.

The purpose of the present work was to study the dependence of the ρ° value on the n-Bu₄NBr and Et₄NBr salt additions for the alkaline hydrolysis of substituted phenyl benzoates.

Experimental

The kinetics of the alkaline hydrolysis of substituted phenyl benzoates C₆H₅COOC₆H₄-X (X=4-NO₂, 3-NO₂, 3-NO₂, 3-Cl, 4-F, 3-NH₂, H) as dependent on the additions of salts n-Bu₄NBr and Et₄NBr was studied in water at 50°C.

Tetra-n-butylammonium hydroxide was used as the reagent. The purification of hydroxide, the preparation and characteristics of the phenyl benzoates studied has been described earlier^{8,9}.

n-Bu₄NBr "pure" grade was recrystallized twice from ethyl acetate and dried in vacuo.² Ethyl acetate was purified as described in reference 10.

Kinetic measurements were carried out under pseudo monomolecular conditions on spectrophotometer SF-4A, equipped with a photoelectric multiplier and a LP type recorder.

In greater detail the method of kinetic measurements has been described earlier⁹.

The alkaline hydrolysis kinetics of phenyl benzoates C₆H₅COOC₆H₄-X was measured on the following wavelengths:

X	λ (nm)
4-NO ₂	404
3-NO ₂	410
3-Cl	293
4-F	306
3-NH ₂	266
H	296

Table 1
 Rate Constants $k(M^{-1} \cdot sec^{-1})$ for Alkaline Hydrolysis
 of Phenyl Benzoates $C_6H_5COOC_6H_4-X$ in the Presence of
 $n-Bu_4NBr$ and Et_4NBr at $50^\circ C$ in Water.^M

X	G_{salt} (M)	Additions of $n-Bu_4NBr$		Additions of Et_4NBr	
		$k(M^{-1} \cdot sec^{-1})$	n^{MSE}	$k(M^{-1} \cdot sec^{-1})$	n^{MSE}
1	2	3	4	5	6
4-NO ₂		13.45 ± 0.62	4	13.45 ± 0.62	4
		10.39 ± 0.72 ^{MSE}			
	1.00	7.34 ± 0.22	9	13.30 ± 0.33	4
	2.25	9.64 ± 1.48	8	10.14 ± 3.75	4
	3.24	-		12.59 ± 0.13	2
3-NO ₂	-	10.58 ± 0.93	3	10.58 ± 0.93	3
		8.59 ± 0.42 ^{MSE}			
	1.00	4.29 ± 0.27	2	10.43 ± 0.16	5
	2.25	6.25 ± 0.75	10	7.29 ± 2.77	4
	3.24	-		9.47 ± 0.075	2
3-Cl	-	3.76 ± 0.11	2	3.76 ± 0.11	2
		3.49 ± 0.32 ^{MSE}			
	1.00	0.749 ± 0.080	8	3.31 ± 0.10	5
	2.25	1.08 ± 0.13	7	1.81 ± 0.74	4
	3.24			2.51 ± 0.26	2
4-F	-	2.25 ± 0.19	3	2.25 ± 0.19	3
	1.00	0.503 ± 0.043	7	1.89 ± 0.13	4
	2.25	0.550 ± 0.055	7	0.939 ± 0.311	5
	3.24	-		1.37 ± 0.33	2
H	-	1.55 ± 0.015	3	1.55 ± 0.015	3
		1.67 ± 0.09 ^{MSE}			
	1.00	0.243 ± 0.004	7	1.37 ± 0.003	5
	2.25	0.241 ± 0.033	6	0.554 ± 0.163	4
	3.24			0.852 ± 0.008	2
3-NH ₂	-	1.39 ± 0.06	3	1.39 ± 0.06	3
		1.40 ± 0.07 ^{MSE}			
	1.00	-		0.985 ± 0.022	5
	2.25	-		0.345 ± 0.133	4
	3.24	-		0.376 ± 0.007	2

Table 1 continued

- Concentration of Bu_4NOH was 0.0126 M in the case of all measurements in presence of salt additions. At measurements without salt additions concentration of Bu_4NOH was 0.00631 M
- Number of measurements at the salt concentration considered.
- Values of k given in reference 9. As hydroxide NaOH was used.

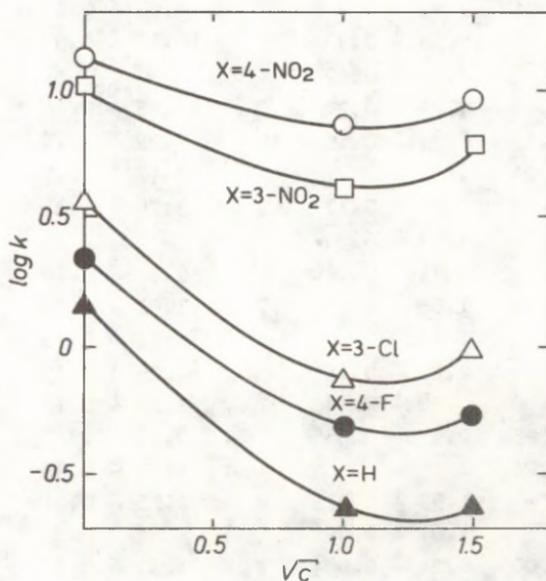


Fig. 1. Dependence of $\log k$ on \sqrt{C} for alkaline hydrolysis of substituted phenyl benzoates $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_4\text{-X}$ in presence of $n\text{-Bu}_4\text{NBr}$ at 50°C

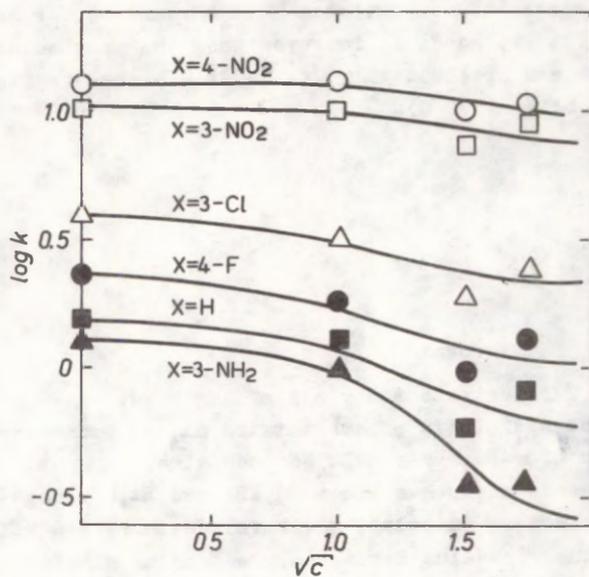


Fig. 2. Dependence of $\log k$ on \sqrt{C} for alkaline hydrolysis of substituted phenyl benzoates $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_4\text{-X}$ in presence of Et_4NBr at 50°C .

The second order rate constants k_2 were calculated by dividing pseudo-first order rate constants k_1 by the alkali concentration. The measurements at each salt concentration were repeated and the arithmetic means of the corresponding second order rate constants k_2 were calculated. The k_2 values found in such way and the number of measurements at each salt concentration are given in Table 1.

It should be noted that the reproducibility of the kinetic data in the case of concentrated $n\text{-Bu}_4\text{NBr}$ and Et_4NBr solution is not quite good. It improves when the salt solution with hydroxide was preliminarily heated at a higher temperature (about 3 hrs. at 70°C).

Discussion.

Fig. 1 and 2 illustrate the plots of $\log k$ vs. \sqrt{C} for the alkaline hydrolysis of substituted phenyl benzoates in the presence of $n\text{-Bu}_4\text{NBr}$ and Et_4NBr additions.

In the presence of both salts $n\text{-Bu}_4\text{NBr}$ and Et_4NBr negative salt effects were detected, their values increased with a decrease in the σ° value for the corresponding substituted phenyl radical.

According to equation

$$\log k_S^X = \log k_S^0 + \rho_S^0 \sigma_X^0 \quad (1)$$

the ρ_S^0 values for every $n\text{-Bu}_4\text{NBr}$ and Et_4NBr salt concentration were calculated. In calculations the "recommended"

values of σ° from Tables¹¹ were used.

The values of ρ_s° and $(\log k_s^{\circ})_{\text{calc}}$ for various concentrations of salts $n\text{-Bu}_4\text{NBr}$ and Et_4NBr as well as the corresponding differences $\Delta\rho_s^{\circ} = \rho_s^{\circ} - \rho_{\text{H}_2\text{O}}^{\circ}$ are reported in Table 2.

The a_{js} and b_{js} values found according to equation (2)

$$\log k_{js}^{\text{X}} = (a_{js} + 1) \log k_j^{\text{X}}(\text{H}_2\text{O}) + b_{js} \quad (2)$$

where

$$a_{js} = \frac{\rho_{js}^{\circ} - \rho_j^{\circ}(\text{H}_2\text{O})}{\rho_j^{\circ}(\text{H}_2\text{O})}$$

are given in Table 2 as well. In equation (2) indexes j and s denote reaction and medium.

The addition of $n\text{-Bu}_4\text{NBr}$ or Et_4NBr to the aqueous solution increases the ρ° value of the phenyl benzoates alkaline hydrolysis reaction by comparison with the same value for water (see Fig. 3 and Table 2). For 2.25 molar $n\text{-Bu}_4\text{NBr}$ solution (corresponds to 6.6 molal solution)

$$\Delta\rho_s^{\circ} = \rho_s^{\circ} - \rho_{\text{H}_2\text{O}}^{\circ} = 0.90$$

An analogous increase in the ρ° value when passing from water to 7.75 molal $n\text{-Bu}_4\text{NBr}$ solution was found for acidic dissociation of aromatic carboxylic acids ($\Delta\rho^{\circ} = 1.15$) and phenols ($\Delta\rho^{\circ} = 0.91$)⁴.

The addition of tetraethylammonium bromide to the reaction mixture has a less considerable influence on the ρ° value (see Table 2). When passing from water to 2.25 molar tetraethylammonium bromide solution the ρ° value increases by 0.67 units.

Using the differences $\Delta\rho_s^{\circ} = \rho_s^{\circ} - \rho_{\text{H}_2\text{O}}^{\circ}$ found in the present work and earlier according to equation (3)¹⁴

$$\Delta\rho_s^{\circ} = \rho_s^{\circ} - \rho_{\text{H}_2\text{O}}^{\circ} = -0.0842(E_s - E_{\text{H}_2\text{O}}) \quad (3)$$

Table 2

Values of p_s° , $(\log k_s^{\circ})_{\text{calc}}$, s , Δp_s° , a_{j_s} and b_{j_s} at Various Concentrations of $n\text{-Bu}_4\text{NBr}$ and Et_4NBr .

C_{salt}	p_s°	$(\log k_s^{\circ})_{\text{calc}}$	s	Δp_s°	a_{j_s}	b_{j_s}
<u>Alkaline Hydrolysis of Phenyl Benzoates at 50°C</u>						
—	1.12 ± 0.06	0.200 ± 0.019	0.050	—	—	—
1M $n\text{-Bu}_4\text{NBr}$	1.85 ± 0.10	-0.683 ± 0.042	0.068	0.73	0.529 ± 0.071	-0.907 ± 0.046
2.25M $n\text{-Bu}_4\text{NBr}$ (6.6 molal solution)	2.02 ± 0.05	-0.660 ± 0.021	0.034	0.90	0.667 ± 0.037	-0.902 ± 0.024
1M Et_4NBr	1.40 ± 0.14	-0.012 ± 0.051	0.100	0.28	0.094 ± 0.020	-0.106 ± 0.011
2.25 M Et_4NBr	1.79 ± 0.19	-0.439 ± 0.070	0.135	0.67	0.400 ± 0.037	-0.560 ± 0.020
3.24 M Et_4NBr	1.74 ± 0.25	-0.295 ± 0.093	0.181	0.62	0.380 ± 0.089	-0.425 ± 0.050
<u>Acidic Dissociation of Benzoic Acids at 25°C</u>						
7.75 molal solution of $n\text{-Bu}_4\text{NBr}$	$2.09^{\text{ref 4}} \pm 0.08$			1.15	$0.99^{\text{ref 4}} \pm 0.16$	$2.09^{\text{ref 4}} \pm 0.62$
<u>Acidic Dissociation of Phenols at 25°C</u>						
7.75 molal solution of $n\text{-Bu}_4\text{NBr}$	$3.27^{\text{ref 4}} \pm 0.09$			0.91	$0.45^{\text{ref 4}} \pm 0.07$	$2.36^{\text{ref 4}} \pm 0.56$

s - s - Standard error at calculation the values of p_s° and $(\log k_s^{\circ})_{\text{calc}}$ according to equation (1).

~~ref 4~~ - Data from reference 4.

~~ref 3~~ - Data from reference 3.

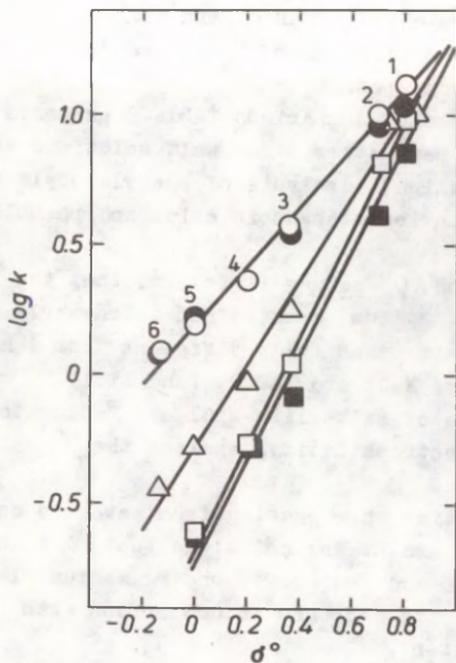


Fig. 3. Dependence of $\log k$ on σ° for alkaline hydrolysis of substituted phenyl benzoates $C_6H_5COOC_6H_4-X$ at $50^\circ C$.

1. $X=4-NO_2$; 2. $X=3-NO_2$; 3. $X=3-Cl$; 4. $X=4-F$;

5. $X=H$; 6. $X=NH_2$

○ - H_2O

● - H_2O , $\log k$ values from reference 9.

△ - 2.25 M Et_4NBr

■ - 1.0 M $n-Bu_4NBr$

□ - 2.25 M $n-Bu_4NBr$

the effective electrophilicity parameters $E^{12,13}$ for salt solutions could be calculated.

Table 3 presents the E parameters for various salt solutions, calculated using the $\Delta\rho_s^0$ values for the alkaline hydrolysis of phenyl benzoates.

For the purpose of comparison Table 3 presents also the electrophilicity parameters E for salt solutions when the data for the alkaline hydrolysis of phenyl tosylates as well as acidic dissociation of benzoic acids and phenols were used.

From the E and $\Delta\rho_s^0$ values it follows that the influence of tetra-*n*-butylammonium bromide and tetraethylammonium bromide to water is essentially different from that in the case of salts like NaCl and NaClO₄ (and LiCl).

The additions of salts like NaCl and NaClO₄ to water increase medium electrophilicity, whereas the ρ_s^0 value was found to decrease.

At the same time when passing from water to concentrated aqueous *n*-Bu₄NBr and Et₄NBr solutions the ρ_s^0 values were found to increase and the corresponding medium electrophilicity parameters E to decrease in comparison with the same parameter for water⁷.

So, for example, when passing from water to aqueous 7.75 molal tetra-*n*-butylammonium bromide solutions the ρ_s^0 value increases about a unit. Effective electrophilicity for such a medium is comparable with the same parameter for binary mixture H₂O-DMSO(50 M%).

The value of $E=11.2$ for 2.25 molar (corresponds to 6.6 molal) Bu₄NBr solution, found from the hydrolysis phenyl benzoates $\Delta\rho_s^0 = \rho_s^0 - \rho_{H_2O}^0$ value, is comparable with the value of $E = 8.1$ and $E = 11.0$ calculated for 7.75 molal Bu₄NBr solution using the respective pK_a values of benzoic acids and phenols. The values of E for tetra-*n*-butylammonium bromide salt solutions reported in the present work are in good agreement with the same parameters published in the present issue¹⁶.

Figure 4 illustrates the dependence of $\log k$ on ρ_s^0 values for the alkaline hydrolysis of phenyl benzoates in

Table 3

Effective Electrophilicities E for Salt Solutions
Found According to Equation (3)

C_{salt}	E_s	$(E_{\text{H}_2\text{O}} = 21.8)^{13}$
1 M n-Bu ₄ NBr	13.1	
2.25 M n-Bu ₄ NBr (6.6 molal solution)	11.1	
1 M Et ₄ NBr	18.4	
2.25 M Et ₄ NBr	13.8	
3.24 M Et ₄ NBr	14.4	
7.75 molal solution n-Bu ₄ NBr	8.1 ^{III} , 11.0 ^{IIII} , 9.6 ⁷	
5.3 M NaClO ₄ ⁴⁻⁶	27.9,	26.6 ^{IIII}
5.3 M NaCl ⁵	24.4,	23.3 ^{IIII} , 24.0 ^{IIII}
5.4 M LiCl	28.3 ¹⁵	

^{II} Found using the data of acidic dissociation of benzoic acid⁴.

^{III} Found using the data of acidic dissociation of phenols⁴.

^{IIII} Found using the data of alkaline hydrolysis of phenyl tosylates^{6,7}.

~~IIII~~ Found using the data of alkaline hydrolysis of phenyl tosylates when $\Delta f_s^0 = a_{js} \cdot \rho_{\text{H}_2\text{O}}^0$ ⁷.

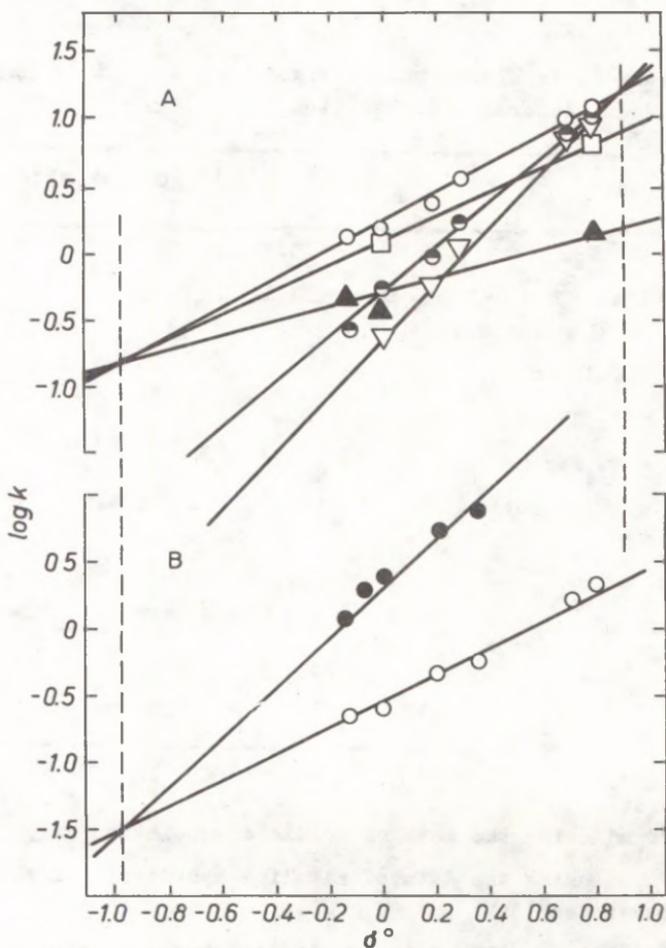


Fig.4. Dependence of $\log k$ on σ° for alkaline hydrolysis of substituted phenyl benzoates $C_6H_5COOC_6H_4-X$ in various media A) at $50^\circ C$ B) at $25^\circ C$

○ $-H_2O$; □ $-5.3 M NaCl^5$; ▲ $-5.3 M NaClO_4^5$;
 ● $-2.25 M Et_4NBr$; ▽ $-2.25 M n-Bu_4NBr$;
 ● $-80\% (volume) aqueous DMSO^8$.

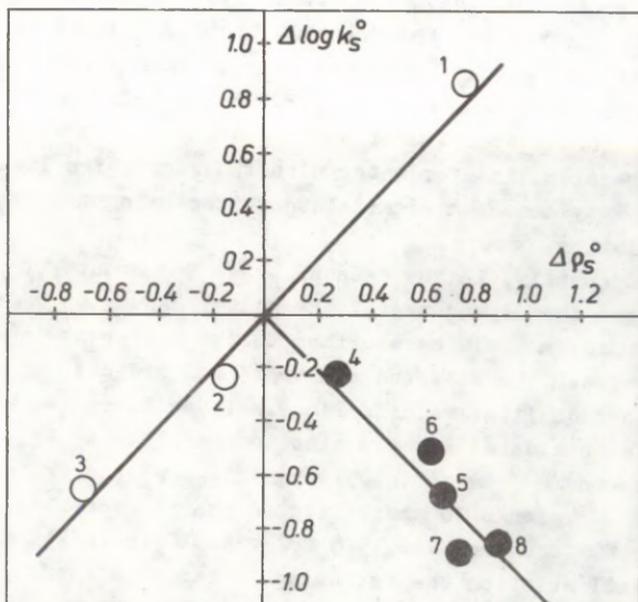


Fig. 5. Dependence of $\Delta \log k_S^0 = \log k_S^0 - \log k_{H_2O}^0$ values on $\Delta \rho_S^0 = \rho_S^0 - \rho_{H_2O}^0$ for alkaline

hydrolysis of phenyl benzoate in various media

1. 80% (volume) aqueous DMSO⁸

2. 5.3 M NaCl⁵

3. 5.3 M NaClO₄⁵

4. 1 M Et₄NBr

5. 2.25 M Et₄NBr

6. 3.24 M Et₄NBr

7. 1 M n-Bu₄NBr

8. 2.25 M n-Bu₄NBr

various media. For the media considered two symmetrical isoparametric points can be observed. The first could be observed at $\hat{\sigma}^0 = -0.95$, the crossing of regression lines for water, 5.3 molar NaCl solution, 5.3 molar NaClO₄ solution and 80% aqueous solution of DMSO.⁸ At $\hat{\sigma}^0 = 0.95$ cross of the regression line for water with the regression lines for tetra-n-butylammonium bromide and tetraethylammonium bromide salt solutions occurs.

Consequently, in the case of these two groups of media considered the dependence of the phenyl benzoates hydrolysis rate on medium could be ascribed to two different interactions between the solvated substrate and medium.

Such a qualitative difference between these two groups of media considered appears also in the $\Delta \log k_S^0$ values dependence on $\Delta \rho_S^0$ (see Fig. 5) where $\Delta \log k_S^0 = \log k_S^0 - \log k_{H_2O}^0$ and $\log k^0$ belongs to unsubstituted phenyl benzoate.

For 80% aqueous DMSO, 5.3 molar NaClO₄ solution and 5.3 molar NaCl solution the following linear relationship takes place:

$$\Delta \log k_S^0 = 0.114(\pm 0.001) + 1.02(\pm 0.01)\Delta \rho_S^0$$

For tetra-n-butylammonium bromide and tetraethylammonium bromide salt solutions the regression line with the slope of the opposite sign was found:

$$\Delta \log k_S^0 = 0.060(\pm 0.111) - 1.12(\pm 0.17)\Delta \rho_S^0.$$

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E_T - PARAMETERS OF AQUEOUS SOLUTIONS OF
SOME STRONG ELECTROLYTES

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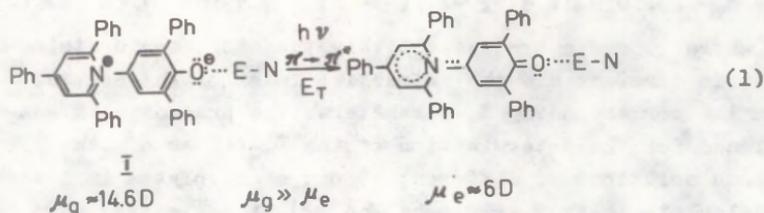
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The E_T - parameters of the gross polarity of the aqueous solutions of some strong electrolytes (Bu_4NBr , $LiCl$, $NaCl$, $NaClO_4$, KBr , Me_4NCl) were determined. It was found that these values depend significantly on the concentration as well as on the nature of the added salt.

It was established that two quaternary ammonium salts - Bu_4NBr and Me_4NCl - drastically (the energy of the long-wavelength $\pi \rightarrow \pi^*$ transition of the pyridinium-N-phenoxide betaine dye drops by 17.9 kcal/mol when water is substituted for the 3.2 M solution of Bu_4NBr) reduce the electrophilicity of water whereas the additions of the rest of the electrolytes lead to the hypsochromic shifts of the E_T -values.

The salt effects of the Bu_4NBr on the UV $n \rightarrow \pi^*$ transitions of acetone and that of Bu_4NBr and some other electrolytes on $\pi \rightarrow \pi^*$ transitions of the picrate-anion were also studied for comparison.

Up to now the E_T -scale of the gross polarity of solvents based on the measurements of the solvatochromic shifts of excitation energies of the long-wavelength absorption maximum of the pyridinium-N-phenoxide betaine dye(I) has been established for a great number of individual and binary solvents (see Refs.1-4 and references therein):



However, as far as we know, still practically untouched⁺ is the problem of the study of the influence of the concentration and chemical nature of various electrolytes on the E_T values of solvents, first of all in aqueous solutions.

On the other hand, the study⁵ of the salt effects on the UV spectra of various classes ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions) shows that the large variations of the concentration and chemical nature of the electrolyte result in rather significant changes of the observed solvating power⁶ (polarity, electrophilicity, etc.) of the solvent itself. In particular, it was shown that the additions of the salts with the relatively small inorganic cations (Li^+ , Na^+ , H^+ , Cs^+ , NH_4^+ , Ca^{2+} , La^{3+} , etc.) lead to the increase of the electrophilic solvating power of water whereas the behavior of the organic tetraalkylammonium cations seemed to be more

⁺ Only the E_T -value for the pure liquid tetrahexylammonium benzoate was reported.¹

complicated⁺

The use of the $\pi \rightarrow \pi^*$ transition of nitrobenzene as a secondary reference served as a base for the preliminary semiquantitative estimates of the electrophilicity E-Parameters⁶ of the aqueous solutions of LiCl and H₂SO₄.

According to the original definition⁶ E-parameters are calculated according to the formula

$$E = E_T - 25.10 - 14.84(\epsilon - 1)/(\epsilon + 2) - 9.59(n^2 - 1)/(n^2 + 2), (2)$$

where ϵ and n are respectively the macroscopic dielectric constant and the refractive index of the solvent from the corresponding E_T -parameters. The present work was designed for the determination of the E_T -values of the aqueous solutions of different strong electrolytes in order to calculate their E-values by Eqn.(2), i.e. on the same scale with the originally⁶ proposed values for the different solvents. The E parameters of these systems are needed also from the viewpoint of some practical considerations. For the sake of comparison with salt effects on the E_T values, the influence of Bu₄NBr on the $n \rightarrow \pi^*$ transitions of acetone and $\pi \rightarrow \pi^*$ transitions of picrate anion was also studied. In both of these cases one might expect^{1,4-6} that the influence of the solvent polarity and electrophilicity would be, in the general features, similar to that in the case of $\pi \rightarrow \pi^*$ transition of the pyridinium-N-phenoxide betaine dye (1).

Experimental

The same sample of pyridinium-N-phenoxide dye as in Ref.4 was used. The salts used were purified by recrystallization from the proper solvents. Meanwhile, the technique recommended by Steigman and Sussman⁸ was used for the purification of Bu₄NBr. The method of consecutive dilutions (by weight) was used for the preparation of the salt solutions of necessary concentration.

⁺ It seems to be firmly established⁷ that the additions of the electrolytes of any nature decrease the static dielectric constant of water.

The concentration of pyridinium-N-phenoxide betaine and picrate-anion was in the range of 10^{-5} - 10^{-4} mole/l and that of acetone about 10^{-3} - 10^{-2} mole/l. As a rule, the addition of small amounts of strong bases (aqueous Bu_4NOH or NaOH) was necessary to guarantee the presence of two of these indicators (betaine dye and picrate) in the anionic form. The solubility of the pyridinium-N-phenoxide betaine in the pure water, as well as in the presence of NaCl , LiCl , KBr , NaClO_4 and Me_4NCl is insufficient for the measurement of its absorption spectrum. Therefore, the study of the salt effects of these electrolytes on the position of the long-wavelength absorption maximum of the pyridinium-N-phenoxide dye was performed in the presence of a relatively small amount of methanol at $N_{\text{MeOH}}=0.218$. The solubility of the betaine dye in the aqueous solutions of Bu_4NBr is, however, sufficient for the corresponding spectral measurements.

The concentrated aqueous solutions of Bu_4NBr are highly viscous liquids. Their density significantly exceeds the density of pure water (e.g., for the 3 molar solution of Bu_4NBr at 50°C $d = 1.046 \text{ g/cm}^3$). The solubility of the much less lipophilic picrate anion in aqueous solutions of other electrolytes was sufficient for the study of its UV-absorption spectrum.

The spectra were recorded using Hitachi EPS-3T spectrophotometer in the thermostated cells (the optical path of the light - 1 cm). The differential technique was used; the solution of the indicator and salt was compared with the blank solution of the aqueous electrolyte of the same concentration.

The results of the experiments are represented in Tables 1-4. The dependence of the halochromic shifts of the spectral transition energies of the indicator studied on the concentration and nature of the electrolytes is shown on Figs. 1-3.

Table 1
Halochromic Shifts of Maxima of Long-Wavelength
Absorption Band of Pyridinium-N-Phenoxide Betaine Dye(I)
in Aqueous Solution of Bu_4NBr at 25, 50 and 75°C.^a

1.	M	m	25°		50°		75°	
			λ_{max}	E_{T}	λ_{max}	E_{T}	λ_{max}	E_{T}
1.	0	0	453	63.1	-	61 ^b	-	59 ^b
2.	0.29	0.31	477	59.9	487	58.7	499	57.3
3.	0.36	0.39	-	-	489	58.4	-	-
4.	0.39	0.43	478	59.8	492	58.1	-	-
5.	0.45	0.50	486	58.8	500	57.2	507.5	56.3
6.	0.61	0.71	494	57.9	503.5	56.8	-	-
7.	0.92	1.20	515	55.5	523	54.7	527	54.3
8.	1.00	1.36	-	-	524	54.6	-	-
9.	1.01	1.40	520	55.0	532 ^c	53.7 ^c	538 ^c	53.1 ^c
10.	1.42	2.40	538	53.1	542	52.7	547	52.3
11.	1.43	2.40	-	-	540	52.9	-	-
12.	1.80	3.83	555	51.5	-	-	-	-
13.	1.86	4.05	-	-	555	51.5	-	-
14.	2.10	5.65	564	50.7	-	-	-	-
15.	2.16	5.93	-	-	566	50.5	-	-
16.	2.36	7.91	576	49.6	577	49.5	-	-
17.	2.54	11.40	587	48.7	-	-	-	-
18.	2.56	11.40	-	-	585	48.9	-	-
19.	2.69	14.80	596	48.0	-	-	-	-
20.	2.88	23.0	614	46.6	613 ^c	46.6 ^c	616 ^c	46.4 ^c
21.	2.90	23.0	-	-	615	46.5	-	-
22.	3.00	30.2	616	46.4	617	46.3	617	46.3
23.	3.20	40.0	-	-	631	45.3	632	45.2

a - λ_{max} is given in nanometer units, E_{T} in kcal/mol.,
M - represents the molar and m the molal concentration of
the salt in H_2O at 25°C. The E_{T} - value for the pure water
(M=m=0) is taken from Refs. 1-3;

b - Extrapolation, this work; c - At M = 1.11; d-At M=2.82.

Table 2

Halochromic Shifts of the Maxima of Long-Wavelength Absorption Band of
 Pyridinium-N-Phenoxide Betaine Dye (1) in Solutions of Some Electrolytes in
 Aqueous Methanol ($N_{\text{MeOH}}=0.218$) at 25°C^a

LiCl			NaCl			NaClO ₄			KBr			Me ₄ NCl			Bu ₄ NBr		
M	λ_{max}	E _T	M	λ_{max}	E _T	M	λ_{max}	E _T	M	λ_{max}	E _T	M	λ_{max}	E _T	M	λ_{max}	E _T
1. 0	483	59.2	0	483	59.2	0	483	59.2	0	483	59.2	0	483	59.2	0	483	59.2
2. 1.29	480	59.6	1.09	482	59.3	0.33	473.5	60.4	0.78	480	59.6	0.42	484	59.1	0.60	508	56.3
3. 1.43	480	59.6	2.10	483	59.2	0.55	472	60.6	0.93	479	59.7	2.06	497	57.5	1.21	522	54.8
4. 2.43	477	59.9	3.10	480	59.6	1.04	468.5	61.0	1.40	479	59.7	2.98	503	56.8	1.66	532	53.7
5. 4.14	472.5	60.5				1.19	468	61.1	1.80	478	59.8						
6. 5.25	469.5	60.9				1.42	467	61.2	2.07	478	59.8						
7. 7.71	463	61.8				1.64	465	61.5	2.22	475	60.2						
8. 8.14	463	61.8				1.81	465	61.5									
						2.51	462	61.9									
						2.97	464	61.6									
						3.79	460	62.2									
						4.82	458	62.3									
						4.94	457.5	62.5									

^a - λ_{max} is given in nanometers, E_T in kcal/mol, M is in moles per liter.

Table 3

Halochromic Shifts of Energies E'_T of $\pi \rightarrow \pi^*$ Transition of Picrate Anion in Aqueous Solutions of Strong Electrolytes.⁹

	Bu ₄ NBr			KBr			LiCl ^b			Me ₄ NCl ^b		
	M	λ_{\max}	E'_T	M	λ_{\max}	E'_T	M	λ_{\max}	E'_T	M	λ_{\max}	E'_T
1.	0	356	80.3	0	356	80.3	0	356	80.3	0	356	80.3
2.	0.45	362	79.0	2.30	359	79.6	2.2	355	80.5	1.63	357	80.1
3.	0.62	363	78.8	4.54	362.5	78.9	4.6	354	80.6	2.44	357	80.1
4.	0.74	364	78.5				7.2	354	80.6	3.25	358	79.8
5.	1.14	369	77.5				9.2	352	81.2	4.07	358	79.8
6.	1.47	371	77.1				11.4	351	81.4	4.89	360	79.4
7.	1.86	372	76.9									
8.	2.19	372.5	76.7									
9.	2.48	372	76.9									
10.	3.00	375	76.2									

a - λ_{\max} is in nanometers, $E'_T = \nu_{\max} (\text{cm}^{-1}) \times 2.859 \times 10^{-3}$ kcal/mol, ν_{\max} is in the reciprocal centimeters, M is in moles per liter

b - Data from Ref. 4.

Table 4
Halochromic Shifts of Energies E_T^H of $n \rightarrow \pi^*$
Transition of Acetone in Aqueous Bu_4NBr ^a

M	λ_{max}	E_T^H	M	λ_{max}	E_T^H		
1.	0	265	107.9	4.	2.27	271.5	105.3
2.	0.81	267	107.1	5.	3.00	274	104.3
3.	1.51	268.5	106.5				

a - λ_{max} is in nanometers, $E_T^H = \nu_{max} (cm^{-1}) \times 2.859 \times 10^{-3}$ kcal/mol., M is in mole/l units.

Discussion

One can see from Tables 1-4 and Figs. 1-3 that the direction as well as the intensity of the halochromic shifts of E_T values of aqueous or aqueous methanolic solutions very strongly depend on the concentration and nature of the electrolytes added. The same is also true for the E_T^I energies of the $\pi \rightarrow \pi^*$ transition of picrate anion and for the $n \rightarrow \pi^*$ transition of acetone.

1. Halochromic Effect of Aqueous Solutions of Tetraalkylammonium Halides on E_T -Parameters

Fig. 1 shows that the additions of Bu_4NBr to aqueous solution of pyridinium-N-phenoxide betaine initiate a very substantial bathochromic shift of frequency of the long-wavelength absorption band of this compound. So, the variation of the concentration of this electrolyte from zero to 3.2 mole/l reduces the energy of the $\pi \rightarrow \pi^*$ transition (1) by almost 18 kcal/mol (or more than 6250 cm^{-1}) which already covers approximately two thirds of all the variation, of the experimentally determined E_T -values! In other words, the additions of Bu_4NBr are able to reduce the gross polarity

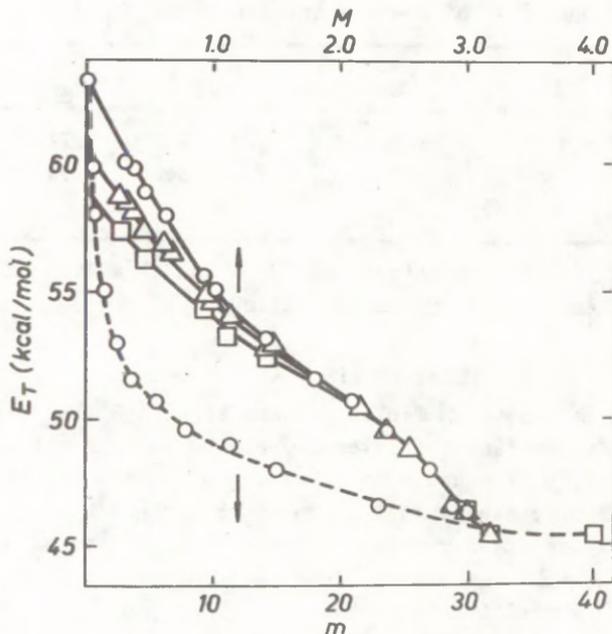


Fig. 1. The dependence of halochromic shifts of E_T -parameters on the molar (M) and molal (m) concentration of Bu_4NBr in water at 25, (\circ), 50 (\triangle), and 75°C (\square). The solid lines refer to the molar concentration of the salt, the dashed line - to the molality of Bu_4NBr .

The plotting of E_T values vs. the square root (\sqrt{M}) of the molar concentration of the salt transfers the present picture into bunch of three straight lines which correspond to three different temperatures and cross at $M=1.8-2.1$ ($\sqrt{M}=1.35-1.45$). At further increase of the salt concentration they become indistinguishable from each other.

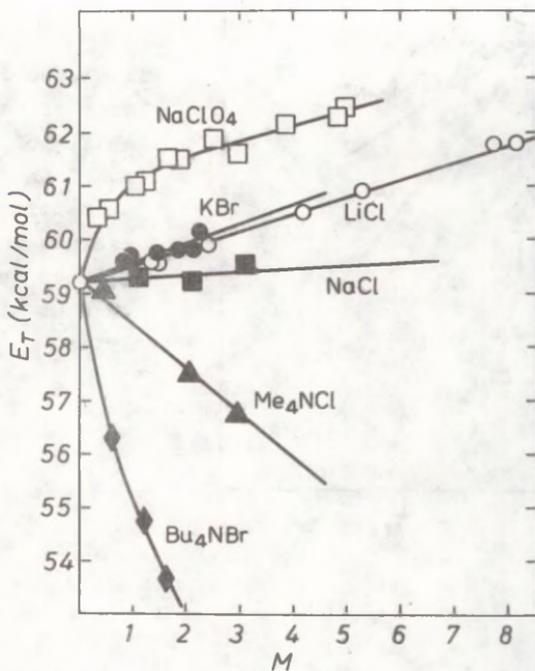


Fig. 2. The dependence of halochromic shifts of E_T - parameters on the molar concentration of some electrolytes in aqueous methanol ($N_{\text{MeOH}}=0.218$) at 25°C .

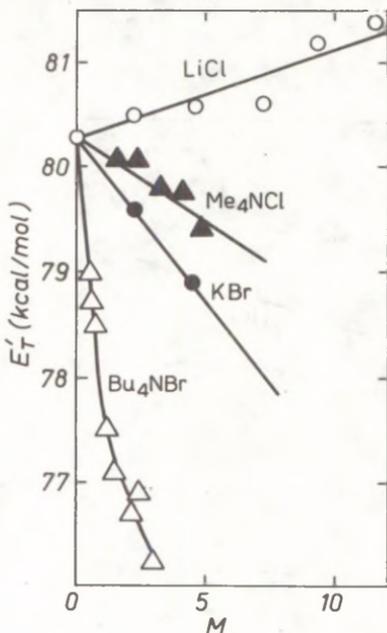


Fig. 3. The dependence of halochromic shifts of energies E_T' of the $\tilde{\pi} \rightarrow \tilde{\pi}^*$ transition of picrate anion in aqueous solutions of some electrolytes.

of water to values which are rather close⁺ to the corresponding values for DMSO ($E_T = 45.0$ kcal/mol)⁴ or acetonitrile ($E_T = 45.7$ kcal/mol)⁴. At least formally, the above-cited facts

+ Quite remarkably, our E_T value (45.2 kcal/mol) for the 3.2 M solution of Bu_4NBr is practically identical to that for the liquid pure $PhCOONHex_4$ (44.3 kcal/mol)¹. It should also be mentioned that the concentration reached for the solution of Bu_4NBr (3.2 M at 50°C) is rather close to the theoretical possible maximum concentration of that salt. In other words, the assumption that the pure (anhydrous) molten Bu_4NBr has the density 1.05-1.06 g/cm³ (see also p. 101) leads to its molarity 3.26-3.29 mole/l.

do not disagree with scheme (1) and Eqn.(2), according to which solvent-solute interactions between betaine dye (1) and medium, including also those modified by the presence of the additions of electrolytes, reduce⁶ to the simultaneous influence of the effects of polarity (represented, e.g., by the function $(\xi-1)/(\xi+2)$ of the dielectric constant of the solvent), polarizability (measured by the function $(n^2-1)/(n^2+2)$ of the refractivity of the given medium) and electrophilicity of the individual (pure) or mixed solvent. In its turn, the simple calculation by Eqn. (2) shows (see Table 5) that despite the rather significant changes in the ξ and n values the above-mentioned huge decrease of E_T -parameters with the increase of the concentration of Bu_4NBr is primarily accounted for by the very substantial decrease of the electrophilicity of the water with the increase of the concentration of that salt. As regards the calculated E -values for this system (see the last column of Table 5) then it is reasonable to exercise some caution. However, even in this case the probable error of their values which is caused by some uncertainty of the procedure of estimation of the contribution of the solvent polarity⁸ does not exceed 1 - 1.5 kcal/mol.

⁸ In the literature⁷ only the dielectric constant of the unimolar aqueous solution of Bu_4NBr is reported. In the present calculations, up to 2 M solution the same rate of the decrease of ξ was assumed (27.7 units of ξ per 1 M). In the range from 2 - 3.2 M the twice lower decrease of ξ by the increase of the concentration of Bu_4NBr was assumed.

Table 5

The Estimation of Contributions of Solvent Polarity ($yY = 14.84(\xi - 1)/(\xi + 2)$), Polarizability ($pP = 9.59(n^2 - 1)/(n^2 + 2)$), and Electrophilicity E of the Aqueous Solution of Bu_4NBr on Gross Solvent Polarity Parameters E_T^a

M	E_T	ξ^b	yY	n^c	pP	E
0	63.1	78.3	14.3	1.333	2.0	21.7
0.5	58.2	(64.5)	14.2	1.358	2.1	16.8
1.0	55.1	50.6 ⁷	14.0	1.383	2.2	13.8
1.5	52.7	(36.8)	13.7	1.410	2.4	11.5
2.0	50.9	(22.9)	13.1	1.433	2.5	10.2
2.25	49.9	(19.5)	12.8	1.447	2.6	9.4
2.35	49.6	(18.1)	12.6	1.453	2.6	9.3 ^d
2.50	48.9	(16.0)	12.4	1.460	2.6	8.8
2.75	47.7	(12.6)	11.8	1.473	2.7	8.1
3.0	46.3	(9.1)	10.8	1.486	2.8	7.6
3.2	45.2	(6.3)	9.5	1.497	2.8	7.8
- 17.9 ^e			-4.8 ^f		+0.8 ^f	-14.1 ^f

- a - E -values are calculated from Eqn. (2) and are given in kcal/mol units.
- b - Estimated values are given in parenthesis; see the text.
- c - This work, 25°C.
- d - In Ref. 9 a rather close E value (9.8 kcal/mol) for this system was suggested on the basis of some indirect data. See also the paper¹⁰ in this issue.
- e - The over-all solvent effect on E_T values on going from pure water to 3.2 M solution of Bu_4NBr .
- f - The over-all contribution of the different types of solvent solute interactions into the gross E_T -values while substituting pure water for 3.2 M solution of Bu_4NBr .

One can see from Table 5 that the decrease of the electrophilicity parameters for the present system is more pronounced at the low and moderate concentrations of Bu_4NBr (up to 1-1.5 M) whereas in the relatively highly concentrated solutions the E-values change at a lower rate.

The nature of the peculiar thermochromic effect the intensity of which^x decreases with the increase of the concentration of the added electrolyte - Bu_4NBr - is complicated. So, one can see from Fig.1 that the intensity of that effect is the highest (up to 2 kcal/mol at $M=0$ for the temperature change by 25°C) for the relatively diluted solutions of Bu_4NBr . With the increase of the concentration of the latter the intensity of the thermochromic effect decreases, and starting approximately from the 2 M solutions of Bu_4NBr the E_T -parameters are practically no longer sensitive to the variation of the temperature factor.

Analogously to the earlier study¹¹ of the thermochromic effect on the solvent E_T -parameters, the increase of the temperature leads also to the decrease of the halochromic effects on those parameters. The latter is, e.g., evidenced by the decrease of E_T -values with the increase of temperature due to the relative destabilization of highly polar and highly basic ground (non-excited) state of the transfer (1) via the decrease of the intensity or even by turning off the solvent-solute interactions of the initial dye with the molecules of electrophiles (hydrogen bond, etc.) or dipolar aprotic solvents.

It seems reasonable to assume that the simplest way to explain the observed dependence of E_T -parameters on the concentration of Bu_4NBr is to accept the hypothesis about the relative destabilization of the solute (dye) molecules, i.e., the ground state of the transition (1) by the additions of Bu_4NBr due to the immobilization and deactivation of the

* As measured by the energy difference between the ordinate of E_T vs. M curves at various fixed concentrations of Bu_4NBr .

water molecules as electrophilically solvating agents via the mechanism^{7,12} of penetration of Bu_4NBr into the three-dimensional clusters of water and by structure-making hydrophobic interactions between the latter and large lyophobic tetraalkylammonium cation. In other words, the substitution of the strong hydrophylic solvation of betaine dye by the molecules of the "ordinary" water for the relatively weak solvent-solute interactions between betaine (1) and water which due to the hydrophobic interactions with quaternary ammonium salts has the increased structuredness is assumed.

A certain role in the variation of the structuredness and solvating power of water belongs also to the bromide anion.¹³

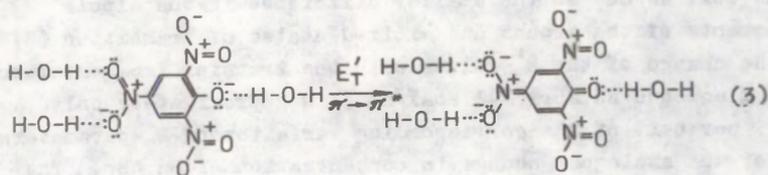
Naturally, these processes result in the significant decrease of the electrophilic solvating power of water (almost down to the level of the electrophilically weakly solvating medium - $t\text{-BuOH}^4$), as well as in the decrease of its dielectric constant (solvent polarity) and in the change of its refractive index (polarizability), which, in their turn, should be responsible for the overall change (decrease) of the gross E_T -values of the medium by the increase of the concentration of Bu_4NBr .¹⁴ One can conclude from Fig. 1 (the pattern of the variation of E_T -values with the concentration of Bu_4NBr and the coincidence of the E_T vs. M plots for different temperatures at high concentrations of that salt) that the transfer from the ordinary three-dimensional water to its state with the reinforced structure will be completed at relatively high concentrations ($> 1.8 - 2.0 M$ solutions) of Bu_4NBr (see Fig. 1 and especially the dependence of E_T -values on the molal concentration of Bu_4NBr).

The latter is in agreement also with the findings¹⁴ which suggest that Bu_4NBr forms the stable clathrate hydrate which involves 14 molecules of water. The further increase of the concentration of Bu_4NBr leads to the additional de-

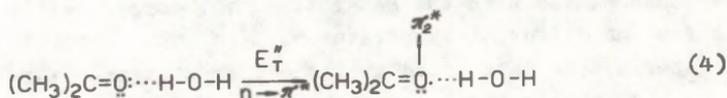
¹⁴ The effect of the direct association of the electrophilic moiety tetrabutylammonium cation - with the anionic betaine according to scheme (1) seems to be negligible.

crease of E_T -values by a few units. However, this is no longer accompanied with the separate E_T vs. concentration plots for the different temperatures. In other words, the E_T -parameters determined at the different temperatures for the high enough fixed concentrations of Bu_4NBr practically coincide with each other. Hence, an inference can be drawn that the intensity of the hydrophilic solvation of the betaine dye by the ordinary water (low concentrations of Bu_4NBr) is more sensitive to the temperature effects than the solvation interactions between that solute and structurally reinforced water (at the high concentrations of Bu_4NBr). The same could be stated also in the alternative way: the temperature of breaking the "normal" hydrogen bonding between the betaine dye and water molecules in relatively dilute aqueous solutions is lower than the temperature necessary for the elimination of the hydrophobic structure-making interactions between water clusters and quaternary ammonium salts at higher concentrations of the latter.

The general pattern of the addition of Bu_4NBr to water on the gross energies E_T' of $\pi \rightarrow \pi^*$ transition (3) of picrate anion (see Fig.3 Table 3, and Ref. 4)



and on the energies E_T'' of the $n \rightarrow \pi^*$ transfer (4) of acetone (see Table 4 and Ref. 4)



is similar to the above-considered case of $\pi \rightarrow \pi^*$ transfer (1) of pyridinium-N-phenoxide betaine. In both cases^{5,6} the decrease of the electrophilicity as well as of the dielectric constant of the solvent should lead to the relative destabilization of the ground state and, therefore, result in the decrease of the energies (E_T' and E_T'') of these transitions (3) and (4). In the case of picrate anion the situation is probably more complicated due to the possibility of the electrophilic solvation by water molecules or other electrophiles EW of three nitro-groups which are located in ortho- and para- positions to the O⁻-group.⁴ This additional solvent-solute interaction should show the counteracting to the electrophilic solvation of the O⁻-group effect and due to its preferred stabilization^{5,6} of the excited state should result in some reduction of the overall energy E_T' of the $\pi \rightarrow \pi^*$ transition (3). Probably on these grounds as well as due to the smaller difference in the dipole moments of the ground and excited states of transition (3) the change of the E_T' -values with the transfer from water to 3 M aqueous Bu₄NBr (4.1 kcal/mol) is approximately only 25 per cent of the corresponding variation of E_T' -parameters for the analogous change in concentration of Bu₄NBr. The decrease of the excitation energies E_T'' of $n \rightarrow \pi^*$ transfer while changing water for 3 M Bu₄NBr is of the same order. The influence of the different contributions of the solvent-solute interactions on the latter process was discussed earlier.^{5,6}

⁴ For the sake of simplicity, the solvation of only one nitro-group is shown on scheme (3)

Concluding the analysis of the dependence of the energies of spectral transfers (1), (3) and (4) in water on the concentration of Bu_4NBr it is necessary to note that the qualitative general pattern of the influence of another electrolyte of that type, Me_4NCl , on these processes is the same: the energies of $\pi \rightarrow \pi^*$ transitions of picrate anion as well as those of $n \rightarrow \pi^*$ transitions of acetone both display⁵ bathochromic shifts.

2. Halochromic Effects on E_T -Parameters in Aqueous Methanol ($N_{\text{MeOH}}=0.218$)

Analogously to the aqueous medium, the addition of Bu_4NBr also induces the significant red shift of the maximum of the long-wavelength $\pi \rightarrow \pi^*$ transfer (1) even in the presence of the relatively small amount of methanol in its binary mixture with water. as a major component. So, in unimolar solution the change in E_T values is 3.9 kcal/mol which is approximately two times lower than the similar shift for the analogous change of the concentration of that salt without the presence of MeOH. The noticeable decrease of the E_T values is also characteristic to the solutions of Me_4NCl where for the change of the salt concentration by 1 M corresponds the reduction of E_T -value by 0.8 kcal/mol. Most probably, these facts evidence that despite that above-mentioned significant decrease of the intensity of the structure-making effect of the quaternary ammonium salts at the presence of 21.8 mole per cent of methanol the substitution of water medium for the aqueous methanol does not change the direction and mechanism of the influence of those salts on the $\pi \rightarrow \pi^*$ transfer of the betaine dye (1).

However, one can see from Fig. 2 that the transfer from the quaternary ammonium salts to the solution of some alkali halides (LiCl , NaCl , KBr) and sodium perchlorate in a radical manner inverts the direction of the observed halochromic effects on E_T values.

In other words, in the latter case the transfer from the aqueous methanol to its concentrated solutions of the above-mentioned inorganic salts already results in the hypsochromic

shifts of the maximum of the long-wavelength absorption band of the $\pi \rightarrow \pi^*$ transfer of pyridinium-N-phenoxide betaine. One can also see that, at the fixed concentration, the change of the quaternary ammonium cation for the small inorganic cation is responsible for the rather significant change in the energy of that spectral transition. So, in the unimolar solutions of Bu_4NBr and KBr , the difference between their E_T -values is 4.3 kcal/mol (in favor of KBr), in the corresponding 2 M solutions of these electrolytes this gap is already 6.8 kcal/mol. Less impressive but still rather definite changes of E_T -parameters occur also for the transfer from Me_4NCl to NaCl and LiCl where the corresponding differences in 2 M solutions are 1.9 and 2.2 kcal/mol (in favor of NaCl and LiCl). On the other hand, the transfer from NaCl to NaClO_4 leads to the comparable change (at 2 M the difference in the E_T -values of their solutions in aqueous methanol is 2.0 kcal/mol) in the gross polarity of the media.

Similar to the above-discussed case of aqueous solutions of Bu_4NBr , it could be shown (see Table 6) in the framework of the formal model represented by Eqn.(2) that the major contribution into the gross halochromic effect ΔE_T in the aqueous methanol also belongs to the change (decrease in the case of Bu_4NBr and Me_4NCl and increase for all other electrolytes considered) of the electrophilic solvating power E caused by the presence of different by their chemical nature electrolytes⁺.

⁺ As in the case of aqueous solutions of Bu_4NBr due to the lack of the experimental data on the dielectric constants and refractivity indexes of the electrolyte solutions of aqueous methanol such a calculation has a nature of rough estimate (see Table 6). However, even in this case, due to the relatively low sensitivity at $\xi > 5$ of $(\xi - 1)/(\xi + 2)$ values⁶ on ξ , and because of the insignificant change of $(n^2 - 1)/(n^2 + 2)$ functions in these systems, the probable uncertainty of the calculated E values hardly exceeds 1-2 kcal/mol.

It is necessary to mention that unlike of the aqueous solutions of quaternary ammonium salts (compare, e.g., with Table 5) the effect of the addition of inorganic salts on the separate contributions of the polarity (dielectric constant) and electrophilicity of the medium shows the opposite, mutually cancelable behavior (see Table 6).

Analogously to the intensity of variation of the electrophilicity parameters of the aqueous Bu_4NBr and aqueous methanolic solution of the same salt, the effect of the addition of LiCl on the E -value of aqueous methanol (3.6 kcal/mol while going into 8 M solution of LiCl) is significantly less pronounced than its effect on the E -parameter of the pure water (according to Ref.5 the E -value of 8 M aqueous LiCl exceeds by 11 kcal/mol the corresponding figure for the pure water).

The mechanism of the mineral salts on the different properties of aqueous solutions seems to be even more complicated than that for the quaternary ammonium salts. It is believed^{7,12} that unlike to the latter the inorganic electrolytes, as a rule, tend to display the water-structure-breaking effect. The overall effect of that type should, naturally, depend on the nature of both the cation and anion. Their strong interaction with the water molecules as building blocks of the three-dimensional clusters of the structured water might destroy the net of the hydrogen bonds between the neighboring molecules of that structure (structure-breaking effect). Simultaneously, as a rule, these processes are accompanied by the increase of the capacity of the molecules of the destructured water to form hydrogen bonds with the other solutes in the given system.(see,however Ref.13 and 15).

So, even the rather primitive ab initio calculation performed in the present work on the STO-3G level shows that the complex-formation of Na^+ ion with one water molecule according to scheme (5)⁸

* On the molecular diagrams the formal Mulliken charges (in the charges of electron) are shown at separate atoms, bond lengths are given in angstrom units, whereas the total energy E_T is given in atomic units .

Table 6

The Estimation of Contributions of Polarity ($yY=14.84(\xi-1)/(\xi+2)$) and Electrophilicity E into the Gross Polarity E_T -Parameters of Solutions of some Strong Electrolytes in Aqueous Methanol ($N_{MeOH}=0.218$).

M	Bu ₄ NBr			Me ₄ NCl			NaCl		
	E_T	yY^b	E	E_T	yY^c	E	E_T	yY^c	E
0	59.2	14.2	17.9	59.2	14.2	17.9	59.2	14.2	17.9
0.5	56.5	14.2	15.2	-	-	-	-	-	-
1.0	55.3	14.0	14.2	58.5	14.2	17.4	59.4	14.2	18.1
1.5	54.2	13.7	13.4	58.0	14.1	16.8	-	-	-
2.0	53.2	13.1	13.0	57.6	14.1	16.4	59.5	14.1	18.3
3.0				56.8	14.0	15.7	59.5	14.0	18.4
4.0							59.6	13.9	18.6
	-6.0	-1.1	-4.9	-2.4	-0.2	-2.2	0.4	-0.3	0.7

- a - E-values are calculated according to Eqn.(2). The dimensions of all quantities given in this Table are in kcal/mol units. The contribution of the medium polarizability ($9.59(n^2-1)/(n^2+2)$) is for all systems taken equal to 2.0 kcal/mol. On the very bottom line of the Table the maximum variations of E_T values as well as those of contributions from medium polarity and electrophilicity are given. The E_T values reported for various values of the molar concentration M of the electrolyte are gotten by interpolation from the E_T vs. M plots in Fig. 2.

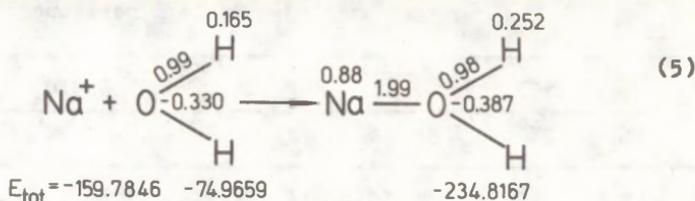
Table 6 continued

M	LiCl			KBr			NaClO ₄		
	E _T	yY ^d	E	E _T	yY ^c	E	E _T	yY ^c	E
0	59.2	14.2	17.9	59.2	14.2	17.9	59.2	14.2	17.9
0.5	-	-	-	-	-	-	60.5	14.2	19.2
1.0	59.5	14.2	18.2	59.6	14.2	18.3	61.0	14.2	19.7
1.5	59.7	14.2	18.4	-	-	-	-	-	-
2.0	59.8	14.1	18.6	60.0	14.1	18.8	61.5	14.1	20.3
3.0	60.2	13.9	19.2	60.3	14.0	19.2	61.9	14.0	20.8
4.0	60.5	13.8	19.6				62.2	13.8	21.3
5.0	60.8	13.6	20.1				62.4	13.6	21.7
6.0	61.2	13.4	20.7						
7.0	61.5	13.3	21.1						
8.0	61.8	13.2	21.5						
	2.6	-1.0	3.6	1.1	-0.2	1.3	3.2	-0.6	3.8

b - The yY values for the aqueous Bu₄NBr were used (see Table 5).

c - The yY values for aqueous NaCl⁷ were used.

d - The yY values for aqueous LiCl⁷ were used.



results in the rather significant change of the Mulliken charge populations on the oxygen, and, especially, on the hydrogen (the increase of the positive charge by 0.087 units) atom.

It is highly probable that alongside with the "indirect" influence via the change of the degree of structuredness and by variation of the electrophilic solvating power of water, the electrophiles E^+ (either free cations E^+ or in the form of the ion-pairs E^+N^- with the anion N^-) can in principle (unlike to the quaternary ammonium salts) change the observed E_T , E_T' , and E_T'' parameters towards their increase² by the direct complex-formation with the solute according to scheme(1). In these terms the increase of the concentration of the mineral salt should shift the solvation equilibrium between the solute and electrophilic component towards the preferred formation of their complexes (relative stabilization of the ground state).

One can see from Table 6 that at the same concentrations of the electrolyte the solutions of NaClO_4 in aqueous methanol display the higher electrophilic solvating power than the corresponding solutions of NaCl . So, in 4M solutions this difference is about 3 kcal/mol which is comparable to the findings of Ref. 9 where it was estimated from the cor-

² In the case of E_T' -values (scheme (3)) KBr somewhat decreases these quantities (bathochromic shift). It is probable that less hard K^+ ion, unlike to Li^+ cation prefers to associate instead of the O^- group with the softer NO_2 group which should result in the overall red shift of the absorption band of the transfer (3) (compare also with Ref. 5).

relation dependence of the ρ^0 -parameters on the electrophilicity parameters that the same gap should be 2.6 kcal/mol in favor of NaClO_4 .

It is possible that the increased electrophilicity of the NaClO_4 solutions is connected with the earlier⁷ noticed capacity of perchlorate anion to break the structure of water clusters. On the other hand, the IR spectroscopy data² on the aqueous solutions of NaClO_4 and the results of the non-empirical quantum-chemical calculations¹⁵ of the hydration complexes of perchlorate ion indicate that the latter shows only a slight trend to form relatively unstable hydrates.

It is also not excluded that the relatively high electrophilicity of NaClO_4 solution (relative to aqueous NaCl) is due to the practically negligible capacity of perchlorate anion to form associates with Na^+ cation. This, in its turn, should result in the enhanced electrophilic stabilization of the ground state of the betaine dye (I) by "free" hydrated sodium cations.¹³

3. Halochromic Shifts of R_T -Parameters in Dimethylsulfoxide

It is evident from the previous sections of this work that the observance of halochromic effects of quaternary ammonium salts as well as inorganic electrolytes is closely related to the influence of the ions on the three-dimensional structure of water clusters by their structure-making or structure-breaking abilities which, in the end, result in the behavior of the indicator of the gross polarity of the media - betaine dye (1).

The structure of the DMSO solutions is probably quite different from that of water. According to the widespread viewpoint¹⁶ the molecules of DMSO are associated into long chain-like polymers for which at least the above-described mechanism of the structure-making seems to be unappropriate. Indeed, the results of our experiments show that in the anhydrous DMSO the influence of quaternary ammonium salt - Bu_4NBr - is almost negligible, whereas NaClO_4 , by the analogy with aqueous solutions, causes the hypsochromic shift of the

E_T -parameter. Analogously, significantly less pronounced blue shift of the absorption maximum of the $\pi \rightarrow \pi^*$ transfer (1) is present also in the DMSO solutions of Et_4NClO_4 , Bu_4NClO_4 , KBr , etc.

The full account of the results of these as well as some other experiments on the influence of the concentration and the nature of several electrolytes in nonaqueous media will be given in one of the future communications.

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13. In principle, the penetration of the electrolyte into the structure of water could be accompanied by the hydrophilic interaction between anion and water molecules. The smaller the ionic radius of the anion and the higher the charge density on its hydration center the higher will be the intensity of this interaction. Simultaneously, the binding of the molecules of water with the anions added reduces the activity of the water molecules as donors of the hydrogen bond. That, in its turn, should result in a certain reduction of the solvent-solute interactions between the anionic solute (e.g. betaine dye (I) and water molecules as electrophiles.

Larger anions with the high degree of charge delocalization (ClO_4^- , tosylate, picrate, etc.) are less inclined towards that kind of hydration. Therefore, assuming the influence of all other factors being the same, one might expect that in this case the reduction of the electrophilicity of water as a solvent will be the smallest. Simultaneously, the association of such an anion with the cation is most probably also suppressed (See also p.121).

An interesting viewpoint on the role of anion in case of aqueous solutions of quaternary ammonium salts is presented in Y.A. Mirgorod, S.I. Sivakova, Zh. Strukt. Khimii., 20, 612 (1979).

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