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DOMBI J., GYULAI J. és KETSKEMÉTY I.

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SPLITTING OF d^n- TERMS OF TETRAGONAL COMPLEXES IN STRONG FIELDS

By F. J. GILDE
Institute of Theoretical Physics, The University, Szeged
and
M. I. BÁN
Institute of General and Physical Chemistry, The University, Szeged

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The *d*-electrons of the central ion play an important role at the development of the properties of complex compounds. In this paper, all the strong field configurations arising from d^n-configurations ($n = 1, \dots 10$) in the complex field of D_{4h} symmetry have been calculated. The irreducible representations and the multiplicity of the splitting products of these terms have been established.

§ 1. *Introduction*

BETHE [1] investigated the splitting of terms of ions in crystals for the first time. He founded the „crystal field method" in 1929 which is also applicable for the theoretical treatment of complex ions. SCHLAPP and PENNEY [2] have used this theory for the calculation of magnetic susceptibilities of crystals containing paramagnetic ions, while FINKELSTEIN and VAN VLECK [3] employed it for the interpretation of the spectrum of chrome alaun in crystalline state. On applying BETHE's crystal field method for electrostatic complexes it is usual to start from the model outlined below. According to the basic assumption of the method the complex ion consists of a central ion being surrounded by the coordination zone. The central ion is a core surrounded by *d*-electrons while the coordination zone is a point charge system or point dipole system having a well-defined geometric shape.

In the approximation suitable for the model one usually considers the interactions among the individual parts. These are as follows: (i) the interaction of the outer electrons of the central ion and (ii) the influence of the coordination zone (complex field) on the outer electrons of the central ion. These interactions can be conceived as representing perturbations. In such calculations the final aim is to determine the wave functions and energy levels of the electrons considered. According to the relative size of the interactions considered[1] one can take steps in two different manners.

1. *Weak field case.* When the influence of the complex field on the outer electrons of the central ion is less than the interaction of these electrons among themselves; there exists a weak field. In such a case, in the first approximation disregarding the influence of the complex field only the interactions of the electrons will be taken into account. Thus, in this approximation, the model is reduced to the problem of the spectroscopic gaseous ion. Then the corresponding RUSSEL—SAUNDERS terms are obtained as energies. In the second approximation, due to the perturbation caused by the complex field, the RUSSEL—SAUNDERS terms split.

2. *Strong field case.* Whenever the influence of the complex field is greater than the mutual interaction of the outer electrons of the central ion; there exists a strong field. As then the complex field is strong the state of the outer electrons of the central ion is modified already before affecting the mutual interaction of the electrons. Hence the strong complex field completely or partly removes the degeneracy of the terms. The mutual interactions of the outer electrons must be investigated taking into account the splitting mentioned above. The configurations obtained in this manner split in the complex field.

ILSE and HARTMANN [4] were in 1951 the first to apply for complex ions the weak field approximation of BETHE's theory. Since this time many authors [5] have dealt with similar problems.

For the interpretation of spectra of transition metal complexes the strong field approximation was applied by ORGEL [6]. Subsequently TANABE and SUGANO [7] and ORGEL [8] have elaborated the theory for octahedral complexes of d^n configurations completely. JØRGENSEN [9] has supplied the size of the splittings of all the d^n-terms in strong fields of O_h symmetry. KISS [10] was one of the first who applied these results for the interpretation of spectra. Since then they are used by numerous other authors for the interpretation of spectroscopic [11], [15] and magnetic [12] phenomena.

In most cases O_h symmetry has been assumed, though this means the extreme simplification of the problem considered. Actually, however, a lower symmetry exists. Sometimes already at the beginning the symmetry is not cubic [3], [6], [13], in other cases owing to the JAHN—TELLER effect distortion takes place. Thus *e. g.* JØRGENSEN [14] has stated that a complex of d^4 and d^9 configurations having six identical ligands with cubic symmetry cannot be stable and therefore the cubic symmetry distorts to tetragonal and in the case of d^1 configuration to rhombic. Considering that the complex compounds which are in the centre of spectroscopic interest have lower symmetries than

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[1] At this point we have to draw attention to the circumstance that we ought still to examine how, owing to the effect of the complex field, the core changes and how this modified core influences the state of the outer electrons. With regard to these problems which appear only in the course of numerical calculations and even then cause changes only in the radial part of the wave functions of the electrons considered, nevertheless, we ought only to deal with these problems if we want to calculate the integrals occurring in the course of the calculation explicitly.

O_h, it seems to be necessary to determine the splittings caused by strong fields of lower symmetries. Such calculations were hitherto only carried out for the case of D_{4h} symmetry [15], however, only the splittings of some strong field configurations for d^6 electron configuration were determined. Under these circumstances it seems necessary to extend these examinations to the other important cases. Therefore, in this paper, to investigate the splitting of d^n configurations ($n=1, 2, \ldots 10$) in complex fields having D_{4h} symmetry the strong field approximation will be applied.

§ 2. *The classification of energy terms corresponding to the symmetry properties of the complex*

It is known that there exist five d wave functions independent linearly of one another, the linear combinations of which belonging to each irreducible representation of the point group D_{4h} will be determined. Accordingly, the five-dimensional space of the d-functions breaks up into sub-spaces being invariant under the operations of the D_{4h} group. Let us designate with Γ_d the representation of the D_{4h} group which is valid in the five-dimensional reducible space, it will be broken up into irreducible representations as follows:

$$\Gamma_d = A_{1g} + B_{1g} + B_{2g} + E_g . \tag{1}$$

In Table I the character system of D_{4h} group is given. In this, the irreducible representations are denoted as usual (*e. g.* [16]).

In the case of a complex field having D_{4h} symmetry one d-electron, in accordance with (1), can stay in four different states. According to the PAULI exclusion principle, two electrons can stay in the states represented by wave functions[2] denoted by a_{1g}, b_{1g} and b_{2g} and four electrons can stay in e_g.

In the case of d^n configurations, apart from the case $n=1$, a many-electron problem has to be dealt with. Thus, to consider the interactions of d-electrons we have to start from many-electron wave functions which can be represented in the usual way as products of one-electron functions. In making these products, of course, the PAULI principle is to be considered and corresponding with the strong field approximation not the original d-functions but the functions suitable for (1) are used. In this manner, the possible configurations of the strong field (strong field configurations) can be obtained. The spaces of the functions belonging to each configuration of the strong field are generally reducible. Since the d-functions contain the coordinates on even power, the reducible spaces can have irreducible components (splitting products or sub-levels) of g type only. The same holds for spaces spanned by linear combinations or products of functions of d-type, respectively. These reducible spaces are to be reduced according to D_{4h}.

In the first place, the number of the functions belonging to each configuration, *i. e.* the total sum of degeneracy numbers should be determined.

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[2] In the following the wave function belonging to a Γ representation will be correspondingly denoted by γ and this γ will be called the function of Γ or γ function as well.

In a state belonging to a j-dimensional irreducible representation $2j$ electrons can stay. If the number of the filled states is k the total sum of degeneracy numbers is given by the formula

$$\frac{(2j)!}{(2j-k)!\cdot k!}. \tag{2}$$

Whenever wave functions of different irreducible representations take part in a given configuration the total sum of the degeneracy numbers is the product of the degeneracy numbers of the states belonging to each configuration. The dimension of the space of the functions belonging to each configuration corresponds to the total sum of degeneracy numbers of the configuration involved. If one knows the total sum of the degeneracy numbers the number and the multiplicity of states belonging to a given configuration may be calculated. To determine the irreducible representations to which these states belong the reduction mentioned above must be carried out in the space of the configurations. To accomplish this the trace system of the representations attained in the reducible space is required. If there is a configuration which comprises only the functions of one-dimensional irreducible representations the traces wanted are given by a product. The factors of this product are the square or the double of the characters if the filling number is 2 or 1, respectively. If, in turn, there are configurations comprising wave functions of multi-dimensional irreducible representations too the question is much more complicated. There appear configurations containing (e_g) and $(e_g)^3$; their traces are equal, on the other hand, as the degeneracy number of the state e_g is 4 the corresponding traces are the double of the characters of representation E_g. Similarly there occur configurations containing $(e_g)^2$ too. In order to determine the traces of the representation belonging to these

Table I

D_{4h}	E	C_2	$2C_4$	$2C_2'$	$2C_2''$	i	iC_2	$2iC_4$	$2iC_2'$	$2iC_2''$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
B_{1g}	1	1	−1	1	−1	1	1	−1	1	−1
B_{1u}	1	1	−1	1	−1	−1	−1	1	−1	1
B_{2g}	1	1	−1	−1	1	1	1	−1	−1	1
B_{2u}	1	1	−1	−1	1	−1	−1	1	1	−1
E_g	2	−2	0	0	0	2	−2	0	0	0
E_u	2	−2	0	0	0	−2	2	0	0	0
$(e_g)^2$	6	6	2	−2	−2	6	6	2	−2	−2

configurations antisymmetrized functions of type $(e_g)^2$ should be formed. Since $j = 2$, $k = 2$, according to (2) the number of the functions is 6. The traces of the representation obtained in the space of these six functions may be got by studying the behaviour of these functions under the symmetry operations of the D_{4h} group (Table I, last row).

The reductions can be performed by means of traces obtained by the above consideration. If these reductions are known, in most cases it can directly be established to which irreducible representations the already counted terms arising from the splitting belong and their multiplicities may also be calculated. In cases, when a configuration breaks up into functions of irreducible representations of various kinds in the above procedure there remains uncertainty. Under these circumstances, BETHE's method is used for establishing the multiplicities. The essence of this method is that the configurations containing the functions of multi-dimensional irreducible representations split into configurations composed of functions of pure one-dimensional representations by diminishing the symmetry. The multiplicity is given directly. In addition the irreducible representation of the group of lower symmetry, to which the state of multiplicity already known belongs, can be determined. One or two irreducible representations correspond to this representation in D_{4h} symmetry. Nevertheless, this method was also unsuccessful. For this reason BETHE's method has been developped by diminishing the symmetry in several different ways. Then the alternatives obtained in different manners were compared. However, we succeeded in obtaining perfect results by making use of the above reduction.

BETHE's procedure outlined previously can be meglected on applying the following — though rather lengthy, but far more direct — considerations. After determining the terms arising from the reduction new functions which span the subspaces invariant under the symmetry operations of D_{4h} group in the space of the configuration should be formed. If these new functions are known the multiplicities wanted are afforded directly.

§ 3. *Summary of results*

In the manner described in § 2 the terms[3] arising from the splitting of the configurations d^1—d^{10} have been determined. The splitting products are the same in configurations d^n and d^{10-n}. The splitting of the configurations d^1 and d^9, respectively, is given by (1). The d^{10} configuration $[(e_g)^4 (a_{1g})^2 (b_{1g})^2 (b_{2g})^2]$ consists of a single term $^1A_{1g}$. The other results are listed in Tables II, III, IV and V. The division of the Tables is as follows. In the first column, one can find the possible strong field configurations of the d^n electron configurations. In the second one, the total sum of degeneracy numbers of each configuration is denoted. In the third, the number of the splitting products grouped according to their irreducible representations and their multiplicities are given. In the last column, the strong field configurations of

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[3] Hereafter referred as to "splitting products" or "sub-levels".

Table II*

d^2	Total sum of $d.n.$	A_{1g}		A_{2g}		B_{1g}		B_{2g}		E_g		d^8
		1	3	1	3	1	3	1	3	1	3	
$(e_g)^2$	6	1			1	1		1				$(a_{1g})^2 (b_{1g})^2 (b_{2g})^2 (e_g)^2$
$(a_{1g})^2$	1	1										$(b_{1g})^2 (b_{2g})^2 (e_g)^4$
$(b_{1g})^2$	1	1										$(a_{1g})^2 (b_{2g})^2 (e_g)^4$
$(b_{2g})^2$	1	1										$(a_{1g})^2 (b_{1g})^2 (e_g)^4$
$(a_{1g}) (b_{1g})$	4					1	1					$(a_{1g}) (b_{1g}) (b_{2g})^2 (e_g)^4$
$(a_{1g}) (b_{2g})$	4							1	1			$(a_{1g}) (b_{1g})^2 (b_{2g}) (e_g)^4$
$(b_{1g}) (b_{2g})$	4			1	1							$(a_{1g})^2 (b_{1g}) (b_{2g}) (e_g)^4$
$(a_{1g}) (e_g)$	8									1	1	$(a_{1g}) (b_{1g})^2 (b_{2g})^2 (e_g)^3$
$(b_{1g}) (e_g)$	8									1	1	$(a_{1g})^2 (b_{1g}) (b_{2g})^2 (e_g)^3$
$(b_{2g}) (e_g)$	8									1	1	$(a_{1g})^2 (b_{1g})^2 (b_{2g}) (e_g)^3$

Table III**

d^3	Total sum of $d.n.$	A_{1g}		A_{2g}		B_{1g}		B_{2g}		E_g		d^7
		2	4	2	4	2	4	2	4	2	4	
$(e_g)^3$	4									1		$(a_{1g})^2 (b_{1g})^2 (b_{2g})^2 (e_g)$
$(a_{1g})^2 (b_{1g})$	2					1						$(b_{1g}) (b_{2g})^2 (e_g)^4$
$(a_{1g})^2 (b_{2g})$	2							1				$(b_{1g})^2 (b_{2g}) (e_g)^4$
$(b_{1g})^2 (a_{1g})$	2	1										$(a_{1g}) (b_{2g})^2 (e_g)^4$
$(b_{1g})^2 (b_{2g})$	2							1				$(a_{1g})^2 (b_{2g}) (e_g)^4$
$(b_{2g})^2 (a_{1g})$	2	1										$(a_{1g}) (b_{1g})^2 (e_g)^4$
$(b_{2g})^2 (b_{1g})$	2					1						$(a_{1g})^2 (b_{1g}) (e_g)^4$
$(a_{1g})^2 (e_g)$	4									1		$(b_{1g})^2 (b_{2g})^2 (e_g)^3$
$(b_{1g})^2 (e_g)$	4									1		$(a_{1g})^2 (b_{2g})^2 (e_g)^3$
$(b_{2g})^2 (e_g)$	4									1		$(a_{1g})^2 (b_{1g})^2 (e_g)^3$
$(e_g)^2 (a_{1g})$	12	1		1	1	1		1				$(a_{1g}) (b_{1g})^2 (b_{2g})^2 (e_g)^2$
$(e_g)^2 (b_{1g})$	12	1		1		1		1	1			$(a_{1g})^2 (b_{1g}) (b_{2g})^2 (e_g)^2$
$(e_g)^2 (b_{2g})$	12	1		1		1	1	1				$(a_{1g})^2 (b_{1g})^2 (b_{2g}) (e_g)^2$
$(a_{1g})(b_{1g}) (b_{2g})$	8			2	1							$(a_{1g}) (b_{1g}) (b_{2g}) (e_g)^4$
$(e_g) (a_{1g}) (b_{1g})$	16									2	1	$(a_{1g}) (b_{1g}) (b_{2g})^2 (e_g)^3$
$(e_g) (a_{1g}) (b_{2g})$	16									2	1	$(a_{1g}) (b_{1g})^2 (b_{2g}) (e_g)^3$
$(e_g) (b_{1g}) (b_{2g})$	16									2	1	$(a_{1g})^2 (b_{1g}) (b_{2g}) (e_g)^3$

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* In the third column the numbers 1 and 3 mean the multiplicities of the terms.

** In the third column the numbers 2 and 4 mean the multiplicities of the terms.

Table IV*

d^4	Total sum of *d. n.*	A_{1g}			A_{2g}			B_{1g}			B_{2g}			E_g			d^6
		1	3	5	1	3	5	1	3	5	1	3	5	1	3	5	
$(e_g)^4$	1	1															$(a_{1g})^2 (b_{1g})^2 (b_{2g})^2$
$(e_g)^3 (a_{1g})$	8													1	1		$(e_g) (a_{1g}) (b_{1g})^2 (b_{2g})^2$
$(e_g)^3 (b_{1g})$	8													1	1		$(e_g) (a_{1g})^2 (b_{1g}) (b_{2g})^2$
$(e_g)^3 (b_{2g})$	8													1	1		$(e_g) (a_{1g})^2 (b_{1g})^2 (b_{2g})$
$(a_{1g})^2 (b_{1g})^2$	1	1															$(e_g)^4 (b_{2g})^2$
$(a_{1g})^2 (b_{2g})^2$	1	1															$(e_g)^4 (b_{1g})^2$
$(b_{1g})^2 (b_{2g})^2$	1	1															$(e_g)^4 (a_{1g})^2$
$(e_g)^2 (a_{1g})^2$	6	1				1		1			1						$(e_g)^2 (b_{1g})^2 (b_{2g})^2$
$(e_g)^2 (b_{1g})^2$	6	1				1		1			1						$(e_g)^2 (a_{1g})^2 (b_{2g})^2$
$(e_g)^2 (b_{2g})^2$	6	1				1		1			1						$(e_g)^2 (a_{1g})^2 (b_{1g})^2$
$(a_{1g})^2 (b_{1g}) (b_{2g})$	4				1	1											$(e_g)^4 (b_{1g}) (b_{2g})$
$(b_{1g})^2 (a_{1g}) (b_{2g}$	4										1	1					$(e_g)^4 (a_{1g}) (b_{2g})$
$(b_{2g})^2 (a_{1g}) (b_{1g})$	4							1	1								$(e_g)^4 (a_{1g}) (b_{1g})$
$a_{1g})^2 (e_g) (b_{1g})$	8													1	1		$(e_g)^3 (b_{1g}) (b_{2g})^2$
$(a_{1g})^2 (e_g) (b_{2g})$	8													1	1		$(e_g)^3 (b_{1g})^2 (b_{2g})$
$(b_{1g})^2 (e_g) (a_{1g})$	8													1	1		$(e_g)^3 (a_{1g}) (b_{2g})^2$
$(b_{1g})^2 (e_g) (b_{2g})$	8													1	1		$(e_g)^3 (a_{1g})^2 (b_{2g})$
$(b_{2g})^2 (e_g) (a_{1g})$	8													1	1		$(e_g)^3 (a_{1g}) (b_{1g})^2$
$(b_{2g})^2 (e_g) (b_{1g})$	8													1	1		$(e_g)^3 (a_{1g})^2 (b_{1g})$
$(e_g)^2 (a_{1g}) (b_{1g})$	24	1	1		1	1		1	1		1	2	1				$(e_g)^2 (a_{1g}) (b_{1g}) (b_{2g})^2$
$(e_g)^2 (a_{1g}) (b_{2g})$	24	1	1		1	1		1	2	1	1	1					$(e_g)^2 (a_{1g}) (b_{1g})^2 (b_{2g})$
$(e_g)^2 (b_{1g}) (b_{2g})$	24	1	2	1	1	1		1	1		1	1					$(e_g)^2 (a_{1g})^2 (b_{1g}) (b_{2g})$
$(a_{1g}) (b_{1g}) (b_{2g}) (e_g)$	32													2	3	1	$(e_g)^3 (a_{1g}) (b_{1g}) (b_{2g})$

the corresponding d^{10-n} configurations are displayed. The splitting products of the strong field configurations are, of course, equal regarding their numbers and multiplicities to the splitting products of the RUSSEL—SAUNDERS terms.

§ 4. *Some generalizing remarks*

Considering the even character of the functions used the above results are directly transmissible by omitting the suffix *g* to the cases of complex fields possessing symmetries D_4, C_{4v} and D_{2d} too. The above considerations

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* In the third column the numbers 1, 3 and 5 mean the multiplicities of the terms.

Table V*

d^5	Total sum of $d. n.$	A_{1g}			A_{2g}			B_{1g}			B_{2g}			E_g		
		2	4	6	2	4	6	2	4	6	2	4	6	2	4	6
$(e_g)^4 (a_{1g})$	2	1														
$(e_g)^4 (b_{1g})$	2							1								
$(e_g)^4 (b_{2g})$	2										1					
$(e_g)^3 (a_{1g})^2$	4													1		
$(e_g)^3 (b_{1g})^2$	4													1		
$(e_g)^3 (b_{2g})^2$	4													1		
$(a_{1g})^2 (b_{1g})^2 (b_{2g})$	2										1					
$(a_{1g})^2 (b_{2g})^2 (b_{1g})$	2							1								
$(b_{1g})^2 (b_{2g})^2 (a_{1g})$	2	1														
$(a_{1g})^2 (b_{1g})^2 (e_g)$	4													1		
$(a_{1g})^2 (b_{2g})^2 (e_g)$	4													1		
$(b_{1g})^2 (b_{2g})^2 (e_g)$	4													1		
$(e_g)^2 (a_{1g})^2 (b_{1g})$	12	1			1			1			1	1				
$(e_g)^2 (a_{1g})^2 (b_{2g})$	12	1			1			1	1		1					
$(e_g)^2 (b_{1g})^2 (a_{1g})$	12	1			1	1		1			1					
$(e_g)^2 (b_{1g})^2 (b_{2g})$	12	1			1			1	1		1					
$(e_g)^2 (b_{2g})^2 (a_{1g})$	12	1			1	1		1			1					
$(e_g)^2 (b_{2g})^2 (b_{1g})$	12	1			1			1			1	1				
$(a_{1g})^2 (b_{1g}) (b_{2g}) (e_g)$	16													2	1	
$(b_{1g})^2 (a_{1g}) (b_{2g}) (e_g)$	16													2	1	
$(b_{2g})^2 (a_{1g}) (b_{1g}) (e_g)$	16													2	1	
$(e_g)^2 (a_{1g}) (b_{1g}) (b_{2g})$	48	3	3	1	2	1		2	1		2	1				
$(e_g)^3 (a_{1g}) (b_{1g})$	16													2	1	
$(e_g)^3 (a_{1g}) (b_{2g})$	16													2	1	
$(e_g)^3 (b_{1g}) (b_{2g})$	16													2	1	

naturally do not depend on the concrete form of the function system used in a given approximation. In the course of the calculations group theoretical considerations were adapted everywhere. Thus the results obtained are quite exact. For the explanation of the spectra of diamagnetic and anomalously paramagnetic complexes this method of strong field approximation can be used with good results. According to PAULING the diamagnetic complexes are covalent, hence according to the statement of STEVENS [17] the strong

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* In the third column the numbers 2, 4 and 6 mean the multiplicities of the terms.

field model can be regarded to be formally equivalent to the covalent model. Consequently the given results can be used in a wide circle of complexes.

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GENERAL MAGNETIC FIELD OF THE SUN — BASED ON MAGNETOGRAMS I

By I. K. CSADA

Institute of Theoretical Physics, The University, Szeged

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The magnetograms made in the Mount Wilson Observatory, the present of H. W. BABKOCK, are investigated. In the first part the mathematical background of the suggested statistical method is summarized, a practical method is presented, furthermore, a numerical prototype is investigated and some preliminary conclusions are suggested.

§ 1. *Introduction*

As is well known the magnetograms show the components of the photospheric magnetic field in the line of sight consisting of the superposition of the general and random field, respectively. The average of the latter vanishes, therefore, the mean value of the photospheric field determines the general field. A suitable way for the determination of the mean values seems to be the calculation of the integral of the magnetic curves along the horizontal traces across the solar disc on a magnetogram from the west limb to the east one. These integrals give, however, only the average of the general field in relation to these lines, therefore, the determination of the characteristics of the general field can be explained only by further analysis of the magnetograms.

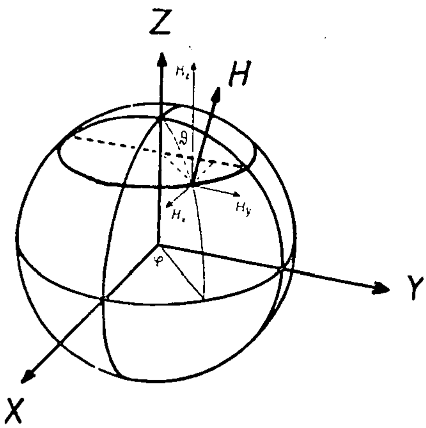

Fig. 1

§ 2. *The components of the general field in the line of sight*

1. Let the general magnetic field be represented by the scalar potential as follows

$$\Phi = \sum \frac{n h_n P_n(\cos\vartheta)}{r^{n+1}}. \tag{1}$$

A system of axes X, Y, Z may be introduced (see Fig. 1) in such a way that the X axis is oriented toward the observer (to Earth), Z to north along the central meridian, and the axis Y to east. The components of the magnetic field in this system are:

$$\mathfrak{H}_x = -\frac{\partial \Phi}{\partial r} \sin \vartheta \cos \varphi - \frac{1}{r} \frac{\partial \Phi}{\partial \vartheta} \cos \vartheta \cos \varphi$$

$$\mathfrak{H}_y = -\frac{\partial \Phi}{\partial r} \sin \vartheta \sin \varphi - \frac{1}{r} \frac{\partial \Phi}{\partial \vartheta} \cos \vartheta \sin \varphi$$

$$\mathfrak{H}_z = -\frac{\partial \Phi}{\partial r} \cos \vartheta + \frac{1}{r} \frac{\partial \Phi}{\partial \vartheta} \sin \vartheta$$

Applying (1) and using some recurrence formulae [1] the expansions

$$\mathfrak{H}_x = \sum \frac{n h_n}{r^{n+2}} P_{n+1}^{(1)} \cos \varphi, \quad \mathfrak{H}_y = \sum \frac{n h_n}{r^{n+2}} P_{n+1}^{(1)} \sin \varphi, \quad \mathfrak{H}_z = \sum \frac{n(n+1) h_n}{r^{n+2}} P_{n+1} \quad (2)$$

can be obtained.

In the magnetograms the horizontal lines correspond to the orthogonal projections of the circle $\varphi = const.$ on the XZ plane. The averages along these circles correspond to an integration of the traces between the limits $-\pi/2$ and $+\pi/2$ divided by the length of the zero-line. This means that

$$\overline{\mathfrak{H}} = \frac{1}{\pi r_\odot \sin \vartheta} \int_{-\pi/2}^{+\pi/2} \mathfrak{H} r_\odot \sin \vartheta \, d\varphi.$$

Taking the average of (2) after some calculations one obtains simply that

$$\overline{\mathfrak{H}}_x = \frac{2}{\pi} \sum \frac{n h_n}{r^{n+2}} P_{n+1}^{(1)}, \quad \overline{\mathfrak{H}}_y = 0, \quad \overline{\mathfrak{H}}_z = \frac{2}{\pi} \sum \frac{n(n+1) h_n}{r^{n+1}} P_{n+1}. \quad (3)$$

In the following we have only to take component $\overline{\mathfrak{H}}_x$ into account as it is the observed one. If on the two hemispheres the magnetic properties are opposite the odd terms of (1) vanish and the remaining first two terms of $\overline{\mathfrak{H}}_x$ will be:

$$\frac{\pi}{2} \overline{\mathfrak{H}}_x = \frac{h_1}{r^3} P_2^{(1)} (\cos \vartheta) + \frac{3 h_3}{r^5} P_4^{(1)} (\cos \vartheta)$$

or introducing the nondimensional parameter $h = h_3/(h_1 r_\odot^2)$

$$\frac{\pi}{2} \overline{\mathfrak{H}}_x = \frac{h_1}{r^3} \left[P_2^{(1)} (\cos \vartheta) + 3h \frac{r_\odot^2}{r^2} P_4^{(1)} (\cos \vartheta) \right] \quad (4)$$

can be obtained which will be the fundamental expression for the practical interpretation.

2. In the above it was implicitly assumed that the magnetic axis coincides with the axis Z. In the case of a more general discussion one has also to take the annual deviations of the solar axis from the axis Z into account.

One can substitute $\cos\vartheta$ by $\cos\vartheta'$ for which

$$\cos\vartheta' = \cos\vartheta\cos q + \sin\vartheta\sin q\cos(\varphi - \Phi)$$

holds, where q and Φ are the polar coordinates of the north solar pole in the system X, Y, Z.

Owing to the additional theorem of the Legendre functions [2]

$$P_n(\cos\vartheta') = P_n(\cos\vartheta)\,P_n(\cos q) +$$
$$+ 2\sum_{m=1}^{n}\frac{(n-m)!}{(n+m)!}P_n^m(\cos\vartheta)\,P_n^m(\cos q)\cos m(\varphi - \Phi),$$

it can be concluded that $\mathfrak{H}_x$ — in this more general form — depends also on the coordinate φ. The x-component of the magnetic strength, will in this case be completed by a term resulting from derivatives of φ, *i. e.*

$$\mathfrak{H}_x = -\frac{\partial\Phi}{\partial r}\sin\vartheta\cos\varphi - \frac{1}{r}\frac{\partial\Phi}{\partial\vartheta}\cos\vartheta\cos\varphi - \frac{1}{r\sin\vartheta}\frac{\partial\Phi}{\partial\varphi}\sin\varphi. \qquad (5)$$

At the deduction of the mean values along the horizontal lines given by $\varphi = const.$, one meets the following integrals

$$\int_{-\pi/2}^{+\pi/2}\cos m(\varphi - \Phi)\cos\varphi\,d\varphi = \begin{cases}\pi/2\cdot\cos\Phi & m = 1\\ 0 & m < 1\end{cases}$$

and

$$\int_{-\pi/2}^{+\pi/2}\cos m(\varphi - \Phi)\sin\varphi\,d\varphi = \begin{cases}\pi/2\cdot\sin\Phi & m = 1\\ 0 & m > 1\end{cases}.$$

It is a general rule of magnetograms that the horizontal lines are perpendicular to the central meridian, *i. e.* $\Phi = 0$. This means that the second integral identically vanishes.

The expansion of $\bar{\mathfrak{H}}_x$ in this more general case is rather complicated but according to the following discussion it can be separated as follows:

$$\bar{\mathfrak{H}}_x = \sum\frac{2nP_{n+1}^{(1)}(\cos\vartheta)}{r^{n+2}}P_n(\cos q) + F(\cos\vartheta), \qquad (6)$$

where $F(\cos\vartheta)$ denotes a function being symmetrical to the equator ($\vartheta = 90°$) for odd n. The first term correspond to the x-component of (3), but has coefficients $P_n(\cos q)$ depending on the position of the solar pole. The second can be eliminated by substraction of the mean values belonging to the horizontal lines given by $\vartheta (< 90°)$ and $180° - \vartheta$. The expression

$$H_x = \frac{\bar{\mathfrak{H}}_{xN} - \bar{\mathfrak{H}}_{xS}}{2} = \sum\frac{2nh_n}{r^{n+2}}P_n(\cos q)\,P_n^{(1)}(\cos\vartheta) \qquad (7)$$

gives the final form for the practical calculation, where $\bar{\mathfrak{H}}_{xN}$ and $\bar{\mathfrak{H}}_{xS}$ denote the values of $\overline{\mathfrak{H}}_x$ at ϑ and at $180° - \vartheta$, respectively. In the case of the two-terms potential function the formula

$$H_x = \frac{2h_1}{r^3} P_1(\cos q)\left[P_1^{(1)}(\cos\vartheta) + 3h \frac{P_3(\cos q)}{P_1(\cos q)} \frac{r_\odot^2}{r^2} P_4^{(1)}(\cos\vartheta)\right] \qquad (8)$$

can be obtained, deviating from the fundamental expression (4) by the coefficient of $P_3(\cos q)/P_1(\cos q)$ corresponding to an annual correction of h.

The order of magnitude of this correction may be estimated when the maximum of q is substituted in the explicit form of the coefficient:

$$P_3(\cos q)/P_1(\cos q) = (1/2)(5\cos^2 q - 3)$$

providing a numerical factor of 0,96 (being $q \sim 7°$ in maximum) which means an additional correction of about 4 *per cent.*

3. A further correction may arise from the effects of the limb-darkening which depends on the position p relative to the centre of the disc in the following form:

$$\mathfrak{H}_x' = \frac{2}{5}\mathfrak{H}_x\left(1 + \frac{3}{2}\cos p\right)$$

where $\mathfrak{H}'$ means the registered value. Owing to the formula $\cos p = \sin\vartheta\cos\varphi$, finally

$$\overline{\mathfrak{H}}_x' = \frac{2}{5}\overline{\mathfrak{H}}_x + \frac{3}{5}\sin\vartheta\,\overline{\mathfrak{H}_x\cos\varphi}$$

can be obtained.

The last term of the right hand side leads to an expression like (6) and it can be eliminated in a similar way.

§ 3. *A practical method for the calculation of averages introduced*

The determination of $\overline{\mathfrak{H}}_x$ can be directly realized by means of a planimeter (2), the calibration of which can be carried out as follows: an area of 5 mm^2 corresponds to 0,1 in the scale which is the lower limit of the measurements, but a copy of 12 cm in diameter from the microfilm of the magnetograms is also suitable (the value of the integral in these cases was between 0,5 an 1,0 in the scale). The repetition of the mesurement has been given a spread of 0,2—0,3 proving the reality of the method suggested.

The calibration in gauss was not performed as the nondimensional parameter h was discussed which is independent of calibration.

According to the expression (7) a condition of symmetry has to be fulfilled by the horizontal lines. An exact elimination of $F(\cos\vartheta)$ is possible only in the case when the traces are lying symmetrical to the centre. However, this condition is not generally realized, therefore the procedure (7) has a systematic error, the approximate values of which are given by

$$F(\cos\vartheta_1) - F(\cos\vartheta_2) = \frac{\partial F(\cos\vartheta)}{\partial\vartheta}\,d\vartheta.$$

Because the derivative is of unit in order, the left hand side depends only on $d\vartheta$. An estimated value of $d\vartheta$ may be about 2°, consequently the assimetry provides an additional term of order of 4 *per cent.* This affects the averages very little and together with the annual variation of h they will not be taken into account in the following discussions.

§ 4. *A numerical illustration of the method*

In order to use the method elaborated above, three different kinds of measurements have to be carried out for the evaluation of the discs: (i) determination of the areas by planimeter, (ii) measurement of the lengths of the horizontal lines and (iii) its heliographical latitudes, respectively. Table I shows these numerical values corresponding to a disc. The coefficient in the last column means the factor of calibration composed by the calibration of magnetograms and that of the planimeter.

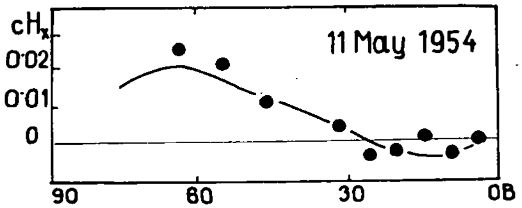

Fig. 2

Owing to the numerical values the coefficients A and B of the formula of interpolation

$$cH_x = AP_2^{(1)} + BP_4^{(1)}$$

are calculated by the method of the least squares, *e.g.* using the numerical values given in Table I., it will be got: $A = 0{,}00716$, $B = 0{,}00465$. According to the definition of h one can easily obtain that $h = B/(3A) = 0{,}216$. Fig. 2 shows a comparison of the measured values of cH_x and its calculated curve. The dots indicate the values of $1/2\,[H_x(\vartheta) - H_x(180° - \vartheta)]$.

Some magnetograms give unacceptable large value for h, illustrated by Fig. 3. One can immediately see that the formula of interpolation is not suitable for these observations and the conclusion can be drawn that the

Table I

11 May 1954

n	Pl	d	B	cH_x	n	Pl	d	B	cH_x
1	1,0	57	66	0,032	11	0,8	120	— 3	0,007
2	1,6	71	55	0,024	12	1,4	118	— 9	0,012
3	1,3	83	46	0,016	13	1,4	116	—14	0,012
4	0,5	95	38	0,005	14	1,3	113	—20	0,012
5	1,0	103	31	0,013	15	1,9	108	—26	0,018
6	1,4	109	24	0,013	16	0,5	102	—32	0,005
7	1,3	114	19	0,011	17	0,5	94	—38	0,005
8	1,8	117	13	0,015	18	—0,7	83	—46	—0,008
9	0,8	118	7	0,007	19	—1,3	69	—54	—0,015
10	0,8	120	2	0,007	20	—1,0	42	—62	—0,020

Pl = areas determined by planimeter, d = length of horizontal lines,
B = heliographical latitude of the lines, cH_x = magnetic strength with calibration factor.

solar magnetic field would not be characterized by (4) in this case. It seems that in this case the usual magnetic field of the Sun would be deformed by an extended unipolar field discovered by H. W. Babcock [3]. These magnetograms, however, may be omitted from our point of wiew as they are incompatible with a statistical evalution of *h*.

§ 5. *Results and conclusions*

Table II contains the values of *h* calculated from 99 magnetograms by the suggested method. The magnetograms were obtained from H. W. Babcock as microfilms. A second series of these magnetograms will be published in the next future.

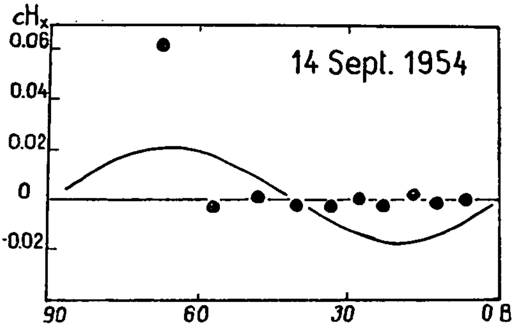

Fig. 3

The conclusions of the present article can be summarized as follows:

(a) Most of the magnetograms permit for *h* values between 0 and 1. But there are some magnetograms with negative values of *h* between 0 and —0,5, taken since Oct. 1, 1954.

(b) Some magnetograms give imcompatible values for *h*. In five cases *h* has a greater value that 1 and in seven cases it is smaller than —0,5. The number of the accepted magnetograms are 87 indicated in Fig. 4 by dots and the rest by circles.

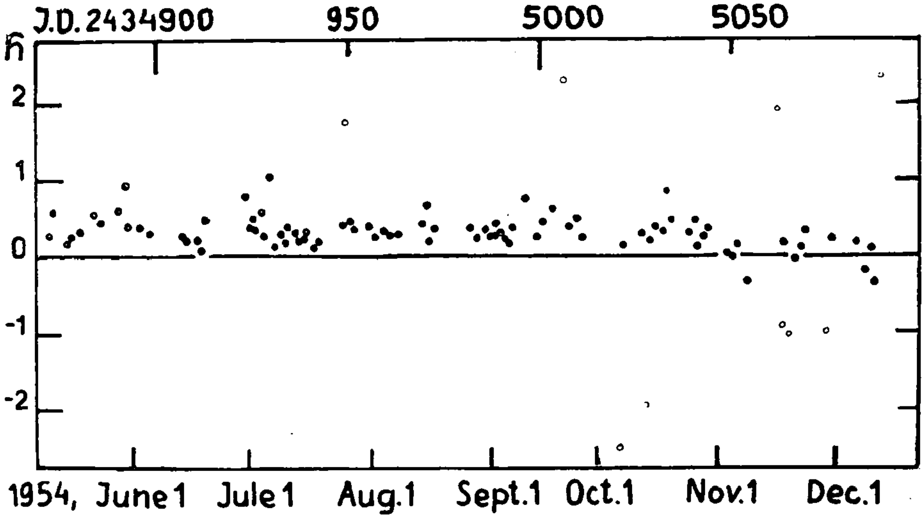

Fig. 4

(c) It seems to be very probable that *h* has a periodical variation of 30 days. However, the present observational material is from the statistical point of view not large enough to draw such a conclusion safely. In the second part of this paper we will have the possibility to investigate a greater observational material and it is hoped that it will be possible to return to this problem. If this periodical variation would be proved it might be concluded that the magnetic axis does not coincide with the rotational one. It can be mentioned that this conclusion would be accepted as the period of 30 days is in good agreement with the rotational period of the photosphere at the polar areas.

(d) The only conclusion which may be obtained from the present material is that the average of *h* is about 0,4 being in good agreement with a pre-

Table II

Date	J. D.	*h*	Date	J. D.	*h*	Date	J. D.	*h*
1954	2434		1954	2434		1954	2435	
May 11.	874	0,216	July 19.	943	0,120	Sept. 27.	013	0,238
12.	875	0,551	20.	944	0,199	Oct. 7.	023	(—2,521)
16.	879	0,134	26.	950	0,418	8.	024	0,213
17.	880	0,230	27.	951	(1,750)	13.	029	0,271
18.	881	(1,171)	28.	952	0,449	14.	030	(—1,950)
19.	882	0,297	29.	953	0,360	15.	031	0,188
23.	886	0,508	Aug. 2.	957	0,368	16.	032	0,362
24.	887	0,416	4.	959	0,228	18.	034	0,335
31.	894	0,919	6.	961	0,308	19.	035	0,857
June 1.	895	0,362	8.	963	0,259	20.	036	0,495
2.	896	(—18,266)	10.	965	0,295	25.	041	0,271
6.	900	0,252	16.	971	0,433	26.	042	0,448
14.	908	0,237	17.	972	0,690	27.	043	0,136
15.	909	0,223	18.	973	0,181	28.	044	0,206
18.	912	0,160	20.	975	0,347	29.	045	0,348
19.	913	0,0965	28.	983	0,374	Nov. 4.	051	0,0388
20.	914	0,476	31.	986	0,238	5.	052	—0,0154
30.	924	0,788	Sept. 2.	988	0,346	6.	053	0,150
July 1.	925	(1,579)	3.	989	0,254	9.	056	—0,341
2.	926	0,361	4.	990	0,260	17.	064	(1,971)
3.	927	0,498	5.	991	0,406	18.	065	(—0,901)
4.	928	0,317	6.	992	0,289	19.	066	0,196
5.	929	0,540	7.	993	0,225	20.	067	(—2,018)
6.	930	0,259	8.	994	0,216	22.	069	—0,0252
7.	931	1,022	9.	995	0,355	23.	070	0,140
9.	933	0,136	13.	999	0,723	24.	071	0,366
10.	934	0,277	14.	5000	(—9,075)	30.	077	(—0,976)
11.	935	0,189	16.	002	0,218	Dec. 1.	078	0,242
12.	936	0,386	17.	003	0,433	8.	085	0,181
14.	938	0,286	20.	006	0,387	10.	087	—0.214
15.	939	0,180	22.	008	(2,333)	11.	088	0,0944
16.	940	0,221	24.	010	0,375	12.	089	—0,348
17.	941	0.293	25.	011	0,485	15.	092	(2,390)

vious result of the author [1], where *h* was derived from the curvature of the polar rays of solar corona and numerical values of the same order of magnitude was obtained.

* * *

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EINE EINFACHE EXPERIMENTELLE METHODE ZUR BESTIMMUNG DER INTENSITÄT DER SEKUNDÄRFLUORESZENZ

Von J. DOMBI, J. HEVESI und R. HORVAI
Institut für Experimentalphysik der Universität Szeged

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Von der Verallgemeinerung der bezüglich der Sekundärfluoreszenz bisher bekannten Zusammenhänge ausgehend, wird eine empirische Methode für die Bestimmung des Intensitätsverhältnisses der sekundären und primären Fluoreszenz angegeben. Die Methode wurde bei mehreren Lösungen in einem breiteren Konzentrationsintervall angewendet.

Die unmittelbaren Meßdaten sind für die molekulare Lumineszenz noch nicht als charakteristisch zu betrachten, da die in den einzelnen Volumenelementen sich abspielenden Prozesse sekundäre Wirkungen auslösen, welche noch durch geeignete Rechnungsverfahren zu berücksichtigen sind.

Die Absorption des in dem untersuchten Material entstandenen Lumineszenzlichtes, die sogenannte Reabsorption kann man unter geeigneten Erregungs- und Beobachtungsbedingungen — wie schon lange bekannt — mit einfachen Verfahren in Betracht ziehen. Das Verfahren zur Korrektion der Wirkung der durch die Reabsorption erzeugten sekundären, sowie der tertiären usw. Lumineszenz — bezüglich deren erst in den letzten Jahren systematische theoretische und experimentelle Untersuchungen durchgeführt wurden [1]—[5] — ist nicht so einfach, wie das auf die Reabsorption bezügliche. Die quantitativen Zusammenhänge für die Wirkungen der Lumineszenzen höherer Ordnung erfordern nämlich als Vorbedingung die Kenntnis der eben gesuchten Charakteristiken, wie z. B. des wahren oder inneren Spektrums, der Abhängigkeit der inneren Quantenausbeute von der Wellenlänge des erregenden Lichtes, usw., und die deshalb anzuwendende sukzessive Approximationsmethode kompliziert die auch sonst ziemlich verwickelten und langwierigen Rechnungsmethoden noch mehr.

Das Gesagte läßt die Anwendung eines Verfahrens angezeigt erscheinen, mit dessen Hilfe man das Verhältnis der Intensität der entstehenden Sekundärfluoreszenz zu derjenigen der Primärfluoreszenz bestimmen kann. Bei Kenntnis dieses Verhältnisses kann man nämlich z. B. bei einer Lösung von bestimmter Schichtdicke diejenige Konzentration (bzw. bei gegebener Konzentration die Schichtdicke) immer angeben, bei welcher die Wirkung der Sekundärfluoreszenz schon vernachlässigt werden kann bzw. ist die Kenntnis des genannten Verhältnisses auch für die genauere Bestimmung der wahren Quantenausbeute benützbar [4]. Unsere Arbeit hatte zum Ziel, die Abhängigkeit des Intensitätsverhältnisses der sekundären und primären Fluoreszenz von der Konzentration bei gleicher Schichtdicke für mehrere organische Farbstofflösungen mit einfachen experimentellen Mitteln zu bestimmen.

Wenn eine optisch hinsichtlich der Absorption isotrope Lösung in einer zylindrischen Küvette durch ein mit der Längsachse der Küvette paralleles monochromatisches Strahlenbündel erregt wird, welches in seinem Querschnitte homogene Intensität hat, und wir in der Mitte der Rückfläche der Küvette ein solches Wellenlängengebiet der entstehenden Lumineszenz longitudinal beobachten, in welchem der Absorptionskoeffizient schon zu vernachlässigen ist, dann ist die Intensität (Quantenstromdichte) der beobachteten Lumineszenz [2] mit guter Annäherung

$$B_{\lambda'} = \text{konst}\, E_{\lambda 0}\, \eta(\lambda)\, (1-e^{-\alpha}) \frac{1}{1-\varkappa}, \tag{1}$$

wobei $E_{\lambda 0}$ die Quantenstromdichte des in die Lösung eintretenden erregenden Lichtes von der Wellenlänge λ, $\eta(\lambda)$ die Quantenausbeute für die Erregungswellenlänge, α das Produkt des bei der Erregungswellenlänge gültigen Absorptionskoeffizienten und der Schichtdicke der Lösung, $\varkappa$ das Intensitätsverhältnis der Sekundär- und Primärfluoreszenz in dem beobachteten Fluoreszenzlichte bedeutet. Der Wert $\varkappa$ ist unter den erwähnten Bedingungen von der Beobachtungswellenlänge λ' unabhängig und hängt nur von der Erregungswellenlänge λ ab.

Bei anisotroper Emission ist das Intensitätsverhältnis der Sekundär- und Primärlumineszenz in dem beobachteten Lumineszenzlichte ebenfalls bestimmbar, doch ergibt es sich nicht einfach aus den Intensitätsmessungsdaten, sondern es ist auf Grund einer komplizierten Formel bei Kenntnis des wahren Polarisationsgrades, sowie des Absorptionsspektrums der Lösung zu ermitteln (siehe die Bedeutung von θ_2 in [5]). Dagegen kann man das Verhältnis $\varkappa^*$ der Anzahl der in dem beobachteten Volumen in der Zeiteinheit entstehenden sekundären und primären Photonen, welches Verhältnis für die relative Intensität der entstehenden Sekundärfluoreszenz ebenfalls charakteristisch ist, schon mittels eines einfacheren Zusammenhanges bestimmen.

Es bedeute $B_p(\lambda')$ die Quantenstromdichte des beobachteten partiell polarisierten Lumineszenzlichtes, von dem wir vorläufig annehmen, daß es nur aus primärer und sekundärer Emission entstammt, I_P und I_S die Anzahl der in dem beobachteten Volumen in der Zeiteinheit entstehenden Photonen, p_P und p_S deren wahren Polarisationsgrad; dann ist nach einer Arbeit von WAWILOW [6]

$$B_p(\lambda') = \text{konst}\left(I_P \frac{3}{3-p_P} + I_S \frac{3}{3-p_S}\right), \tag{2}$$

anderseits ist der Polarisationsgrad des aus den Anteilen I_P und I_S herrührenden beobachteten Lichtes

$$p' = \frac{I_P \frac{3}{3-p_P} p_P + I_S \frac{3}{3-p_S} p_S}{I_P \frac{3}{3-p_P} + I_S \frac{3}{3-p_S}}. \tag{3}$$

Auf Grund der beiden letzteren Zusammenhänge ist die Richtigkeit der folgenden Gleichung leicht zu verifizieren:

$$B_p(\lambda') = \frac{3}{3-p'}(I_P + I_S) = \frac{3}{3-p'} I_P(1+\varkappa^*), \tag{4}$$

wobei $\varkappa^*$ den Quotienten I_S/I_P bedeutet.

Wenn wir einerseits die Wirkung der in dem beobachteten Lumineszenzlichte außer der primären und sekundären Strahlung vorhandenen Komponenten von höherer Ordnung dadurch annähernd berücksichtigen, daß wir in (4) $1/(1-\varkappa^*)$ statt $(1+\varkappa^*)$ schreiben, was nach den Überlegungen in [1] im allgemeinen gerechtfertigt erscheint, anderseits die Proportionalität von I_P mit $E_{\lambda 0}\eta(\lambda)(1-e^{-\alpha})$ benützen [7] (dieser Faktor ist auch in der Konstante in (2) und (4) enthalten), dann wird die Anzahl der in dem beobachteten Volumen in der Zeiteinheit entstehenden Photonen mit guter Annäherung durch folgende Formel gegeben:

$$I = \text{konst}\, E_{\lambda 0}\eta(\lambda)\,(1-e^{-\alpha})\frac{1}{1-\varkappa^*} = \text{konst}\,\frac{1-e^{-\alpha}}{1-\varkappa^*}, \tag{5}$$

und die Größe I läßt sich leicht bis auf eine multiplikative Konstante durch Polarisationsmessungen bestimmen.

Was den Zusammenhang zwischen $\varkappa$ und $\varkappa^*$ betrifft, ist es auf Grund von (2) leicht einzusehen, daß

$$\varkappa = \frac{I_S}{I_P}\,\frac{3-p_P}{3-p_S} = \varkappa^*\,\frac{3-p_P}{3-p_S} \tag{6}$$

ist. Bei nicht zu hohen Polarisationsgraden ist der Quotient $(3-p_P)/(3-p_S)$ mit guter Annäherung gleich 1 zu setzen, wodurch $\varkappa \approx \varkappa^*$ wird.

Die Bestimmung von I in (5) ist durch die Messung der relativen Fluoreszenzintensität in der in [8] beschriebenen Weise leicht durchführbar. Nach diesem Verfahren können wir das Verhältnis der Anzahl der in einer die zu untersuchende Lösung enthaltenden Küvette K_2 in der Zeiteinheit entstehenden sämtlichen Lumineszenzlichtquanten zu der Anzahl derjenigen bestimmen, welche in einer, das untersuchte Material in geeignet gewählter Schichtdicke und Konzentration enthaltenden Küvette K_1 entstehen, und zwar nach der folgenden Beziehung

$$I = C\,\frac{D_{2i}+2}{D_{1i}-D_{2i}}, \tag{7}$$

wenn die Lichtquelle, die Küvette K_1, ein Polarisator, die Küvette K_2 und das Polarisationsmeßapparat sich längs der optischen Achse der Versuchseinrichtung in der hier angegebenen Reihenfolge befinden; D_{2i} bzw. D_{1i} bedeuten die reziproken Depolarisationsgrade des beobachteten Lumineszenzlichtes bei der Anwendung der mit der i-ten Lösung gefüllten Küvette K_2 allein bzw. gemeinsam mit der Küvette K_1.

Die Werte D waren an der bei unseren Untersuchungen verwendeten Meßeinrichtung [9] unmittelbar abzulesen. An dieser Versuchsanordnung haben wir aber, um sie auch für Absorptionsmessungen verwenden zu können, kleinere Veränderungen vorgenommen: die zur Erregung dienende Lichtquelle (Quecksilberhöchstdrucklampe HBO 500) wurde durch Gleichstrom gespeist, als Meß- bzw. Nullinstrument ein Galvanometer von der Empfindlichkeit 10^{-9} A/Skt verwendet, und der Dunkelstrom der Sekundärelektronenvervielfacher mittels einer besonderen Batterie kompensiert. So kann nämlich — nach Austauschen des kreuzenden Filters (Sperrfilters) auf ein Grauglas — der Wert $e^{-\alpha}$ mittels des Erregungslichtes selbst mit Hilfe der Ausschlagsmethode bestimmt werden, indem wir nur den Photostrom des einen Sekundärelektronenvervielfachers messen. Die so gewonnenen Größen waren allerdings — infolge der durch den Interferenzfilter gesicherten geringeren Monochromasie — von den mit Spektrophotometer gemessenen merklich verschieden.

Bestimmt man die Werte I und $e^{-\alpha}$ auf die angegebene Weise, so läßt sich auf Grund von (5) die Größe konst. $(1-\varkappa^*)$ und daraus — da für $\alpha \rightarrow 0$ auch $\varkappa^* \rightarrow 0$ gilt — auch $\varkappa^*$ selbst bestimmen.

Bei unseren Untersuchungen verwendeten wir die wässerigen Lösungen von Fluoreszein (mit einem NaOH-Gehalt von 3 Gewichtsprozenten), Äthylalkohol-Lösungen von Rhodamin B, Trypaflavin und Al-Morin (die beiden ersten mit $3 \cdot 10^{-3}$ Mol/l HCl-Gehalt, die letzte mit 1 volumenprozentigem Essigsäuregehalt). Die Grundstoffe wurden durch mehrfache Umkristallisierung gereinigt. Die Konzentrationen c_i der Lösungen waren bei sämtlichen Farbstoffen die folgenden (in Mol/l): $c_1 = 5{,}6 \cdot 10^{-6}$, $c_2 = 1 \cdot 10^{-5}$, $c_3 = 1{,}8 \cdot 10^{-5}$, $c_4 = 3 \cdot 10^{-5}$, $c_5 = 5{,}6 \cdot 10^{-5}$, $c_6 = 1 \cdot 10^{-4}$, $c_7 = 1{,}8 \cdot 10^{-4}$, $c_8 = 3 \cdot 10^{-4}$, $c_9 = 5{,}6 \cdot 10^{-4}$. Die Erregungswellenlänge war bei sämtlichen Lösungen 436 mμ, außerdem wurde die Konzentrationsabhängigkeit von $\varkappa^*$ im Falle von Rhodamin B auch mit der Erregungswellenlänge 546 mμ bestimmt.

Zur Filterung des Erregungslichtes dienten bei der Hg-Linie 436 mμ: ein Interferenzfilter SIF 436 + eine $CuSO_4 \cdot 5H_2O$-Lösung von 5 cm Schichtdicke und der Konzentration von 2% Gewichtsprozent mit 20 gew. %-igem NH_4OH-Gehalt; bei der Hg-Linie 546 mμ: ein Interferenzfilter SIF 546 + ein Schottfilter BG 18 von 2 mm Dicke + eine 20%-ige $CuCl_2$-Lösung von 3 cm Schichtdicke. Als Sperrfilter wurden verwendet: im Falle von Fluoreszein ein Interferenzfilter SIF 548 + ein Schottfilter GG 14 von 2 mm Dicke; im Falle von Rhodamin B bei 436 mμ Erregungswellenlänge ein Schottfilter RG 1 von 2 mm Dicke, bei 546 mμ deren zwei, bei Trypaflavin und Al-Morin ein Interferenzfilter SIF 518 + + ein Schottglas GG 14 von 2 mm Dicke.

Die erwähnte Kombination der Sperrfilter sicherte, daß der durchdringende, zu dem Sekundärelektronenvervielfacher gelangende Teil des Erregungslichtes, sowie die eventuelle Lumineszenz der optischen Elemente der Versuchsanordnung (Linsen, Filter) keinen stärkeren Photostrom verursachte, als 1% des durch den aus K_2 austretenden Fluoreszenzlichtes hervorgebrachten.

Bei allen Versuchsreihen wurden die Seitenflächen bzw. die für die Erregung und Beobachtung nicht in Betracht kommenden Teile der Vorder- und Rückfläche der Küvette K_2 — zwecks Eliminierung der Reflexions-Sekundärfluoreszenz — mit Tusche bedeckt.

Sämtliche Messungen — für welche übrigens die strenge Konstanz der Temperatur nur eine untergeordnete Rolle spielt — wurden bei Zimmertemperatur (cca 20° C) durchgeführt.

Nach unseren Meßergebnissen kann die Fluoreszenzstrahlung bei den untersuchten Lösungen als annähernd isotrop betrachtet werden; im Falle eines Erregungslichtes von 436 mμ erhielten wir für p' bei Fluoreszein den Wert 2%, bei Rhodamin B 0%, bei Trypaflavin 3%, bei Al-Morin 6,5%, im Falle der Erregungswellenlänge 546 mμ für Rhodamin B 5%. (Die Tatsache, daß die Werte p' für Rhodamin B bei den verschiedenen Erregungswellenlängen einen derartigen Unterschied zeigten, scheint mit FEOFILOW's diesbezüglichen Ergebnissen im Einklang zu stehen [10].)

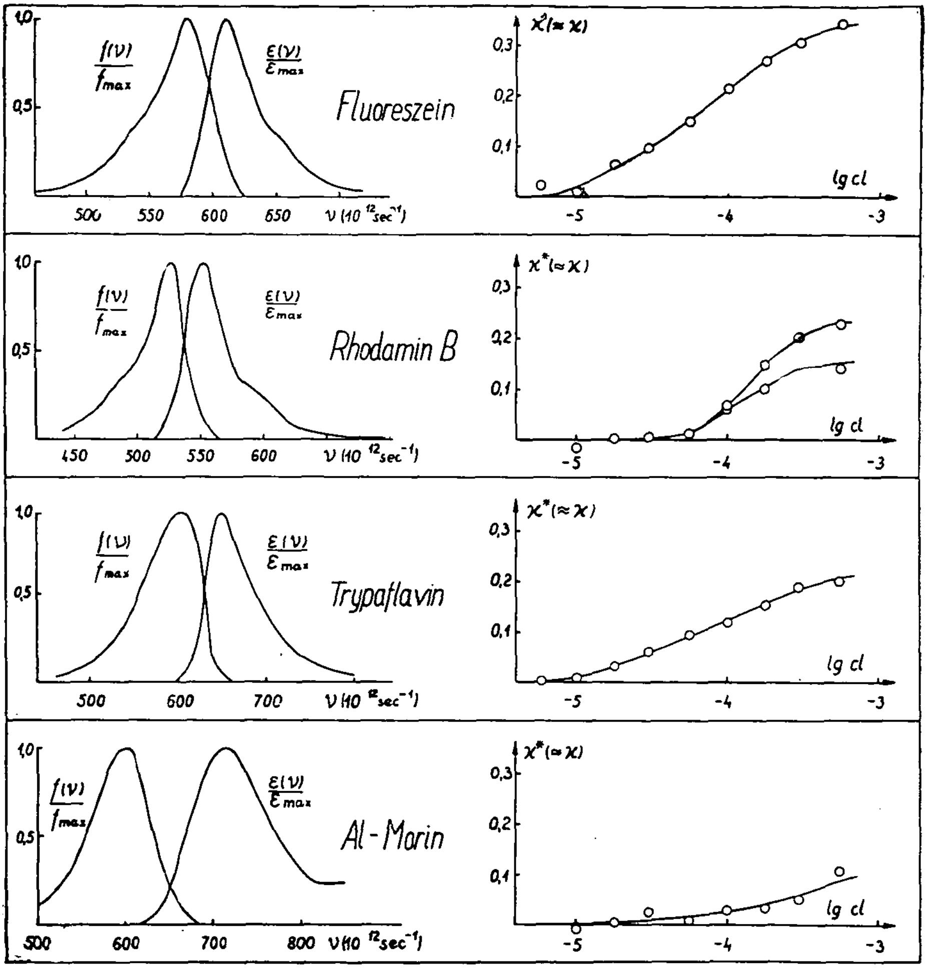

Fig. 1. Intensitätsverhältnis $\varkappa^*$ des sekundären und primären Fluoreszenzlichtes von verschiedenen Lösungen als Funktion der mit der Schichtdicke multiplizierten Konzentration. Links: die Emissionsspektren (Quantenspektren) und die Absorptionsspektren der Lösungen.

Unsere Meßergebnisse bezüglich der Konzentrationsabhängigkeit von $\varkappa \approx \varkappa^*$ wurden im Fig. 1 dargestellt. Diese Figur enthält auch die Absorptions- und Emmissionsspektren der einzelnen Farbstoffe als Funktion der Frequenz ν. $\varkappa$ selbst ist in Abhängigkeit von den dekadischen Logarithmen der Mol-Konzentration aufgezeichnet. Die ersten drei Absorptions- und Emissions-Kurvenpaare der Figur sind auf Grund unveröffentlicher Meßergebnisse von A. Budó und J. Dombi, das vierte Kurvenpaar nach [11] dargestellt.

Wie aus der Figur ersichtlich, zeigt der Ablauf der Kurven mit den in [3] für den Spezialfall des Fluoreszeins durch Rechnung ermittelten eine qualitativ gute Übereinstimmung. Es ist weiterhin zu sehen, daß der Maximalwert von $\varkappa$ bei denjenigen Lösungen größer ist, bei denen die Überlappung der Spektren mehr ausgeprägt erscheint. Was die Abweichung der $\varkappa$-Kurven bei Rhodamin B für die zwei verschiedenen Erregungswellenlängen 436 bzw. 546 $m\mu$ betrifft, ergab sie sich in der Richtung der auf Grund theoretischer Überlegungen erwarteten: unter sonst gleichen Bedingungen war bei kleinerem α der Wert von $\varkappa$ größer.

Zusammenfassend kann gesagt werden, daß unsere empirische Methode zur Verfolgung der Energieübergabe durch Strahlung mit den bei früheren Untersuchungen durch Rechnung erhaltenen Funktionen gut übereinstimmende Kurven für die Konzentrationsabhängigkeit von $\varkappa$ ergab und deshalb — obzwar es nur annähernde Daten liefert — doch als ein hinsichtlich der unmittelbaren Untersuchung der Sekundäreffekte zuverlässiges Verfahren erscheint.

* * *

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ÜBER DIE LICHTELEKTRISCHE LEITUNG AN DEN MIT SINTERN HERGESTELLTEN CdS-SCHICHTEN

Von L. GOMBAY und M. ZÖLLEI
Institut für Experimentalphysik der Universität Szeged

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Im stationären Zustand von durch Sintern hergestellten CdS-Schichten ohne und mit Cl-Zusatz wurde der Anteil [δ] der Photoelektronen am Gesamtbestand der Leitungselektronen als Funktion der Belichtungsstärke mit Hilfe der relativen Widerstandsänderung bei Belichtung durch Licht von verschiedenen Wellenlängen gemessen. Diese Meßergebnisse konnten mit der Funktion $\operatorname{th} E_0 Q$ besser als mit der bisher verwendeten Funktion $\frac{E_0}{b} \ln(1 + bQ)$ angenähert werden. Der δ-Wert, bezogen auf die gleiche Bestrahlungsleistung als Funktion der Wellenlänge des Bestrahlungslichtes zeigte ein Maximum, während dieselbe Größe, bezogen auf die gleiche Photonenzahl je Zeit- und Flächeneinheit, mit der Wellenlänge monoton abnahm. Bei Beginn und Ende der Belichtung wurden die üblichen An- und Abklingoszillogramme gewonnen, die bei gewissen Umständen positive und negative Vorbelichtungseffekte zeigten. Qualitativ konnten diese Meßergebnisse einfach gedeutet werden.

Einleitung

Es wurde von einem der Verfasser durch Entwässerung und darauf folgendes Sintern aus einer wässerigen Kolloidlösung von CdS eine CdS-Halbleiterschicht hergestellt, die besonders dann in großem Maße lichtempfindlich war, wenn zuvor Halogene — hauptsächlich Cl — zugesetzt wurden und dann eine entsprechende Formierung bei geeigneter Temperatur vorgenommen wurde [1]. In der vorliegenden Arbeit wurden die stationären Werte des Photostromes der so hergestellten CdS-Halbleiterschicht sowie der zeitliche Verlauf des Photostromes bei Beginn und Ende einer Belichtung gemessen, um Anhaltspunkte für die Deutung der bei der Photoleitung sich zeigenden Erscheinungen zu gewinnen. Die Resultate, die sich bei der Untersuchung der Photoleiter ergeben, können durch verschiedene [2] Theorien erklärt werden. Die auf die aus Mikrokristallen bestehenden Halbleiterschichten bezüglichen Ergebnisse scheinen mit der von GIBSON ausgearbeiteten Sperrschichttheorie der Halbleiter am besten deutbar zu sein, besonders dann, wenn die Schichten bei mittlerer Temperatur (einige Hundert °C) in Sauerstoff oder Luft empfindlich gemacht werden; die Ergebnisse der an solchen Halbleiterschichten erfolgten Messungen stehen nämlich bisher am besten mit der Sperrschichttheorie im Einklang [3].

Meßmethoden

Es wurden die stationären Werte von δ, d. h. der relative Anteil der lichtelektrischen Elektronen am Gesamtbestand der Leitungselektronen, mit Hilfe der relativen Stromzunahme oder der relativen Widerstandsabnahme bestimmt. Es gilt nämlich [4]

$$\delta = \frac{n}{n+m} = \frac{I_H - I_D}{I_H} = \frac{R_D - R_H}{R_D};$$

dabei sind: n die Zahl der Photoelektronen, m die Zahl der Dunkelelektronen, I_H bzw. R_H der Strom bzw. der Widerstand der Schichten bei Belichtung, I_D bzw. R_D der Dunkelstrom, bzw. der Dunkelwiderstand der Schichten.

Zur Bestimmung der Widerstände diente eine Gleichstromwiderstandsbrücke, deren Nullinstrument ein Spiegelgalvanometer mit der Empfindlichkeit 10^{-11} A/Skt/m war.

Bei der Verwendung unzerlegten Lichtes wurde eine Wolframspirallampe von 90 W als Lichtquelle benutzt. In diesem Fall betrug die Belichtungsstärke 8,2 Wcm^{-2}. Die monochromatische Belichtung lieferte ein mit einer Xenonhöchstdrucklampe XBO 500 belichteter Monochromator. Die Bestrahlungsstärke wurde durch ein mit einer Hefnerkerze geeichtes Thermoelement [5] gemessen. Die verschiedenen Bestrahlungsstärken wurden mit Hilfe eines rotierenden Sektors hergestellt. Den bei Beginn und Ende der Belichtung entstehenden, zeitlichen Stromverlauf haben wir mit Hilfe eines mit einem Synchronmotor getriebenen Sektors untersucht, der ein Wechsellicht mit rechteckiger Modulation herstellte. Die Belichtung der Schicht dauerte 6,6 μsec, die Dunkelpause 13,3 μsec. Der bei diesem Wechsellicht von der Frequenz 50 Hz entstehende Photostrom wurde mit einem Katodenstrahloszillographen untersucht, und die Kurven der nennenswerteren Ergebnisse wurden photographiert. In diesem Fall wurde die Belichtungsstärke durch einen Stufengraukeil verändert.

Die Tieftemperatur wurde mit Hilfe von Trockeneis hergestellt. Die Temperatur der Halbleiterschicht wurde mit einem mit ihr in Berührung stehenden geeichten Fe-Ko Thermoelement gemessen. Die Messung der durch einen Kanthalofen gelieferten höheren Temperatur der Schichten erfolgte in ähnlicher Weise.

Meßergebnisse

a) *Lichtelektrische Leitung im Gleichgewichtszustand.* Kurve *a* in Figur 1 zeigt den δ-Wert der CdS-Schicht ohne Zusatz[1] als Funktion der Belichtungsstärke bei der Belichtungswellenlänge $\lambda = 500$ mμ. Die CdS-Schicht ist sehr empfindlich für Licht von dieser Wellenlänge; wenn die Belichtung der Intensität von ungefähr 10^{10} Photonen cm^{-2} sec^{-1} um eine Größenordnung wermehrt wird, dann steigt δ von einigen %-en über 90 %. Genauer gesagt, bedeutet dies in unserem konkreten Fall, daß wenn die Belichtungsstärke den Wert $2{,}5 \cdot 10^{12}$ Lichtquanten cm^{-2} sec^{-1} bei $\lambda = 500$ mμ erreicht, die Zahl der Pho-

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[1] Dieser CdS-Schicht wurde später Cl zugesetzt.

toelektronen nur ungefähr um 2 % kleiner ist als die der sämtlichen Leitungselektronen, d. h. in diesem Fall kann der Dunkelstrom gegen den Photostrom vernachlässigt werden.

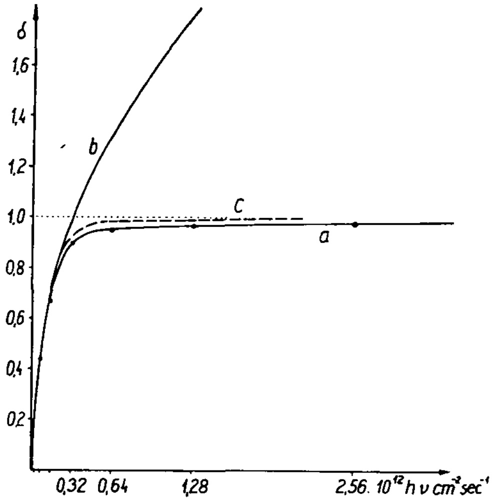

Fig. 1. Die δ-Kurven der CdS-Schicht ohne Zusatz bei Belichtungswellenlänge $\lambda = 500$ mμ; *a:* Die gemessenen δ-Werte, *b:* die Annäherung durch $\frac{E_0}{b}(1 + bQ)$, *c:* die Annäherung durch th $E_0 Q$

Kurve *a* in Figur 2 gibt die δ-Werte gemessen bei 500 mμ an den CdS-Schichten mit Cl-Zusatz wieder; während Kurve *b* dasselbe bei 650 mμ darstellt. Im Falle einer Belichtungsstärke von $0{,}3 \cdot 10^{12}$ Lichtquanten $cm^{-2} sec^{-1}$ bei 500 mμ bzw. einer Belichtungsstärke von $4{,}6 \cdot 10^{12}$ Lichtquanten $cm^{-2} sec^{-1}$ bei 650 mμ nähert sich der Photostrom den Gesamtstrom mit einer Abweichung von 2 %. Aus Figur 2 ist ersichtlich, daß die Zunahme der Kurve bei der Belichtung einer Wellenlänge von 500 mμ steiler ist als bei der Belichtung mit einem Licht von 650 mμ. Im Fall von beiden Wellenlängen erreicht die CdS-Schicht mit Cl-Zusatz bei einer schwächeren Belichtung den Anteil von 98 % der gesamten Stromstärke, wie im Fall der CdS-Schicht ohne Zusatz.

In Figur 3 ist die spektrale Verteilung der photoelektrischen Empfindlichkeit, bezogen auf gleiche Energiewerte, bei CdS-Schicht ohne Zusatz (Kurve *a*) und bei CdS-Schicht mit Cl-Zusatz (Kurve *b*) sichtbar. Aus den Kurven ist ersichtlich, daß die Empfindlichkeit beider Schichten bei 510 mμ ein Maximum erreicht und ferner, daß die Empfindlichkeit der Schicht mit Cl-Zusatz größer ist, als die der

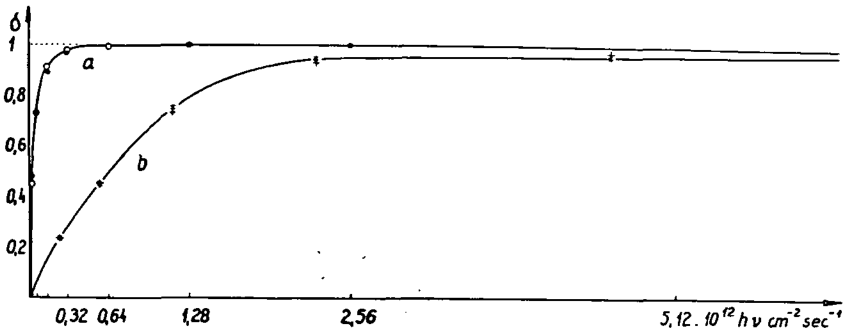

Fig. 2. Die gemessenen δ-Kurven der CdS-Schicht mit Cl-Zusatz bei Belichtungswellenlänge $\lambda = 500$ mμ (*a*) und $\lambda = 650$ mμ (*b*). Die ausgezogenen Kurven zeigen die Annäherung durch th $E_0 Q$

Schicht ohne Cl-Zusatz. Außerdem zeigt die CdS-Schicht mit Cl-Zusatz bei 600 mμ das für den Cl-Zusatz charakteristische Maximum [1].

Figur 4 stellt die Empfindlichkeit der spektralen Verteilung derselben Schichten, aber bezogen auf die Zahl der Lichtquanten je Zeit- und Flächeneinheit dar. In dieser Darstellung verschwindet das Maximum und man erhält eine mit wachsender Wellenlänge monoton abnehmende Kurve; Kurve *a* zeigt die Empfindlichkeit der CdS-Schicht ohne Zusatz, Kurve *b* die der CdS-Schicht mit Cl-Zusatz.

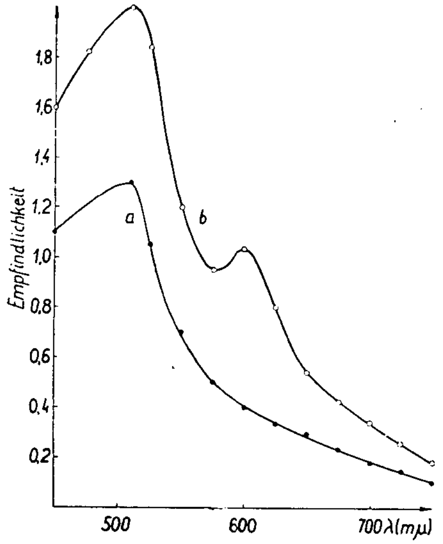

Fig. 3. Die spektrale Verteilung der Empfindlichkeit bei einer CdS-Schicht ohne Zusatz (*a*) und mit Cl-Zusatz (*b*), bezogen auf die gleiche Strahlungsleistung

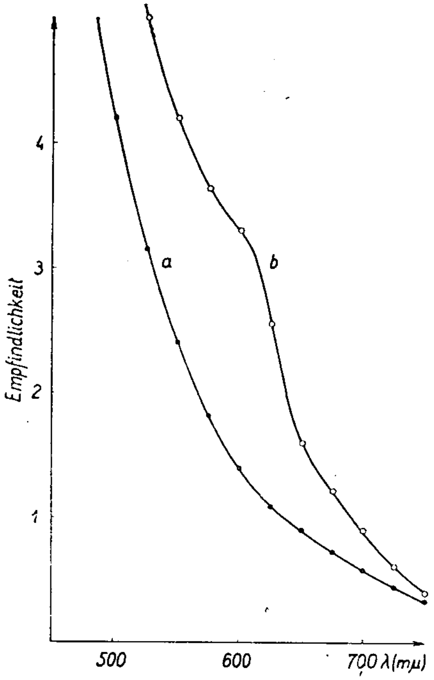

Fig. 4. Die spektrale Verteilung der Empfindlichkeit bei einer CdS-Schicht ohne Zusatz (*a*) und mit Cl-Zusatz (*b*), bezogen auf $\frac{\text{Zahl der Lichtquanten}}{\text{Zeit. Fläche}}$

b) *Lichtelektrische Leitung bei Beginn und Ende einer Belichtung.* Figur 5 gibt die An- und Abklingkurven der CdS-Schicht ohne und mit Zusatz bei höheren (200° C), Zimmer- (20° C) und tieferen (—80° C) Temperaturen bei einer Belichtungsstärke von 8,2 W cm^{-2} wieder. Der Zeitmaßstab der Abszisse ist durch die Periodenlänge der rechteckigen Lichtimpulse gegeben und beträgt 6,6 μsec. Die Ordinaten sind δ proportional, aber bei verschiedenen Oszillogrammen nicht untereinander vergleichbar, weil in den verschiedenen Fällen die Verstärkung so geregelt wurde, daß das Oszillogramm immer die gleiche maximale Ablenkung zeigte; dann ist nämlich der Vergleich des Verlaufes der Kurven besser durchführbar. Aus allen Kurven ist ersichtlich, daß sowohl bei den CdS-Schichten ohne Zusatz wie bei denjenigen mit Zusatz und bei jeder Temperatur die Anklingkurve kürzer als die entsprechende Abklingkurve ist. Der Vergleich der Kurven *a* und *d*, *b* und *e* sowie *c* und *f* zeigt, daß bei allen Temperaturen die An- und Abklingkurven der CdS-Schichten mit Cl-Zusatz kürzer sind als dieselben der entsprechenden CdS-Schichten ohne Zusatz. Anderseits ergibt sich aus dem Vergleich der Oszillogramme *a*, *b*, *c* und *d*, *e*, *f*, daß bei wachsender Temperatur die An- und Abklingkurven immer kürzer werden.

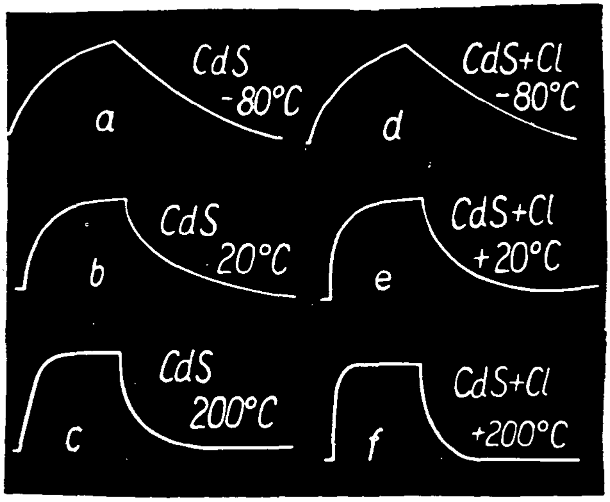

Fig. 5. An- und Abkligkurven der CdS-Schichten bei verschiedenen Temperaturen

Bei monochromatischer Belichtung wurden die An- und Abklingkurven der CdS-Schichten mit Cl-Zusatz bei Zimmertemperatur, ferner auch bei tieferen und höheren Temperaturen untersucht. Da der Verlauf der Kurve keine bedeutendere Wellenlängenabhängigkeit zeigt, wurde die An- und Abklingkurve der CdS-Schichten mit Cl-Zusatz nur bei 600 mμ (bei Zimmertemperatur) in Figur 6 dargestellt.

Fig. 6. Die An- und Abklingkurve der CdS-Schicht mit Cl-Zusatz bei Zimmertemperatur und 600 mμ

Das in Figur 7 ersichtliche Oszillogramm *a* gibt die An- und Abklingkurven der CdS-Schichten mit Cl-Zusatz bei einer Belichtungsstärke von $Q_W = 8{,}2$ W cm^{-2} des unzerlegten Wechsellichtes wieder. Bei der Aufnahme des Oszillogrammes *b* wurde außer der Belichtung mit demselben Wechsellicht auch ein Gleichlicht der Intensität $Q_G = 8{,}2$ W cm^{-2} (im folgenden Vorbelichtung) verwendet, damit der durch die Wirkung der zwei verschiedenen Belichtungen entstehende Photostrom untersucht werden kann. Alle, mit Vorbelichtung aufgenommenen Oszillogramme wurden mit derselben Verstärkung, wie die ohne die entsprechende Vorbelichtung aufgenommenen Oszillogramme untersucht, bzw. photographiert, damit das Maß der durch die Vorbelichtung bewirkten Abnahme oder Zunahme auf den Oszillogrammen treu wiedergegeben wird. Bei dem Vergleich der zwei Oszillogramme ist ersichtlich, daß die starke Vorbelichtung die Wirkung des Wechsellichtes bedeutend vermindert. Die Angaben der Oszillogramme in Figur 7 sind in Tab. 1 zusammengefaßt.

Man sieht, daß eine, relativ zum unzerlegten Wechsellicht sehr starke Vorbelichtung (mit unzerlegtem Licht) die Wirkung des Wechsellichtes vernichtet, während eine relativ schwache Vorbelichtung die Wirkung verstärkt.

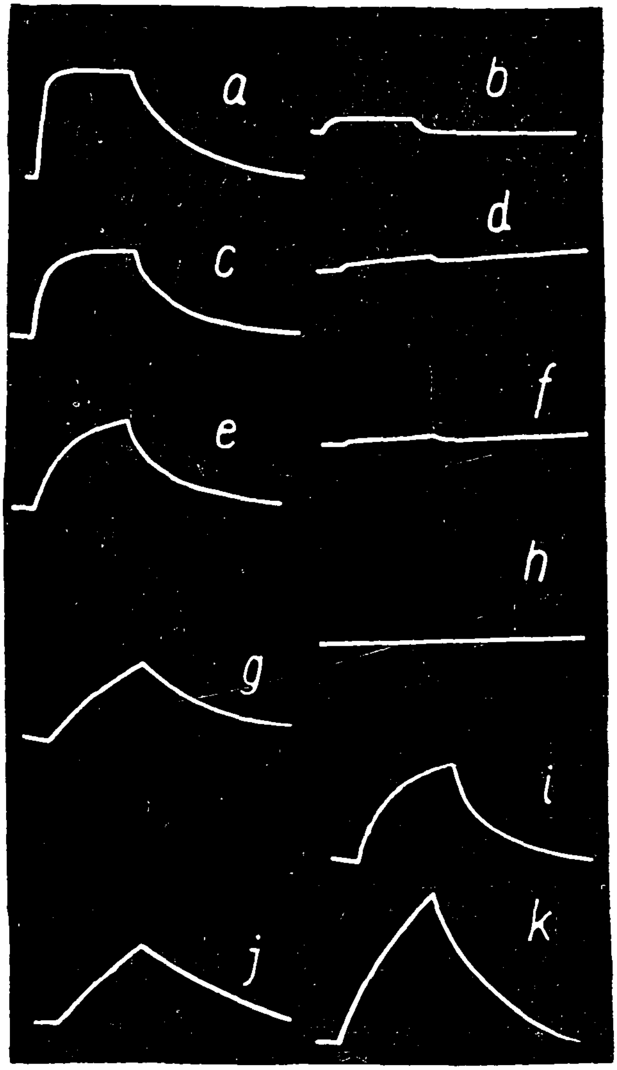

Fig. 7. An- und Abklingkurven bei verschiedenen Wechsel- und Vorbelichtungen

Tabelle 1

Die Benennung der Oszillogramme	Die Belichtungsstärke des Wechsellichtes (Q_W) Einheit: 1 Wcm^{-2}	Die Belichtungsstärke des Gleichlichtes (Q_G) Einheit 1 Wcm^{-2}	Die Wirkung der Vorbelichtung
a	8,2	0	—
b	8,2	8,2	negativ
c	4,1	0	—
d	4,1	8,2	negativ
e	0,82	0	—
f	0,82	8,2	negativ
g	0,082	0	—
h	0,082	8,2	negativ
i	0,082	0,82	positiv
j	0,02	0	—
k	0,02	0,082	positiv

Wenn man die Oszillogramme *a, c, e, g, j*, die mit der 100, 50, 10, 1 bzw. 0,5 %-igen Belichtungsstärke der ursprünglichen aufgenommen wurden, vergleicht, wird es klar, daß mit abnehmender Belichtungsstärke die Länge der Anklingkurven zunimmt und die Steigung der An- und Abklingkurven abnimmt.

Deutung der Meßergebnisse

Wenn die gemessenen δ-Werte als Funktion der Belichtungsstärke Q dargestellt werden, kann die gewonnene Kurve in einem gewissen Belichtungsintervall mit einer empirischen Formel $\frac{E_0}{b}\ln(1+bQ)$ angenähert werden [4]. E_0 ist gleich der Anfangssteigung der Funktion δ, und $1/b$ gibt den Wert von Q an, bei dem die Steigung der Kurve die Hälfte ihres Anfangswertes annimmt. In unserem Fall ist diese logarithmische Annäherung nur bis $\delta \sim 0{,}7$ gut, wenn die gute Annäherung durch ein Höchstunterschied von $\pm 3\,\%$ zwischen den gemessenen und berechneten Werten definiert wird. Daher wurde statt der logarithmischen Annäherung eine Annäherung der Form th $E_0 Q$ verwendet, die die Meßergebnisse bis $\delta = 1$, d. h. im ganzen Intervall ziemlich gut wiedergibt. Die Meßergebnisse und deren Annäherung durch die Funktionen $E_0/b \ln(1+bQ)$ und th $E_0 Q$ zeigen die Kurven *a, b, c* von Figur 1. Die Bedeutung der in der Funktion th $E_0 Q$ vorkommenden Konstante E_0 ist gleich derjenigen in der logarithmischen Funktion.

Aus dem Vergleich der Kurven in Figuren 3 und 4 ist ersichtlich, daß die spektrale Verteilung der Empfindlichkeit, bezogen auf die gleiche Strahlungsleistung, ein Maximum zeigt, aber bezogen auf die gleiche Zahl der Lichtquanten je Sekunde und cm^2 mit zunehmender Wellenlänge monoton abnimmt; was soviel bedeutet, daß die Wirkung der Photonen größerer Frequenz größer ist.

Der Unterschied der Längen der An- und Abklingkurven kann durch die zwischen den Mikrokristallen bestehende Sperrschicht erklärt werden [3]. In unserem Fall hatten die Quotienten τ_{ab}/τ_{an}, die sich bei großer Belichtungsstärke ergaben, wesentlich höhere Werte als die bisher in der Literatur mitgeteilten, während die Quotienten bei mittlerer und kleiner Belichtungsstärke die erwarteten Werte zwischen 1,2—2,5 annahmen [3].

Unser experimentelles Ergebnis, daß die CdS-Schicht mit Cl-Zusatz eine kürzere An- und Abklingkurve als die CdS-Schicht ohne Zusatz gab, ferner, daß unter gleichen Verhältnissen bei höherer Temperatur die An- und Abklingkurve auch kürzer ist, d. h. daß unter den erwähnten Bedingungen die Lebensdauer τ der Photoelektronen kleiner ist, kann mit der Theorie von MOSS [6] gedeutet werden, nach der

$$\tau = \frac{1}{B(M+2n_0)}$$

gilt, wobei B der Rekombinationskoeffizient, M die Anzahl der Störstellen pro cm^3 und n_0 die Anzahl der Dunkelelektronen pro cm^3 sind.

Die Wirkung der Vorbelichtung wurde mit unzerlegtem Licht untersucht, da nach den bisherigen Versuchen [3] dieselbe von der Wellenlänge unabhängig ist. Unsere Experimente weisen darauf hin, daß eine schwache Vorbelichtung im Falle einer sehr starken Belichtung (mit Wechsellicht) keine wesentliche Änderung hervorruft, eine starke Vorbelichtung dagegen die Wirkung der Belichtung bedeutend verkleinert (siehe die Kurven von Fig. 7). Dieses Meßergebnis kann so gedeutet werden, daß die starke Belichtung die sämtlichen erregbaren Ladungsträger erregt hat, und daß die weitere Vorbelichtung nur Ladungsträger von entgegengesetztem Vorzeichen befreit. Auf den entsprechenden Rekombinationsstellen erfolgt die Rekombination der beiden Ladungsträger, die die Anzahl der Ladungsträger vermindert, d. h. der Photostrom nimmt ab (negativer Vorbelichtungseffekt). Die Annahme, daß die entsprechend starke Vorbelichtung bei einer starken Belichtung hauptsächlich Ladungsträger von entgegengesetztem Vorzeichen befreit, kann mit dem Versuchsergebnis unterstützt werden, daß der Photostrom bei schwächerer Belichtung und entsprechend starker Vorbelichtung abnimmt und sogar verschwinden kann, wenn dagegen eine verhältnismäßig schwache Vorbelichtung bei schwacher Belichtung verwendet wird, verstärkt die Vorbelichtung den Photostrom, was dem Umstand zugeschrieben werden kann, daß bei schwacher Stromdichte die Rekombination von geringer Wahrscheinlichkeit ist. (Positiver Vorbelichtungseffekt.)

Bei monochromatischem Licht stimmen die An- und Abklingkurven mit den bei unzerlegtem Licht aufgenommenen überein; dies steht mit den bisherigen Erfahrungen [3], wonach der Wert der Zeitkonstante durch die Wellenlänge des Lichtes nicht beeinflußt wird, im Einklang.

* * *

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ON THE HIGHER OXIDATION STATES OF SILVER

By L. J. CSÁNYI and F. SOLYMOSI

Institute of Inorganic and Analytical Chemistry, The University, Szeged

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Experimentally has been proved that the black product obtained from the oxidation of silver nitrate with peroxydisulfate contains silver(III) and silver(II) oxide, the composition of which greatly depends on the concentration-ratio of the reactants. On mixing silver nitrate and peroxydisulfate in a mole ratio of 2:1 and 4:1 resp. at pH 3

$$2\,Ag_2O_3 \cdot Ag_2SO_4 \quad \text{and} \quad Ag_2O_3 \cdot 2\,AgO \cdot Ag_2SO_4$$

are formed and these after a longer standing decompose into

$$4\,AgO \cdot Ag_2SO_4 .$$

It has also been shown that due to the presence of silver(I) ions only the standard potential of silver(II) and silver(I) can be measured although these compounds contain trivalent silver.

In the early years of the last century it had been observed that when electrolyzing a solution of silver salt between Pt electrodes a black product forms on the anode. Soon after this a method had been developed to prepare this substance in greater amount so it became possible to determine its composition. This black product was firstly investigated by E. WALLQUIST [1] and according to him its composition was Ag_2O_2. But his analytical data proved to be inaccurate as later papers show. Detailed literature see in papers of O. SULC [2] and F. JIRSA [3].

In 1880 M. BERTHELOT [4] suggested a formula containing trivalent silver oxide. The existence of di- and trivalent silver ions seemed to be very likely on the basis of MENDELEIEFF's periodic system.

In the last decades of the century it had been observed, too, that it is possible to obtain a black coloured silver compound by oxidation with potassium peroxydisulfate, ozone or some other strongly oxidizing materials *e. g.* bismuth dioxide, fluorine and others.

The analyses of compounds so prepared even in the case of a substance obtained with the same procedure resulted in the most various formulas. The cause of this fact apparently is that there was not paid sufficient attention to the experimental conditions which may influence the composition of the compounds concerned. The disagreement in analytical data explains that most of the handbooks of inorganic chemistry give data on the higher oxidation states of silver with an attitude of reserve. In some books we can find not a single reference about them and in others we can read only about the properties of silver(II) compound (*e. g.* RIESENFELD, NJEKRASOW, MACHU, SIDGWICK, *Mellors' Modern Inorganic Chemistry*).

In the present paper we are dealing with the properties and analysis of oxide compound from the reaction silver and peroxydisulfate ions. Besides we give a short communication on the higher silver oxide prepared by the reaction between silver(I), ozone and formic acid, respectively.

Data on the behaviour and composition of the black coloured compound obtained from the reaction between silver and peroxydisulfate ions are given up to 1925 in the papers of H. MARSCHALL and others (see references in F. JIRSA's report, loc. cit.).

Later M. YOST [5] has carried out investigations with similar purposes and found that independently from the concentration ratio of silver and peroxydisulfate, Ag_2O_3 or basic sulfate of trivalent silver: $Ag_2O_3 \cdot Ag_2(SO_4)_3$ are formed. Soon after this $3\,Ag_2O_3 \cdot AgNO_3$ was formulated by BARBIER [6] and Ag_2O_2 by PINKUS [7]. K. KIMURA and Y. MURAKAMI [8] reporting the analytical application of silver oxide prepared by peroxydisulfate assume that in the first stage of reaction silver peroxydisulfate is formed, the hydrolysis of which results in Ag_2O_2.

Results and discussion

The reaction between silver nitrate and peroxydisulfate

At first it was investigated how the composition of the oxidation product is influenced by the way of preparation. We found that the oxidizing power of silver compound greatly depends on the ratio of the reactants. Further it was found that in a neutral medium the reaction takes place in few hours therefore a favourable concentration of hydrogen ions was chosen.

The preparation of silver(x) oxide by mixing silver nitrate and peroxydisulfate at a mole ratio of 2:1

On mixing the diluted solution (*M*/10 and *M*/20 resp.) of silver nitrate and peroxydisulfate at pH 3 the solution soon turned to brown colour and a greyish black product separated. The mixture was vigorously stirred for 20—25 minutes till the formation of the solid product visibly ceased. Then the solution containing the precipitate was centrifuged. After manifold washing with water the substance was dried in desiccator over calcium chloride and phosphorus pentoxide, resp. and was kept in darkness.

If the mixture of silver nitrate and peroxydisulfate solutions was allowed to stand on the precipitate more than half an hour, strong evolution of oxygen was observed. Similar gas evolution appeared when the washing was not carried out with sufficient quickness.

Testing the brown greyish solution it was found that it oxidizes momentarily the chloride, bromide and iodide ions into chlorine, bromine and iodine and it turns chromic ions into chromate and manganous ions into permanganate. Pouring this solution into ammonium hydroxide the ammonia smell disappears with vigorous gas evolution *i. e.* ammonia is oxidized into nitrogen.

Concerning the behaviour of the solid material mention may be done that its colour does not change during few weeks. Keeping it in desiccator the greyish tint fully disappears within a few months and we got a loose soot-like velvety black dust. The material dissolves in concentrated mineral acids with a violent gas evolution.

The test of the precipitate with titanic sulfate to hydrogen peroxyde was negative. Similarly no formation of peroxychromic acid was observed. The solution of potassium permanganate is not decolourized by silver(x) oxide. The substance reacts with hydrogen peroxyde with effervescence; it does not give peroxydisulfate reaction with Zwicker-reagent and oxidizes the oxalic acid to carbon dioxide immediately.

The reactions above prove that the solid substance obtained is neither peroxydisulfate nor peroxide so the high oxidizing power can be attributed to silver ions of higher valency. To prove this the total silver and oxygen content of the compound, the oxidizing power and the quantity of other ions present were analyzed, too. From this we hoped to make deductions on the ratio of silver ions in I,.II and III valency states which may be present in the compound.

The total silver content was measured gravimetrically. About 0,1 g of the dry and carefully homogenized substance was dissolved in diluted nitric acid. After manifold treating with nitric acid the silver transferred to silver nitrate and from this silver chloride was precipitated with diluted hydrochloric acid. Results are summarized in Table I.

Table I

Determination of total silver content

Taken g	Found Ag g	Ag content %
0,1106	0,0849	76,79
0,1010	0,0776	76,90
0,1056	0,0813	76,98
0,1003	0,0770	76,80
0,1009	0,0776	76,93
	average value:	76,90 %

The filtrate obtained after the precipitation of the silver ions was evaporated. The dry residue was dissolved in water and detected whether it contains other anions besides chloride. The solution gave with barium nitrate a sulfate reaction. Then the quantitative determination of sulfate content was carried out gravimetrically. The determination resulted in 11,44% of SO_4 content.

To clear up whether the compound contains other ions, perchloric acid was applied in the solvent. In the solution obtained after the precipitation of Ag^+ with hydrochloric acid NO_3^- and K^+ ions were detected as impurities (0,2—0,5 mg NO_3^- and K^+ in 1 g solid material).

To determine the oxygen content the compound was reduced with hydrogen gas. About 20—25 mg solid material was measured into porcelain boat and heated in hydrogen current in a tube. The end-temperature was about 450°C. The water formed by the reduction was absorbed with phosphorus pentoxide. The amount of oxigen was estimated from the increase of weight. During the reducion the oxigen of the sulfate was reduced, too. After heating pure silver remained in the boat. The reduction of silver sulfate carried out under similar condition resulted in pure silver similarly. The result of the determination was in average 18,92% oxygen.

To determine the oxidizing capacity of the compound oxalic acid was found to be the most suitable. The mean value of the oxidizing capacity was equivalent to 9,70 ml 0,1 potassium permanganate (in 0,1 g silver(x) oxide).

Some of our data are shown in Table II.

To evaluate our analytical data a comparative table was made in which the silver, oxygen and sulfate content and oxidation capacity of the different compounds were given.

Table II

Taken g	Total Ag %	Oxidizing capacity ml	Sulphate content %	Total O %
0,1000	76,79	9,65	11,93	19,06
0,1000	76,90	9,81	11,80	—
0,1000	76,98	9,70	11,99	18,91
0,1000	76,80	9,66	11,90	—
0,1000	76,93	9,70	11,92	18,80
average value:	76,90	9,70	11,91	18,92

On comparing data of Table III with results of analyses given in Table II it seems to be very probable that the composition of the compound investigated is

$$2\,Ag_2O_3 \cdot Ag_2SO_4$$

We can write the following overall equation for the formation of this compound:

$$6\,AgNO_3 + 4\,K_2S_2O_8 + 6\,H_2O = 2\,Ag_2O_3 \cdot AgSO_4 + 6\,KNO_3 + 6\,H_2SO_4$$

According to this equation 6 molecules of sulfuric acid are formed. Thus to settle the correctness of this equation we measured the change of the concentration of hydrogen ion during the reaction. To this end the neutral solutions of silver nitrate and peroxydisulfate were mixed and with a glass electrode the pH of the solution was measured. It was found that the pH of the solution decreased rapidly from the initial value of 6,8 and after 10 minutes 2,23 pH was measured. Then the silver oxide formed was collected on a filter and its oxidation capacity determined. From this data it was computed that according to the equation above what amount of sulfuric acid was to be formed. The calculation resulted in $1{,}4 \cdot 10^{-2}$ *M* sulfuric acid concentration.

Considering the mean activity coefficient of sulfuric acid of 0,02 *M* (f = 0,453), 2,35 pH was computed. The value thus obtained is in a good agreement with the measured 2,23 pH.

Supposing that the reaction takes place through formation of silver peroxydisulfate

$$6\,AgNO_3 + 3\,K_2S_2O_8 = 3\,Ag_2S_2O_8 + 6\,KNO_3$$

what on the effect of water and further peroxydisulfate turns

$$3\,Ag_2S_2O_8 + K_2S_2O_8 + 6\,H_2O = 2\,Ag_2O_3 \cdot Ag_2SO_4 + K_2SO_4 + 6\,H_2SO_4.$$

This way of reaction seemed to be proper because it gives explanation of our observation that in the presence of less quantity of peroxydisulfate a product of lower oxidizing capacity is formed.

Table III

Table for comparison of the composition of various higher silver oxide compounds

Supposed formule	Total Ag	Oxidizing* capacity ml	Sulphate content %	Total O %
$2\,Ag_2O_3Ag_2SO_4$	72,12	9,55	11,44	19,06
$Ag_2O_3 \cdot 2\,AgO \cdot Ag_2SO_4$	78,62	7,29	11,67	17,49
$4\,AgO \cdot Ag_2SO_4$	80,18	4,95	11,90	15,85
$(AgO)_2SO_4 \cdot 6\,AgO$	79,39	9,20	8,84	17,66
$3\,Ag_2O_2 \cdot AgNO_3$	82,69	6,57	—	—
$Ag_2O_3 \cdot Ag_2SO_4$	74,98	6,95	16,69	19,46
$2\,AgO \cdot Ag_2SO_4$	77,12	3,57	17,17	17,15
$Ag_2O_3 \cdot 2\,AgO \cdot AgSO_4$	75,39	8,34	13,42	20,12
$2\,Ag_2O_3 \cdot AgSO_4$	73,74	12,30	13,14	21,87

* Related to 0,1 g of material

NB. In total O % the oxygen content of anions is taken into consideration, too.

The possibility of the presence of trivalent silver in the compound is supported by the following experience, too. It had been supposed that silver(III) oxide compound obtained by peroxydisulfate is not stable and on having boiled with water decomposes to silver(II) oxide. As it had been expected, on heating the compound with water considerable decrease in the oxidizing capacity was found. The oxidizing capacity of 0,1 g substance boiled in 10—15 ml water for 4—5 minutes was equal to 4,64 ml. Supposing that all silver(III) was decomposed into silver(II) oxide the calculation resulted in 4,67 ml. During a longer standing the $2\,Ag_2O_3 \cdot Ag_2SO_4$ compound also decomposes. In the course of the decomposition a composition of

$$Ag_2O_3 \cdot 2\,AgO \cdot Ag_2SO_4$$

could be obtained. We succeded in obtaining such a composition using less peroxydisulfate. When 0,1 *M* silver nitrate reacts with 0,025 *M* peroxydisulfate at pH 3 also a solid greyish black material is formed. The substance obtained was analyzed again and we received the results summarized in Table IV. On comparing these results with data in Table III the best agreement was found with the composition

$$Ag_2O_3 \cdot 2\,AgO \cdot Ag_2SO_4$$

The formation of this compound may take place through the following reactions:

$$6\,AgNO_3 + 3\,K_2S_2O_8 + 5\,H_2O = Ag_2O_3 \cdot 2\,AgO \cdot Ag_2SO_4 + 6\,HNO_3 + 5\,H_2SO_4$$

or supposing silver peroxydisulfate as intermediate:

$$6\,AgNO_3 + 3\,K_2S_2O_8 = 3\,Ag_2S_2O_8 + 6\,KNO_3$$

which hydrolizes:

$$3\,Ag_2S_2O_8 + 5\,H_2O = Ag_2O_3 \cdot 2\,AgO \cdot Ag_2SO_4 + 5\,H_2SO_4$$

The oxidizing capacity of this substance after boiling was found 5,06 ml of 0,1 *N* potassium permanganate. Comparing this datum with the calculated one, 4,86 ml, we can say that most of Ag_2O_3 present was decomposed into AgO. The obtained silver(II) oxide had yet a very strong oxidizing pover *e. g.* it oxidizes manganous ion to permanganate rapidly. The compound of $Ag_2O_3 \cdot 2\,AgO \cdot AgSO_4$ composition was kept in desiccator and after 2—3 months its oxidizing capacity determined. The measured data were in good agreement with the composition of $4\,AgO \cdot Ag_2SO_4$. Thus during this time the silver(III) oxide decomposed quantitatively into silver(II) oxide meanwhile the substance became loose and of velvety black colour.

Table IV

Summary of the average values of analytical data

Taken g	Total Ag %	Oxidizing capacity ml	Sulphate content %	Oxygen %
0,1000	78,45	7,40	11,91	17,40

To these previous results also a supplementary observation must be mentioned. During the preparation it had been experienced in every case that the amount of silver(x) oxide was nearly constant. On centrifuging the precipitate a water-pure solution had been obtained which after a short time became brownish and precipitate was formed again. Changing the mole ratios of reactants the quantity of the oxide obtained changed, too. The fact that the amount of oxide compound formed is always less than that of which may be formed from the reagents present can be attributed to the potential equilibrium of the solution.

Oxidation potentials of di- and trivalent silver compounds

In order to give a sufficient explanation of the phenomena that in the course of the reaction between silver nitrate and peroxydisulfate always a definite quantity of silver(x) oxide is formed — namely less than may be expected on the basis of the amount of reactant present — we tried to estimate the oxidation potentials:

$$Ag^{3+} + 2e \rightleftharpoons Ag^{+}$$

$$Ag^{3+} + e \rightleftharpoons Ag^{2+}$$

First the dependence of the potential of the system was measured on the hydrogen ion concentration of the solution. In connection with this it was found that the oxidation potential does not change practically in 0,6—3,0 *M* perchloric acid solution and independently from the amount of $2\,Ag_2O_3 \cdot Ag_2SO_4$ in every case 1,561 V vs. S. C. E. was measured. The circumstance that the measured potential was independent from the taken amount of higher silver oxide (0,020—0,1000 g) shows that the solid material does not play any role in the potential controlling processes.

To estimate the standard oxidation potentials 50—100 mg silver(III) oxide was added to perchloric acid and the equilibrium potential of the following cells was recorded:

Pt	silver(III)oxide, $x\,n$ $HClO_4$	$x\,n$ $HClO_4$	sat. KCl	sat. Hg_2Cl_2	Hg
		a	*b*		

The setting in of the potential needs in most of the cases 10—15 minutes. The electrolyte contact between the half cells was made at place *a* with a sintered glass bridge of porosity G5, filled with x *N* $HClO_4$ and at place *b* with agar-agar gels in saturated $Ba(ClO_4)_2$.

After reading the equilibrium potential the solution was filtered on a sintered glass an the potential of the pure solution measured anew. No considerable difference between the potentials was found.

To estimate the oxidation potential one needs to determine the concentration of silver(I) and silver(III) ions. Since the determination of such a small silver(I) amount furnishes erroneous data, silver nitrate of great quantity was added to the solution.

Being the amount of silver nitrate added more than hundredfolds of the concentration of silver(I) ions originally present the latter quantity may be left out of consideration. On the effect of addition of silver nitrate the potential decreased in a small extent and this decreased value was taken as a basis for the calculations.

In order to determine the amount of silver(III) oxide, oxalic acid was pipetted into the solution the excess of which was back-titrated with potassium permanganate.

Substituting the data obtained into the well known Peters' equation

$$E = E_0 + \frac{0{,}0591}{n} \log \frac{[Ag\,(\text{higher})]}{[Ag^{+}]}$$

we received 1,92 V value for the standard oxidation potential vs. N H_2 electrode. This value is in a good agreement with 1,914 V, determined by NOYES and KOSSIAKOFF [9] for the system

$$Ag^{2+} + e \rightleftharpoons Ag^{+}.$$

Therefore we must suppose that under experimental condition applied the trivalent silver ions are reduced by silver(I):

$$AgO^{+} + Ag^{+} + 2\,H^{+} = 2\,Ag^{2+} + H_2O.$$

From this follows that the original purpose *i. e.* to determine the standard potential of Ag(III)/Ag(II) and Ag(III)/Ag(I), resp. in the presence of silver(I) ions is not possible.

Preparation of higher silver oxide with ozone

The higher valency state of silver may be obtained easily with ozone. Bubbling ozone into acidified solution of silver nitrate greyish black dust-like substance forms which is very similar to that of obtained with peroxydisulfate. The progress and velocity of the oxidation depend on the concentration of ozone, silver and hydrogen ions.

It had been also observed that there did not form more than a definite quantity of higher silver oxide in spite of bubbling forth ozone through the silver nitrate solution. Removing the precipitate the reaction between silver nitrate and ozone starts anew. This shows that the product formed gets into equilibrium with the oxidizing agent.

Since the properties of the substance formed by ozone were similar to higher silver oxide prepared by peroxydisulfate we disregard to give back these reactions in detail.

The product obtained with ozone was analysed and the total silver content was 79,90%. The oxidizing capacity was equal to 8,57 ml 0,1 potassium permanganate. These data prove a composition

$$Ag_2O_3 \cdot AgO \cdot AgNO_3.$$

(The calculated total silver content is 80,37%, the oxidizing capacity 8,69 ml.)

To decide the correctness of the ratio of silver(II) oxide thermal decomposition was applied. After boiling the oxidizing capacity was determined. It was found to be 6,62 ml while the calculated datum 6,45 ml.

Preparation of higher silver oxide with formic acid

On treating a freshly prepared silver(I) oxide with diluted formic acid visible change takes place: the brownish compound turns into black dust-like substance. The colour of the compound depends on the amount of the oxide added and on the time of shaking. After a longer shaking whitish grey metal silver was formed.

To prepare a higher silver oxide, 10 g silver(I) oxide was shaken with 60—70 ml formic acid of 2% for a few minutes and the product obtained centrifuged and dried in desiccator.

The substance thus obtained oxidizes mangan(II) and cerium(III) ions in acidic medium into permanganate and cerium(IV) ions. Ammonia is transformed into nitrogen. Iodides and bromides are oxidized into iodine and bromine but the oxidation of chloride cannot be observed. With titanium(IV) sulphate it does not give peroxide reaction. With hydrogen peroxide it reacts with vigorous gas evolving.

It had been also investigated whether the oxygen had any role besides formic acid in the formation of this compound. To this end silver(I) oxide was made react with formic acid in oxygen, nitrogen and carbon dioxide atmosphere. In all the three vessels a greyish-black substance was formed. The most black coloured substance was obtained in oxygen atmosphere but in presence of nitrogen and carbon dioxide the product also had the mentioned oxidizing properties. Thus for the formation of the oxidizing power of the compound formic acid is of first importance.

The analytical data of the compound prepared with formic acid do not permit to decide whether Ag(II) or Ag(III) are there present.

* * *

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INVESTIGATION OF THE FORMATION OF N—SUBSTITUTED CARBOXYLIC ESTERS WITH THE USE OF VARIOUS HALOID CARBOXYLIC ESTERS

By S. FÖLDEÁK and B. MATKOVICS
Institute of Organic Chemistry, The University, Szeged

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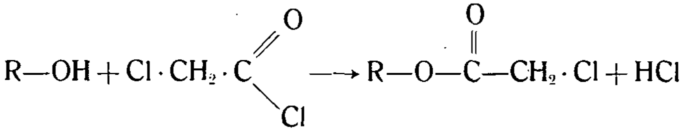
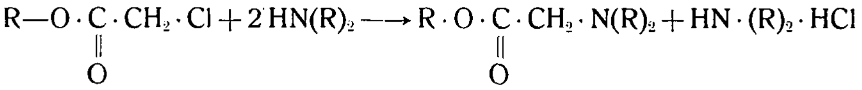
On preparing, under identical conditions, by condensation with various haloid acetic esters, the ethylates of N-piperidine-, morpholine- and pyrrolidine-acetic acid, the highest yields were observed in the cases when bromo-acetic ethylate as a tertiarizing agent was applied. In the group of cyclic secondary amines, the order of reactivity proved to be piperidine > pyrrolidine > morpholine.

A great number of methods are known in literature for the synthesis of aminoacetic esters, a group of compounds of great interest, due to their valuable pharmacological properties. Aminoacetic esters were synthesized by REMIZOV and co-workers [1] with the use of the general method:



$$R{-}OH + Cl\cdot CH_2\cdot C\begin{matrix}{/\!\!/}O\\ \diagdown Cl\end{matrix} \longrightarrow R{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_2\cdot Cl + HCl$$

The second step of preparing esters consisted in a condensation with secondary amine:



$$R{-}O\cdot \underset{O}{\underset{\|}{C}}\cdot CH_2\cdot Cl + 2\,HN(R)_2 \longrightarrow R\cdot O\cdot \underset{O}{\underset{\|}{C}}\cdot CH_2\cdot N(R)_2 + HN\cdot(R)_2\cdot HCl$$

It can be seen from tho above equation that, in addition to N-tertiary carboxylic ester, also the haloid hydrogen salt of the secondary amine forms.

N-piperidine-acetic ethylate was first prepared by WEDEKIND [2] in 1902, from piperidine and chloroacetic ethylate.

In the course of our researches of pharmacological nature, we set us the aim of preparing the N-carboxylic esters of pyrrolidine, piperidine and morpholine. In this connection we investigated what haloid carboxylic ester should be used to obtain the tertiary carboxylic ester in the highest yield, and which conditions affect the formation of the desired end product.

The applied various haloid carboxylic esters were prepared from chloroacetic acid [3], bromoacetic acid [4] by subjecting them to esterification, or from chloroacetic ethylate. [5], by subjecting this latter to a halogen exchange, with the use of potassium iodide.

For this purpose, one mole of the haloid acetic ester was reacted in a benzene solution with 2 moles of the adequate base. The haloid salt of secondary amine obtained as a by-product was removed by filtering the tertiary N-carboxylic ester isolated and converted into hydrochloride.

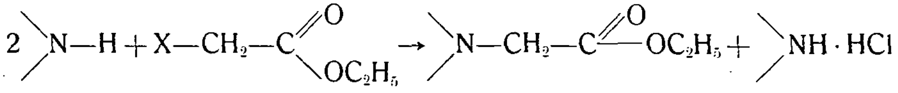
No essential differences exist between the nucleophilic activity of various amines, and their dissociation constants disclose values adjacent to each other (*e. g.* $k = 1{,}3 \cdot 10^{-3}$ in the case of pyrrolidine whilst $k = 1{,}28 \cdot 10^{-3}$ in the case of piperidine). Accordingly, when differences are observed in the reaction rates and in the ratios of end products, respectively, of the reactions with different haloid esters, obviously the different reactivities of the various haloid compounds are responsible for these differences.

On examining the refraction constants and the values of bond energies of the various haloid derivatives [6]:

Type of haloid C—X	Bond energy Kcal	Refraction constant
C—Cl	66,5	5,933
C—Br	54,0	8,803
C—I	45,5	13,757

we find that, on applying the same base, reaction rates should increase in the order Cl < Br < I. Thus, if no side reaction would occur, under identical experimental conditions, the percentage ratio of the obtained product should follow the same order.

The obtained experimental results are summarized on the basis of the equation



$$2\,{>}N-H + X-CH_2-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown OC_2H_5\end{matrix} \rightarrow {>}N-CH_2-\overset{\displaystyle O}{\overset{\Vert}{C}}-OC_2H_5 + {>}NH\cdot HCl$$

in the following table.

N—H	Percentage of yield with haloid X		
	Cl	Br	I
Pyrrolidine	52	77	57
Piperidine	84	85	78
Morpholine	42	71	68

The values of the table prove that in the case of the chloro- and bromo-acetic esters, changes in yields correspond to changes of polarizability. In the reaction with iodo-acetic ester, the amount of formed product decreased with each compound tested. This may be interpreted by the observation that always iodine precipitated when derivatives of iodoesters entered reactions.

Experimental

The ethylates of N-piperidino-, morpholino- and pyrrolidino-acetic acids were prepared and identified as picrates. Also the hydrochlorides and quaternary iodine salts of tertiary bases were produced. In order to make possible the comparison of reaction rates and yields, reactions were carried out with all three cyclic amines identical conditions, as follows.

A reflux condenser with a calcium chloride tube and a dropping funnel were attached to a ground threeneck flask equipped with stirrer. The flask was placed ice-water. On transferring 2 moles of freshly distilled anhydrous amine into the flask, together with 2,5 moles of anhydrous benzene, the solution of one mole of chloro-, bromo- or iodo-acetic ethylate in 2,5 moles of anhydrous benzene was dropwise added from the dropping funnel, under continuous stirring, at a slow rate. When the addition of the haloid ester was completed, stirring was continued for 15 minutes, and the solution was heated on the water bath. On cooling, the precipitate was filtered and repeatedly washed with some benzene. If further precipitate appeared during standing, it was similarly filtered and washed. The combined and dried benzene solutions were distilled under a pressure of 40 mm Hg. The appearing small amount of precipitate was filtered and the oily residue subjected to fractionation under a pressure of 2—5 mm Hg.

The hydrochlorides of the amine esters were prepared by treating the ethereal solution of the obtained tertiary amine esters with the calculated amount of ethereal hydrochloric acid, whilst the quaternary salts were precipitated from the solutions in anhydrous ethanol by methyl iodide.

The physical constants of the initial substances are as follows.

	b. p.	n_D^{20}	mol. weight
Piperidine	106,3°C	1,4534	85,15
Morpholine	128°C	1,4540	87,12
Pyrrolidine	88,5°C	—	71,12
Chloro-acetic ethylate	144—146°C	1,42274	122,51
Bromo-acetic ethylate	159°C	n_D^{15}: 1,45420	166,97
Iodo-acetic ethylate	178—180°C	$n_D^{12,7}$: 1,50789	203,92

N-*piperidino-acetic ethylate*

Prepared from piperidine and haloid acetic ethylate by the previously described method.

$C_9H_{15}O_2N$ (171,18) b. p, 68°C; n_D^{25}: 1,4525.

Picrate $C_9H_{15}O_2N$. $C_6H_3O_7N_3$ m. p. 122°C.
Calcd.: C 44,99% H 5,04% N 13,99%.
Found: C 44,70% H 4,86% N 14,3%.
45,00% 4,80%

Hydrochloride: $C_9H_{17}O_2N \cdot HCl$ (mol. wt. 208,07) m. p. 117°C N-methyl, N-(acetic ethylate)-piperidinium iodide $C_{10}H_{20}O_2NI$ (mol. wt. 160—160,3°C.
Calcd.: C 38,35% H 6,44% I 40,53%.
Found: C 38,22% H 6,82% I 40,70%.

N-*(morpholino)-acetic ethylate*

Prepared from morpholine and haloid acetic ethylate by the method given previously (an oily liquid).

$C_8H_{15}O_3N$ (mol. wt. 173,12) b. p. 81° n_D^{25} 1,4531.

Picrate: $C_8H_{15}O_3N$. $C_6H_3O_7N_3$ (mol. wt. 402,14) m. p. 136°C.
Calcd.: C 41,79% H 4,48% N 13,93%.
Found: C 41,82% H 4,50% N 14,29%.

Hydrochloride: $C_8H_{15}O_3N \cdot HCl$ (mol. wt. 209,68) decomp. at 176° N-methyl, N-morpholinium iodide-acetic ethylate.
$C_9H_{18}O_3NI$ (mol. wt. 315,05) m. p. 132,5°C.
Calcd.: C 34,28% H 5,71% I 40,32%.
Found: C 34,47% H 5,19% I 40,50%.

N-*(pyrrolidino)-acetic ethylate*

Prepared from pyrrolidine and haloid acetic ethylate by the previously described method (oily liquid).

$C_8H_{15}O_2N$ (mol. wt. 157,12) b. $p._2$: 59—59,5° n_D^{25} 1,4460.

Picrate $C_8H_{15}N$. $C_6H_3O_7N_3$ (mol. wt. 386,14) m. p. 118,5°C.
Calcd.: C 43,52% H 4,66% N 14,50%.
Found: C 43,23% H 4,37% N 14,65%.

Hydrochloride $C_8H_{15}O_2N \cdot HCl$ (mol. wt.: 193,59) m. p. 133,5°C.
Attempts to isolate the methoiodide quaternary salt of the pyrrolidine derivative so far failed.

* * *

Tanks are expressed to the workers of the Analytical Laboratory of this Institute for carrying out the required analyses.

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SYNTHESIS OF SOME QUATERNARY GRANATANOL ESTERS OF PHARMACOLOGICAL ACTIVITY

By B. MATKOVICS

Institute of Organic Chemistry, The University, Szeged

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In order to clear up the nature of the correlation between pharmacological activity and stereostructure in the case of the esters of such compounds of granatane skeleton where the ring is longer by a methylene group than that of the group of alkaloids of tropane skeleton, certain granatanol esters were prepared which were isomeric as regards the configuration of the C(3) atom. The comparative study of these compounds, together with that of other derivatives, is expected to result in valuable data, complementing our knowledge of stereo-structure and pharmacological effect.

Of the tropan alkaloids, many compounds of intensive pharmacological activity are known. These can be classified, in essence, in three main groups, according to the representative members of outstanding effect which occur in nature: 1) the group of atropine and ist derivatives, 2) hyoscine and its derivatives and 3) cocaine and the group of substances derivable from it or being in close relation to it.

Differences exist also in the pharmacological activities of the members of these groups [1].

Quaternary tropan esters are similarly discussed in literature in detail.

The quaternary methylate of atropine has been prepared already in 1869 [2]. The curare-like effect of these substances was reported by HILDEBRAND [3]. Studies in detail were carried out by ISSEKUTZ and associates [4, 5, 6] with the scope to clear up the curare-like effect of quaternary tropeins. In the case of quaternary tropeins of the atropine group, ganglion blocking action was observed by GYERMEK and SZTANYIK [7]. The investigations of other authors [8] in the field of the quaternary derivatives of the hyoscine group resulting in discovering important therapeutics such as butyl scopolammonium bromide.

Aliphatic tropin esters proved to show a parasympathicomimetic activity.

The afore-mentioned observations, together with the synthesis of a great number of compounds of tropan skeleton made possible to disclose in detail the correlation of pharmacological activity and chemical structure. It appears practical to mention here only a few of these observations. It was found *e. g.* that the characteristic effect of atropine on ganglions is due to the ester nature of the compounds. Another observation of interest is that in the groups of atropine and hyoscine, respectively, the activity is reduced to 1/8 by converting the substances into norcompounds.

According to the mentioned authors, *e. g.* the quaternary nitrogen of hyoscine is, from the aspect of activity, more essential than the epoxy group, in that the effectiveness was in some cases reduced by introducing an epoxy group [9].

The hydroxyl group on the C(3) atom of the tropan skeleton may be either cis (β) or trans (α) positioned with respect to the methyl group on the nitrogen atom of the ring. In order to secure the pharmacological activity of atropine, an optimum distance between the nitrogen and oxygen atoms is essential [10]. Whilst this is present in the case of α-tropine, the β-isomer is lacking that property [1], and this is the cause why the activities of both isomers are different. The ganglion blocking and the curare-like effects are not influenced by the steric position of hydroxyl group 3. From the aspect of the local anesthetic effect of cocaine, the steric position of the C(2)-carbomethoxy group of cocaine has no essential role. Moreover, the presence of the carbomethoxy group is not necessary at all for securing a local anesthetic activity [1].

The steric position of the substituent groups of the C(3) atom is, in turn, of appreciable importance from the point of view of ganglion blocking effect. In this aspect, α-tropine esters proved to possess lower activities than β-tropine esters. The effect is, in general, reduced in these cases by quaterneration. However, quaternary derivatives disclose certain favourable properties in that they dissolve and are assimilated more readily.

We carried out experiments in the first line with alkaloids of granatane skeleton, *i. e.* alkaloids possessing a ring system longer by a methylene group than that of the tropan skeleton. The scope of our investigations was on one hand to clear up the configuration of the hydroxyl group of the C(3) atom with respect to the methyl group of the N atom, and, on the other hand, to prepare ecgonine analogs on the granatane skeleton [11]. At the same time, also a group of salts of granatanium esters were produced. These latter seem to be promising in studies into the various effects of α- and β-esters.

Experimental

Acetone dicarboxylic acid was prepared according to Organic Syntheses Coll. Vol. I [12].

Glutaric aldehyde dioxime was prepared according to the prescriptions by COPE and associates [13].

Pseudo-pelletierine. Glutaric aldehyde required for condesation was prepared from glutaric aldehyde dioxime according to COPE and associates [13] and applied without isolation. Condensation was carried out by the ZIEGLER and WILMS method [14]. The obtained crude product was distilled under reduced pressure. B. p.$_{4\,\mathrm{mm\,Hg}}$: 98—100 °C. Yield 54 %.

Pseudo-pelletierine was quantitatively determined in form of its reineckate. On applying a 1 % solution of Reinecke's salt in an excess of 30 %, pseudopelletierine was quantitatively precipitated as a violet crystalline powder, m. p. 193—194 °C.

Prior to analysis, the product was dried for 4 hours at 78 °C under reduced pressure.

$C_{13}H_{22}ON_7S_4Cr$ (472,53)

Calcd. C 33,01; H 4,69; N 20,75; Cr (as Cr_2O_3) 16,09 %.

Found C 32,81; H 5,05; N 21,12; Cr 16,30 %.

The precipitation of pseudo-pelletierine as reineckate lends itself as well to the quantitative determination of aminoketone of the reaction mixture [15].

Granatan—3 β-ol. Prepared according to CIAMICIAN and SILBER (16), and, respectively, to ALDER and DORTMANN (17). The prescriptions were slightly modified in that the crude crystalline granatane—3 β-ol obtained on processing the reduction mixture was extracted with benzene, the benzene solution dried with $MgSO_4$ *siccum*, evaporated and distilled under reduced pressure.B. p. 8 mm Hg: 128—130 °C. On crystallizing the distillate from the mixture of 2 parts by weight of anhydrous benzene and 4 parts by weight of petroleum ether, yield 80 % of perfectly pure granatane—3 β-ol, m. p. 99—100 °C.

$C_9H_{17}ON$ (155,2)

Calcd. C 69,63; H 11,04; N 9,02 %

Found C 69,50; H 11,20; N 8,70 %.

The picrate, m. p. 264—265 °C (from water)

$C_9H_{17}ON \cdot C_6H_3O_7N_3$ (384,3)

Calcd. C 46,87: H 5,25; N 14,58 %

Found C 47,10; H 5,43; N 14,40 %.

Granatane—3 β-ol. Prepared by reduction with Raney-nickel, as prescribed by ALDER and associate (18). The substance is extremely hygroscopic.

$C_9H_{17}On$ (155,2)

Calcd. C 69,63; H 11,04; N 9,02 %

Found C 69,60; H 11,15; N 9,20 %.

The picrate, on recrystallisation from ethanol, showed m. p. 275—276 °C.

$C_9H_{17}ON \cdot C_6H_3O_7N_3$ (384,3)

Calcd.: C 46,87; H 5,25; N 14,58 %

Found: C 47,01; H 5,43; N 14,70 %.

O-acetyl—3 β-granatanol. Prepared by dissolving 1 mole of 3 β-granatanol in 20 moles of acetic anhydride and refluxing the solution for 5 hours in a Babo funnel. On removing excess glacial acetic acid by distillation under reduced pressure, the residue was treated with double volume of distilled water and processed with potassium carbonate. After extraction with 5—6 portions of 50—100 ml of ether, the ethereal solutions were dried with $MgSO_4$ *siccum,* evaporated and the obtained O-acetyl compound distilled from oil bath under reduced pressure. Straw-yellow viscous liquid, b. p. 9 mm Hg: 135—150 °C.

$C_{11}H_{19}O_2N$ (197,27) n_D^{25}: 1,4849

Calcd.: C 66,66; H 9,62; N 7,19 %

Found: C 66,50; H 9,27; N 7,11 %.

The picrate showed m. p. 201 °C.

$C_{11}H_{19}ON \cdot C_6H_3O_7N$ (410,38)

Calcd.: C 49,75; H 5,40; N 13,65 %

Found: C 49,66; H 4,94; N 13,61 %.

O-acetyl—3 β-granatanol. Prepared by refluxing for 5 hours the solution of 1 mole of freshly distilled 3 α-granatanol in 2 moles of acetic anhydride. Excess glacial acetic was removed by distillation under reduced pressure. On treating the residue with double volume of distilled water, the aqueous solution was saturated with potassium carbonate and the alkaline solution extracted with 5—6 portions of 50—100 ml of ether. The combined ethereal solutions were dried with $MgSO_4$ *siccum,* the solvent removed by distillation under reduced pressure and the obtained viscous residue distilled on the oil bath under reduced pressure. Light yellowish liquid, b. p. 10 mm Hg: 172—190 °C.

$C_{11}H_{19}O_2N$ (197,27) n_D^{25}: 1,4849

Calcd.: C 66,66; H 9,62; N 7,19 %

Found: C 66,06; H 9,56; N 7,17 %.

The picrate disclosed m. p. 204 °C.

$C_{11}H_{19}O_2N \cdot C_6H_3O_7N_3$ (410,38)

Calcd.: C 49,75; H 5,40; N 13,65 %

Found: C 50,02; H 5,06; N 13,58 %.

O-α-acetyl-N-dimethyl granatanium iodide. Prepared by treating the solution of 1 mole of O-acetyl-3 α-granatanol in 100 ml of anhydrous ethanol with one mole of methyl iodide. On allowing the mixture to stand for a short time, the crystalline product quantitatively precipitated, m. p. 329 °C

$C_{12}H_{22}O_2NI$ (339,22)

Calcd.: C 42,48; H 6,53; $I^{(-)}$ 37,01 %

Found: C 42,72; H 6,24; $I^{(-)}$ 37,21 %.

O-α-acetyl-N-methyl-ethyl granatanium iodide. Prepared by processing one mole of O-acetyl—3 α-granatanol, dissolved in 10 ml of anhydrous ethanol, with one mole of ethyl iodide [18]. Allowing the mixture to stand for 24 hours in a dark place, the quaternary iodide crystallised almost quantitatively, m. p. 337,5 °C.

$C_{13}H_{24}O_2NI$ (353,25)

Calcd.: C 44,19; H 6,85; $I^{(-)}$ 35,82 %

Found: C 43,96; H 7,02; $I^{(-)}$ 36,18 %.

O-α-acetyl-N-methyl-propyl granatanium iodide. Prepared by quaterneration of one mole of O-acetyl—3 α-granatanol with one mole of propyl iodide [18] in the previously described way. On allowing the mixture to stand for several days, the quaternary salt crystallized. On filtering and washing with anhydrous ethanol, m. p. 240 °C.

$C_{14}H_{26}O_2NI$ (367,28)

Calcd.: C 45,76; H 7,01; $I^{(-)}$ 34,54 %

Found: C 45,66; H 7,17; $I^{(-)}$ 34,24 %.

O-β-acetyl-N-dimethyl granatanium iodide. Prepared by processing the solution of one mole of O-acetyl—3 β-granatanol in anhydrous ethanol with one mole of methyl iodide. The formed quaternary salt immediately precipitates and can be filtered, m. p. 331 °C, The reaction is quantitative.

$C_{12}H_{22}O_2NI$ (339,22)

Calcd.: C 42,48; H 6,24; $I^{(-)}$ 37,01 %

Found: C 42,62; H 6,53; $I^{(-)}$ 37,14 %.

O-β-acetyl-N-Methyl-ethyl granatanium iodide. Prepared by processing one mole of O-acetyl—3 β-granatanol with one mole of ethyl iodide. Allowing the mixture to stand for several days, the crystalline product almost quantitatively precipitates. On filtering and drying, m. p. 289,5 °C.

$C_{13}H_{24}O_2NI$ (353,25)

Calcd.: C 44,19; H 6,85; $I^{(-)}$ 35,92 %

Found: C 44,06; H 7,05; $I^{(-)}$ 35,76 %.

O-β-acetyl-N-methyl-propyl granatanium iodide. Prepared by treating one mole of O-acetyl—3 β-granatanol with one mole of propyl iodide in the afore-mentioned way. On allowing the mixture to stand for some days, the precipitated crystals are filtered. The product is obtained in theoretical yield. On recrystallisation from anhydrous ethanol, m. p. 290 °C.

$C_{14}H_{26}O_2NI$ (367,28)

Calcd.: C 45,90; H 7,14; $I^{(-)}$ 34,42 %

Found: C 45,50; H 7,10; $I^{(-)}$ 34,60 %.

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APPARATUS, BASED ON A NEW PRINCIPLE OF OPERATION, FOR CARRYING OUT HETEROGENEOUS CATALYTIC PROCESSES IN THE VAPOUR PHASE[1]

Preliminary Communication

By L. MÉSZÁROS

Institute of Organic Chemistry, The University, Szeged

(Received April 2, 1959)

On conducting heterogeneous catalytic processes in the vapour phase, the effectiveness of the reaction and the preciseness of reproducibility are reduced to a great extent by the experimental fact that in the case of strongly exothermic and endothermic reactions, appreciable differences of temperature exist between the different points of the catalyst space. These differences of temperature are responsible for the local overheating and cooling, respectively, of the catalyst. Around these points of too high and too low temperature, respectively, the reactions do not take the desired course. A great number of attempts have been made to secure the desired direction of reactions in the vapour phase: among others, the tube bundle, the moving and the fluid bed types of reactors were evolved. Reactors consisting of tube bundles are expensive and their operation is inconvenient whilst reactors of moving and fluid bed suffer from the disadvantages of possessing high operating costs, due to the quick wear out of catalysts, further of having a complicated mechanism. A common disadvantage of all three methods is that difficulties are encountered when plants are to be enlarged.

The above-mentioned disadvantages are eliminated by the new type „melt-bed“ reactor evolved by the author. Melted catalysts are applied in place of the solid ones so far used. The method consists, in essence in bubbling the gas-phase mixture of the components to be reacted through a melt of 200—600°C temperature which acts as catalyst. The components of the adequately distributed gaseous mixture, on passing the melted catalyst, react with each other under the catalytic effect when they reach the boundary of the gaseous and the liquid phase. The quick conductance of the heat of reaction is secured by the fair conductivity and movement of the catalyst applied. In order to promote the quickness of heat transfer, the melt is maintained in a constant circulation or stirred in an adequate way.

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[1] Patent application filed under ME-362/1958.

Metals of low melting point, such as lead, zinc, tin, bismuth and their mixture, respectively, or nonmetallic inorganic substances and their mixture, respectively, with melting points in the temperature interval 200—600°C may serve as melts. It is possible to affect in this way the various reactions to a remarkable extent, depending on the nature and ratio of the gaseous mixture applied, and on the state and electronic system of catalysts.

After introducing the new principle at the design of reactors, it was extremely difficult to secure an adequate contact time and surface. The problem was solved with success by the application of a fixed bed of pumice stone, immersed in the melt, further of a column of ceramic bodies.

The proposed new method has the advantage of maintaining an approximately identical temperature in the whole catalyst space *i. e.* both in a vertical and in a horizontal direction. Individual temperature gradients of catalysts consisting of pieces of substances are also eliminated in this way. Namely, in the melt-bed reactor, the reaction takes place on the boundary of phases which serves at the same time also as a heat exchange surface. The favourable heat exchange conditions make possible, in contrast to other types of reactors, that melt-bed reactors can be easily enlarged, a fact of great importance from the point of view of chemical engineering. Easiness of operation, cheapness of construction and long duration of the catalysts applied are similarly properties of a favourable nature.

On using the proposed method, we succeeded *e. g.* in carrying out the conversion furfural → furane at a conversion rate of 93% in the presence of metallic lead as catalyst.

* * *

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INVESTIGATIONS ON YEASTS PRODUCING RED PIGMENTS

I. Effect of diphenylamine on the carotenoids produced by Yeasts

By GY. SCHNEIDER[1]
Institute of Chemistry, Medical University, Pécs
B. MATKOVICS
Institute of Organic Chemistry, The University, Szeged
and J. ZSOLT
Institute of Plant Physiology, The University, Szeged

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Qualitative and quantitative investigations were carried out by the authors with the scope to study the production of carotenoids in nutrient cultures of yeast poisoned by diphenylamine, in comparison to that observed in untreated blanks.

Untreated blank cultures of yeast proved to contain torulin, β-carotene, γ-carotene and torularhodin whilst in nutrients poisoned by diphenylamine the content of torulin appreciably decreased and torularhodin was completely absent.

A remarkable decrease was also observed in the total concentration of carotenoid pigments produced. Namely, the concentration of carotenoid pigments was in cultures of media poisoned by diphenylamine lower by a whole order of magnitude than that of blanks without diphenylamine.

Already several authors observed [1]—[4] that the synthesis of carotenoid pigments in micro-organisms is inhibited by certain concentrations of diphenylamine. The strong effect of diphenylamine on carotenoid pigments is often visually perceptible, due to fading of the colour of micro-organisms. In the present paper, we deal with investigations of yeasts extremely rich in carotenoids and capable of fixation of atmospheric nitrogen, isolated from the root nodules of *Lupinus luteus* [7]. The scope of our investigations was to follow the effect of diphanylamine by the qualitative and quantitative analysis of carotenoid pigments produced. In order to identify in an unambigous manner a carotenoid pigment with pigments of already disclosed structure, isolation of crystalline substances of the cultures would be required. Howerer, we did not dispose of a quantity of substances needed for this completely exact method. Therefore, identification of carotenoid pigments was carried out on the basis of following data:

1. behaviour at distribution between solvents,
2. position in chromatograms,

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[1] Now at the Institute of Organic Chemistry, The University, Szeged.

3. data of chromatogram of mixtures,
4. data of spectra in the visible region (absorption maxima).

On the basis of the mentioned data, it is our intention to present informative values on the changes in the production of carotenoids pigments by yeasts under the effect of diphenylamine.

Experimental

GY. NÉMETH succeeded in 1953 in isolating from the root nodules of *Lupinus luteus* some yeasts strains that produce red pigment and capable of fixation of atmosperic nitrogen [5]—[6]. The present investigations were carried out with these strains [7].

The cultures were prepared in Roux flasks in the nutrients as follows:

Nutrient I.:

5	g	of bean extract
2	g	of sucrose
0,2	g	of KH_2PO_4
0,3	g	of NaCl
0,2	g	of $CaCO_3$
2	g	of agar-agar
100	ml	of distilled water

Nutrient II.:

same as Nutrient I, complemented, however, by 5 mg of diphenylamine

Nutrient III.:

1	g	of dried yeast
1	g	of sucrose
0,5	g	of $(NH_4)_2SO_4$
0,1	g	of KH_2PO_4
0,05	g	of $MgSO_4 \cdot 7\,H_2O$
0,01	g	of $CaCl_2 \cdot 2\,H_2O$
0,01	g	of NaCl
2	g	of agar-agar
100	ml	of distilled water
20	mg	of diphenylamine

On sterilizing nutrients at 110°C for 20 minutes, they were inoculated by test tube cultures, followed by incubation for 10 days at 20°C. No differences were perceptible in the rate of growth of cultures containing diphenylamine and of the blanks. However, the colour of the cultures was different. Whilst the colony grown in nutrient I. was vivid red, that grown in nutrient II. disclosed a faded cream colour and the colony developed in nutrient III. was entirely colourless.

After the tenth day, the colonies were scraped of the surface of the nutrient, washed with a physiological solution of sodium chloride, centrifuged and the sedimented portion dried under an infrared lamp in the presence of $Na_2S_2O_4$.

The following method, which according to data of literature is mostly used when processing carotenoids [8], proved to be suitable for extracting, separating and identifying pigments.

The dried samples were finely rubbed with quartz sand in an ethanolic medium and the pigments extracted from the obtained pulp by ether. The ethanol containing ethereal solution was washed with water and saponified by allowing it to stand overnight at room temperature with 20% methanolic potassium hydroxide. The dry residue obtained in this way was then dissolved in a 1 : 1 mixture of petroleum ether : methanol and some water added, in order to separate pigments into epiphasic and hypophasic ones (distribution between solvents). Epiphasic pigments were chromatographed in a solution of petroleum ether, using a column of calcium hydroxide whilst hypophasic components were chromatographed in a mixture of benzene and petroleum ether, applying a column of calcium carbonate. Absorption maxima (AM) of the spectra of pigments were determind in the visible region, with a Löwe—Schumm, spectroscope. After establishing the spectra, the fractions were further chromatographed until completely homogeneous pigments were obtained. These latter were identified by preparing a mixture of them with already known pigments and establishing the chromatograms and spectra, respectively.

Processing of sample I. 10 g of dried red preparation was extracted as described previously and prepared for chromatography. Prior to chromatography, the concentrations of epiphasic and hypophasic pigments were determined.

Quantity of epiphasic pigments:	255 μg in 10 g
Quantity of hypophasic pigments:	30 μg in 10 g
Total:	285 μg in 10 g

Chromatogram of epiphasic pigments

E 1	30 mm	dark pinkish
	5 mm	empty layer
E 2	30 mm	cyclamen coloured
	10 mm	light cyclamen coloured
E 3	30 mm	light yellow
E 4	5 mm	yellow

Chromatogram of hypophasic pigments

H 1	10 mm	pink

Epiphasic pigments		μg in 10 g	AM in benzene		AM in petroleum ether	
E 1	Torulin	34	536	499	518,5	485
E 2	Torulin	97	536	499	*518*	485
E 3	γ-Carotene	55	508	476	492	460
E 4	β-Carotene	44	497	462	483	452
Hypophasic pigment						
H 1	Torularhodin	25	558	(519)	*539*	503

Processing of sample II. 10 g of product of light cream colour was extracted and prepared for chromatography as described. Owing to the scarcity of material, only the quantities of groups could be determined, the amount of separated pigments was not measured.

Quantity of epiphasic pigments:	95 μg in 10 g
Quantity of hypophasic pigments:	15 μg in 10 g
Total:	110 μg in 10 g

Chromatogram of epiphasic pigments

E1	3 mm pink
E2	2 mm yellow
E3	3 mm yellow

Chromatogram of hypophasic pigment

H1	5 mm pink

Epiphasic pigments		AM in benzene		AM in petroleum ether	
E1	Torulin	536	(498)	518	484
E2	γ-Carotene	508	476	492	(460)
E3	β-Carotene	497	(462)	483	452
Hypophasic pigment					
H1	Torularhodin	558	(518)	539	503

Processing of sample III 10 g of colourless product which contained no hypophasic pigment. The concentration of epiphasic pigments was extremely low.

Quantity of epiphasic pigments: 40 μg in 10 g

Chromatogram of epiphasic pigments

E1	2 mm pink
E2	2 mm yellow

Epiphasic pigments		AM in benzene		AM in petroleum ether	
E1	Torulin	536	(498)	518	484
E2	β-Carotene	(496)	(462)	483	452

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KINETICAL DATA TO ACYL MIGRATION N→O

By Á. FURKA

Institute of Applied Chemistry, The University, Szeged

(Received March 14, 1959)

The rate of rearrangement of (±) cis- and trans-2-benzamido-cyclohexan-1-ol *on the effect of hydrogen chloride in dry* dioxan at 71° C, 81° C and 91° C was measured. From data of measurements the rate constants of the reactions and also their activation energies were calculated.

The rearrangement of 2-acylamido-alcohols into 0-acyl-2-aminoalcohols due to the effect of acids and the revelsal of this process in alkali media are long well known [1]—[5]. In order to elucidate the mechanism of the process, kinetical investigations were carried out by WELSH [6] and MCCASLAND [7]. The former followed the rearrangement of N-acyl-ephedrine on the effect of hydrochloric acid in ethanol, back-titrating the excess of acid, while the latter investigated the change of 2-acetamino-cyclohexanols using water as solvent, so that the nitrogen content of the compound formed during the rearragement was determined by VAN SLYKE's method.

This paper contains data obtained by the author's investigation on the rearrangement of (±) cis- and trans-2-benzamido-cyclohexan-1-ol. Measurements were carried out in dry dioxan in presence of 8—60 times excess of hydrogen chloride, at 71° C, 81° C and 91° C. Dry dioxan was chosen

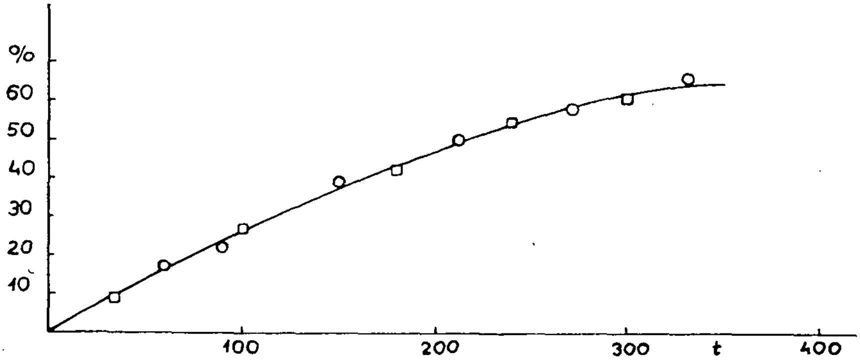

Fig. 1. □ : $a = 0{,}100$; $b = 1{,}4363$ (temp. = 71° C)
○ : $a = 0{,}050$; $b = 0{,}7810$

as solvent in order to avoid side processes which may take place on the effect of water (*e. g.* hydrolysis of 0-benzoyl compound). The great excess of hydrogen chloride mentioned above was claimed by the fact that cis modification has only a slight solubility in dioxan containing less HCl than it was applied. It seemed reasonable to study the rearrangement of trans modification also at such hydrogen chloride concentration. The process was followed by the determination of primer aminonitrogen. Deductions concerning the mechanism of the process, made on the basis of these and É. FODOR—VARGA's measurements [8] had been published [9].

Results[1]

Rearrangement of (±) *trans-2-benzamido-cyclohexan-1-ol*

It has been attempted to determine the order of the reaction by several methods. Fig. 1 shows that 2-fold change in the volume of the solvent has no effect on the rate of formation of the end-product when expressed it in per cent of the initial quantity of starting material. This indicates that the reaction may be of first order.

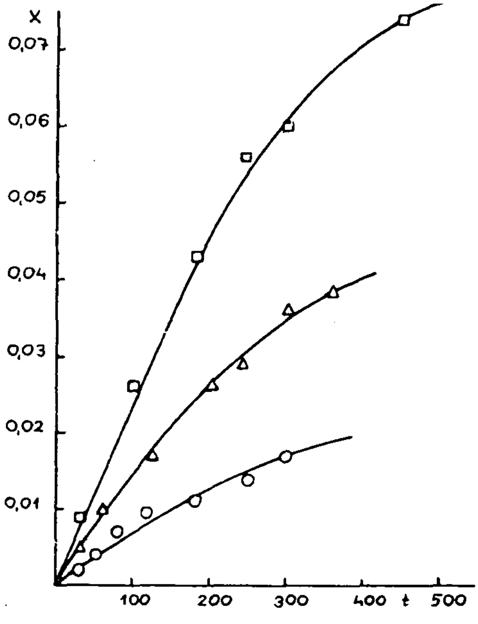

Fig. 2.

○ : $a = 0{,}025$; $b = 1{,}2754$ (temp. = 71° C)
△ : $a = 0{,}050$; $b = 1{,}4721$
□ : $a = 0{,}100$; $b = 1{,}4363$

Further it was investigated how the rate of formation of the end-product depends — at nearly the same initial hydrogen chloride concentrations — on the initial concentration of substrate (Fig. 2). Plotting the logarithms of initial rates, graphically determined, against the logarithms of concentrations, with good approximation, a straight line was obtained. The order referred to the substrate was obtained from the slope of this plot giving a value of about 0,8.

In order to determine the partial order referred to hydrogen chloride it was examined how the changes of the initial concentration of hydrogen chloride influence the rate of rearrangement (Fig. 3). The figure illustrates that the rate of rearrangement increases only to a very small extent with the increase of the hydrogen chloride concentration. The extent of the increase was not sufficient for the graphical determination

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[1] Symbols: a — initial concentration of substrate, x — concentration of substrate, b — initial concentration of hydrogen chloride
Units: concentration — mole/l, time — minute, rate constant — l. mol.$^{-1}$·min.$^{-1}$.

of partial order referred to hydrogen chloride, *i. e.* to yield values strictly differing from zero.

Each data, shown above, indicate that the process is of first order. However, there are data suggesting that the existence of the first order found is not sufficiently proved. On the one hand, hydrogen chloride was applied, from practical viewpoints, in great excess, and this may cause the result obtained at the determination of partial order of hydrogen chloride to be doubtful. Here it may be mentioned that É. FODOR—VARGA [8] in a series of measurements carried out with the same model — in the course of which the initial hydrogen chloride concentration was investigated at a wider range (measurements were performed with back-titrating of the excess of hydrogen chloride) — found the partial order of hydrogen chloride to be almost unit. At the same time constants found by her and calculated from second order equations show a better agreement than those calculated from first order equations. Table I contains some data which illustrate that in measurements carried out by the author the values of rate constants (k_2) calculated according to second order do not show in every case worse agreement than those calculated according to first order (k_1).

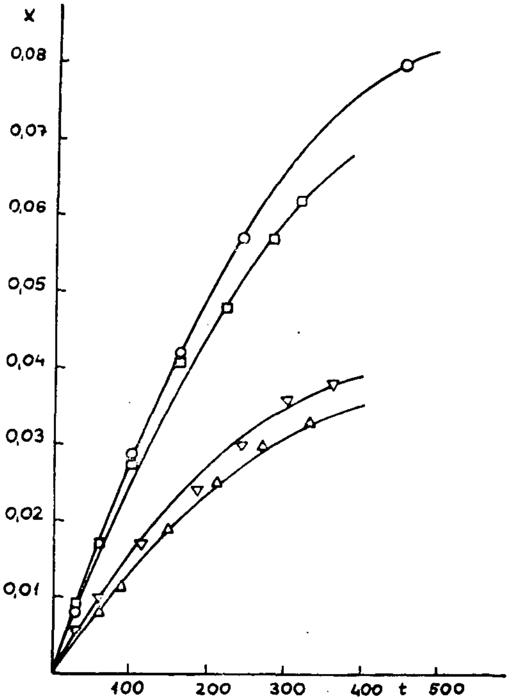

Fig. 3.

□ : $a = 0{,}100$; $b = 1{,}0330$ (temp. = 71° C)
○ : $a = 0{,}100$; $b = 1{,}4363$
△ : $a = 0{,}050$; $b = 0{,}7810$
▽ : $a = 0{,}050$; $b = 1{,}4721$

It must be noted that some difficulties arise from the fact that the activity coefficients referring to dioxan solution are not known, thus in the calculations instead of them the concentrations were used. On the other hand when calculating activation energies it became apparent that values obtained from k_2 instead of k_1 do not show considerable difference.

Fig. 4 shows results of measurements at different temperatures. It is seen that as the temperature rises there is a marked increase in the rate of acyl migration. The value of activation energy, evaluated from dependence of rate constants on the temperature is 18.5 Kcal/mole.

Further it was investigated how the presence of water influences the rate of the process. To dioxan containing hydrogen chloride, 2 % of water was added, then the initial substance was solved in it. The dissolving was

Table I

$a = 0{,}100$ $b = 1{,}436$ temp. = 71°C		$a = 0{,}050$ $b = 0{,}781$ temp. = 71°C		$a = 0{,}050$ $b = 1{,}514$ temp. = 71°C		$a = 0{,}050$ $b = 0{,}847$ temp. = 81°C		$a = 0{,}050$ $b = 1{,}751$ temp. = 91°C	
$k_1 \cdot 10^3$	$k_2 \cdot 10^3$	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$
2,97	2,08	3,16	4,06	2,80	2,32	6,08	7,22	17,94	10,27
3,22	2,26	2,90	3,83	3,02	2,00	5,52	6,57	19,17	11,50
3,19	2,25	3,17	4,14	3,90	2,59	5,70	6,79	19,04	10,93
3,38	2,37	3,30	4,30	4,12	2,74	5,84	7,00	19,73	10,82
3,23	2,31	3,34	4,40	4,27	2,85	5,69	6,83	19,02	10,95
3,01	2,16	3,30	4,33	3,95	2,64	5,87	7,08	18,84	10,90

Table II

temp. °C	a	b	H_2O %	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$
71	0,100	1,033	—	3,17	3,53
71	0,100	1,436	—	3,33	2,26
71	0,050	0,780	—	3,19	4,18
71	0,050	0,997	—	3,11	3,14
71	0,050	1,514	—	3,68	2,52
71	0,025	1,275	—	3,53	2,77
71	0,100	0,893	2	1,82	2,06
81	0,100	0,924	—	6,11	6,80
81	0,100	1,440	—	7,51	5,34
81	0,050	0,847	—	5,78	6,91
91	0,100	1,040	—	12,67	12,41
91	0,100	1,507	—	17,09	11,54
91	0,050	1,751	—	18,96	10,69
91	0,025	1,346	—	15,56	11,52

Table III

$a = 0{,}050$ $b = 1{,}782$ temp. = 71°C		$a = 0{,}050$ $b = 1{,}786$ temp. = 81°C		$a = 0{,}050$ $b = 1{,}765$ temp. = 91°C	
$k_1 \cdot 10^3$	$k_2 \cdot 10^3$	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$	$k_1 \cdot 10^3$	$k_2 \cdot 10^3$
16,08	8,66	34,13	19,19	58,85	38,00
14,77	8,33	34,75	19,66	57,91	33,04
18,87	10,70	37,79	21,40	58,70	33,67
16,37	9,29	35,67	20,30	59,36	33,96
17,02	9,70	40,53	23,15	59,97	34,43
16,10	9,17	38,28	21,91	58,03	33,38
16,53	9,31	36,85	20,93	58,80	34,41
16,53	9,31	36,85	20,93	58,80	34,41

not perfect, an opalescent solution was obtained. Fig. 5 shows that water content of 2 % resulted in a considerable decrease of the rate of rearrangement.

The mean values of rate constants calculated from measurements, carried out at different temperatures and initial concentrations are summarized in Table II. It can be seen that k_1 values in general increase with the increase of concentration of hydrogen chloride, while k_2 values decrease. This indicates that the real value of the order of overall reaction is about between 1 and 2 and this refers — together with facts mentioned above — to the existence of a more complex process.

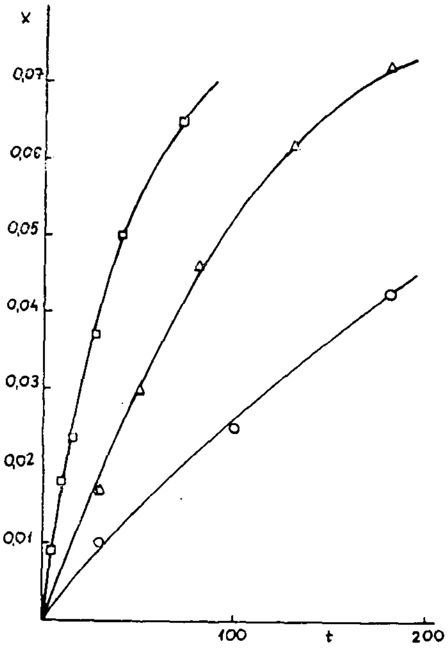

Fig. 4.

○ : $a = 0{,}100$; $b = 1{,}4363$; temp. = 71° C
△ : $a = 0{,}100$; $b = 1{,}4404$; temp. = 81° C
□ : $a = 0{,}100$; $b = 1{,}5070$; temp. = 91° C

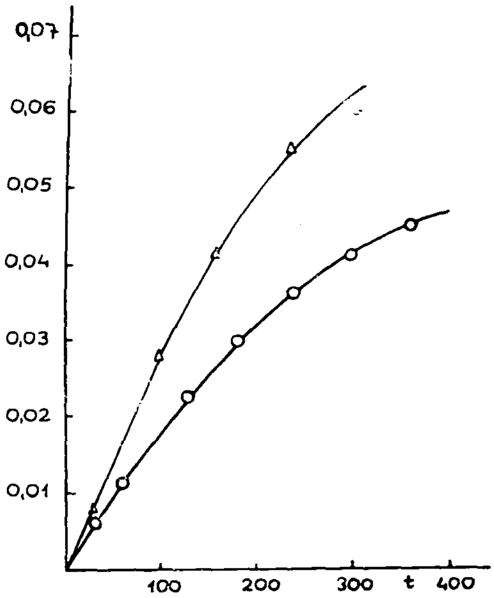

Fig. 5.

○ : $a = 0{,}100$; $b = 0{,}8933$;
△ : $a = 0{,}100$; $b = 1{,}0330$
H_2O : 2% ; (temp. = 71° C)

Rearrangement of (±) cis-2-benzamido-cyclohexan-1-ol

Measurements were carried out — in view of the low solubility of substrate — in the presence of about 1,7 mole/l of hydrogen chloride at 71° C, 81° C and 91° C. Rate constants and their mean values are summarized in Table III. The activation energy was found to be 15,8 Kcal/mole.

Experimental

Materials

Both of (±) cis- and trans-2-benzamido-cyclohexan-1-ol were prepared according to McCasland [10], then several times recrystallized from dioxan and held in desiccator filled with phosphorous pentoxide.

Dry dioxan was prepared from azeotropic aqueous dioxan [11]. Its purity was controlled by measuring the refractivity while its dryness checked by Karl Fischer's reagent.

Dioxanic hydrogen chloride was prepared from dry dioxan by saturating with dry hydrogen chloride in the following way: dry dioxan was introduced into a flask provided with magnesium perchlorate protecting tube through which hydrogen chloride, formed from ammonium chloride, was bubbled. Previously this hydrogen chloride was carried through two towers filled with sulphuric acid and a column filled with phosphorous pentoxide. The hydrogen chloride content of dioxan was determined by titration and hydrogen chloride concentration applied at the measurements was adjusted from time to time by dilution of it with dry dioxan. Both dioxan and dioxanic hydrogen chloride were held in waxed glass vessel to keep off wetting.

To controll the dryness of dioxanic hydrogen chloride (*e.g.* with Karl Fischer's reagent) did not succeed.

Materials consumpted by the determination of nitrogen with Hussey—Maurer's [12] apparatus were all of corresponding to the description of authors mentioned quality.

Measurements

Solutions of different concentrations were all prepared so that samples were weighed into a 50 ml. containing volumetric flask, solved in dioxanic hydrogen chloride at room temperature, then filled to the mark. After the stock solution was prepared, the ground-glass stopper of the flask was replaced by a groundglass stopper of an authomatic buret of 10 ml capacity divided into 0,02 ml and provided with a drying tube (P_2O_2). In the place of the outlet there was a glass capillar, pulled to 10 cm out, connected with the buret with a rubber tube closed by a glass-bead. The solution was measured by 5 mls into glass balls of 10 ml volume. They were immediately soldered, care was taken to prevent loss of hydrogen chloride. In the residue of the solvent hydrogen chloride content was titrimetrically determined and this was considered to be the initial concentration of hydrogen chloride. The soldered balls were placed into Höppler thermostat set in at corresponding temperature so that they suspended on a thread into the liquid of the inner vessel of the thermostate. The replacing of the cover of thermostate was considered as the starting point of the reaction. At corresponding intervals a ball was taken out and immediately sunk into salted ice where the reaction mixture shortly freezed. The placing into the ice was considered as the end point of the reaction. Balls taken out of ice and carefully cleaned were smashed in a flask containing 5 ml water and after shaking, a corresponding amount was pipetted out from the solution, its nitrogen content determined in a Hussey—Maurer apparate [12].

* * *

The author wishes to express his gratitude to G. FODOR, member of the Hungarian Academy of Sciences and É. FODOR—VARGA for their kind interest in this work and also for their valuable advices.

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NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF ESTERS IN THE PRESENCE OF ALUMINIUM CHLORIDE

By Á. FURKA and T. SZÉLL

Institute of Applied Chemistry, The University, Szeged

(Received March 14, 1959)

A method has been suggested for quantitative determination of esters in nitrobenzene solution containig aluminium chloride. The method which is based on the application of NaF may be used for avoiding the interfering effect of $AlCl_3$ by transforming it into a water-soluble complex (Na_3AlF_6) making possible the alkalimetric determination of esters.

In order to follow FRIES reactions and FRIEDEL—CRAFTS reactions of phenols, respectively, it may be necessary to determine the ester-content of the reaction mixtures. Methods used so far all agree in the first step being the isolation of ester from the mixture decomposed with dilute acid. Then ester isolated was either directly measured quantitatively, or it was hydrolysed and the products were determined in a suitable way [1]—[4]. Without the isolation of ester a number of interfering factors emerge generally when determining alkalimetrically the esters. In this case the medium is heterogeneous and this fact renders difficult the titration or boiling. Also the aluminium chloride content of the system may be the source of different problems, since it undergoes hydrolysis even in neutral medium and the precipitate formed makes uncertain the detection of the end points of titrations. Nor is the isolation of esters a simple task, for it is a lengthy one and since it consists of more steps, due to the inevitable losses, its accuracy is unsatisfactory.

To eliminate these difficulties a new method has been evolved by the authors, which renders possible the determination of the ester content relatively rapid, with an error less than 2%. Using this method the isolation of ester from reaction mixture hydrolysed is not necessary. The method is based on the transformation of aluminium chloride with aqueous solution of sodium fluoride into a water-soluble complex (Na_3AlF_6). This reaction has already been used in analytical chemistry in the determination of aluminium [5]—[8]. Under the suggested conditions in the presence of ethanol the well-known alkalimetric determination of esters can be performed in homogeneous medium. Using this method, resins and tars, being always present in such reaction mixtures which cause some trouble in other cases, do not disturb. It is a great advantage of this method that the determination of ester can be connected with the isolation of products formed during the reaction giving in an easier way products less contaminated than those obtained without applying sodium fluoride [9]. When applying the proposed method care must be taken that in the presence of Na_3AlF_6 complex the acid or alkali content of aqueous solutions cannot be exactly determined in one step by titration, at least in the concentration range of our measurements, applying phenolphtalein as indicator. *E. g.* when determining the acid content of such a solution by titration with alkali, the acid content measured is less than the real one. The cause of this may be that the rate of neutralisation reaction greatly decreases near the equivalence point. This error of the determination can be eliminated by measuring blank value and taking it into consideration. Results of measurements carried out by this method, as well as examples for its application (determination of thymylacetate) are given in the experimental part.

Experimental

A) *Materials*

Solutions. 0,1 *N* and 0,75 *N* carbonate-free NaOH solution, 0,1 and 1 *N* HCl solution, neutral NaF solution of 3,4—3,9%.

Nitrobenzene. Twice distilled, held over $CaCl_2$.

Ethanol. Commercial grade of 96%.

Aluminiumchloride. VEB. Feinchemie z. synth.

Thymylacetate. Prepared according to A. SPASOV's method [10]. Its ester content was found, by measuring the amount of NaOH needed for saponification, to be of 99,14%.

B) *Quantitative determination of thymylacetate*

The method was applied in kinetical investigations of Fries reaction of thymylacetate as follows: from a reaction mixture, being the initial concentrations both of aluminium chloride and thymylacetate in nitrobenzene solution 0,5 mole/1, 2 ml was removed and poured into a 100 ml conical flask with ground neck, containing 2 ml of ethanol. To the homogeneous solution 0,3 ml 1 *N* of HCl solution, 2 drops of phenolphtalein indicator, pumice, 12 ml of NaF solution and at last 6 ml distilled water were added. Should the indicator change its colour when adding NaF solution the determination must be repeated giving more hydrochloric acid. The mixture, already consisting of two phases was shaken two minutes, it was allowed to stand for about 2 minutes, four drops of phenolphtalein were introduced and the mixture neutralized with 0,1 *N* NaOH till attained 3 minutes' standardization of colour. (To take care of the period is very necessary.) After pipetting 2 ml of 0,75 *N* NaOH and adding 17 ml of ethanol, the solution was boiled for 45 minutes under a reflux condenser (during boiling the mixture became homogeneous), then the hot solution was estimatedly neutralized with 0,1 *N* hydrochloric acid adding at the same time 2 ml excess (altogether "*a*" ml). The change of the indicator was hardly noticeable, due to coloured sideproducts of FRIES reaction which are soluble in medium containing ethanol. After adding new pumice, in order to expel carbondioxide, the solution was boiled for 3 min. and then cooled at room temperature. The content of the flask was poured into a measuring flask of 100 ml volume, filled at mark (because of 2 ml nitrobenzene present the volume of the solution was considered to be 98 ml), then transferred into a glass cylinder of 2,5 cm diameter, in which it was allowed to stand for about an hour. During this time both nitrobenzene and colourized materials disturbing the titration separated. 50 ml of the clear solution was removed and adding 4 drops of indicator titrated with 0,1 *N* NaOH till standard colour was obtained ("*c*" ml). The result of the determination was calculated on the basis of equation (1) where "*b*" signifies the blank value

$$\text{thymylacetate mmole} = 1{,}5 + \frac{9{,}8}{50} c - 0{,}1\ a - 0{,}1\ b. \qquad (1)$$

C) *Determination of blank value*

From a solution containing the same quantity of aluminium chloride as that mentioned above, 2 ml was removed and exactly the same procedure performed as with the reaction mixture, described under B). The value of the blank ("*b*" ml) was calculated from equation (2), where c_b and a_b mean the corresponding acid and alkali consumption, respectively, at the determination of the blank

$$b = 15 + \frac{98}{50} c_b - a_b. \qquad (2)$$

At analyses of reaction mixtures of different concentrations of aluminium chloride (A_0) to use quantities of materials in Table I seemed to be the most purposeful.

Table I

A_0 mole/l	1 *N* HCl ml	NaF solution ml	Water ml	Ethanol ml
0,25	0,2	6	10	17
0,50	0,3	12	5	17
0,75	0,4	18	—	20
1,00	0,5	24	—	20
1,25	0,6	30	—	24
1,50	0,7	36	—	30

D) *Controlling of reliability of the method*

Into conic flask of 100 ml volume thymylacetate was measured with 0,1 mg accuracy, then nitrobenzenic aluminium chloride solution of corresponding amount and concentration was pipetted into it. Further the procedure was the same as described above. Carrying out a number of measurements it was concluded that the average error of the determination is less than 2% and never greater than 4%.

* * *

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NEUE NITRO—CHALKONE III[1]

Von GY. SIPOS und T. SZÉLL

(Eingegangen am 14. Märcz 1959)

Institut für Angewandte Chemie der Universität Szeged

Es wurden im Laufe unserer Untersuchungen vier, in der Literatur bisher nicht beschriebene, neue Nitro-hydroxy-chalkone hergestellt. Bei zweien dieser Nitro-hydroxy-chalkone wurde die Synthese mit Hilfe eines sauren Katalysators ($AlCl_3$) verwirklicht. Es konnte festgestellt werden, daß die Ausbeute verhältnismäßig gut ausfällt, wenn die Substituenten des Aldehydanteils die Herausbildung des elektrophilen Kohlenstoffes der Aldehydgruppe nicht hemmen.

Als Fortsetzung unserer vorangehenden Arbeiten [1], [2] haben wir weitere neue Nitro-hydroxy-chalkone dargestellt.

Vorliegende Arbeit ist ein weiterer Beweis für die Richtigkeit unserer früheren Beobachtung [3], daß die Synthese der Nitro-hydroxy-chalkone nicht nur mit Hilfe basischer, sondern auch mit sauren Katalysatoren zu verwirklichen ist. Es scheint aber, daß — in Gegenwart von $AlCl_3$ — auch die Dypnonbildung stattfindet. Wir werden bezüglich der Bildung von Dypnon weitere Untersuchungen ausführen.

Bereits die vorliegenden Versuche lassen feststellen, daß die Chalkonbildung auch im Falle der Nitro-hydroxy-chalkone mit relativ guter Ausbeute einhergeht, wenn die Substituenten des Aldehydanteiles in Anbetracht ihrer Lage und ihres Charakters die Entstehung des elektrophilen Kohlenstoffs an der Aldehydgruppe nicht verhindern. Diese experimentelle Tatsache steht im Einklang mit der Theorie von HAUSER und Mitarbeitern [4] bezüglich des Mechanismus der „Aldol"-Kondensation.

Es gelang durch Kondensation des 3-Nitro-4-hydroxy-acetophenons mit 4-Chlor-benzaldehyd sowohl in Gegenwart von wässerigem NaOH, als auch von $AlCl_3$ (ohne Lösungsmittel) das 3′-Nitro-4′-hydroxy-4-chlor-chalkon (I) herzustellen. Ferner wurde auch das 3′-Nitro-4′,4-dihydroxy-chalkon (II) durch Kondensation in Gegenwart von Alkali des 3-Nitro-4-hydroxy-acetophenon mit 4-Hydroxy-benzaldehyd, sowie das 4′-Nitro-2′-hydroxy-4-chlor-chalkon (III) mittels alkalischer Kondensation des 4-Nitro-2-hydroxy-acetophenons mit 4-Chlor-benzaldehyd und das 5′-Nitro-2′-hydroxy-4-chlor-chalkon (IV) durch Kondensation in Gegenwart von $AlCl_3$ des 5-Nitro-2-hydroxy-acetophenons mit 4-Chlor-benzaldehyd gewonnen.

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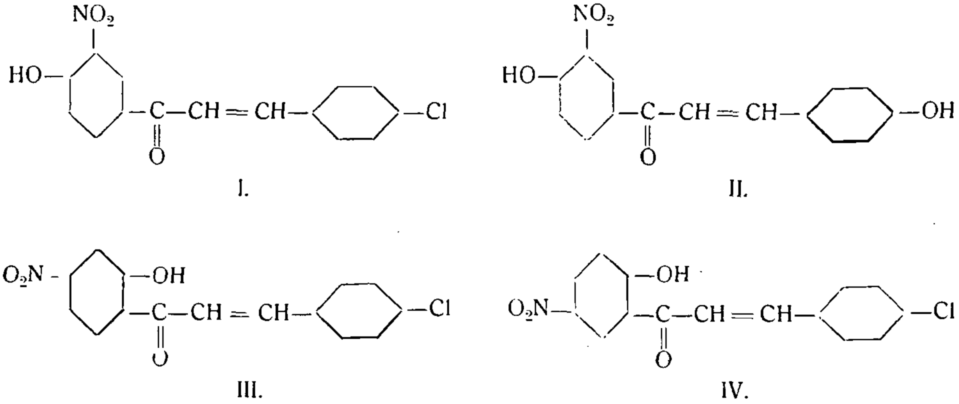

Fig. 1

Experimenteller Teil[2]

a) *Durchführung der Kondensation in Gegenwart von Alkali.* 0,55 g Nitro-hydroxy-acetophenon[3] (3 mMol) wurden mit 1 ml 96-proz. Aethanol benetzt und in 30 ml 1*n* NaOH gelöst. Hinzugefügt wurden äquivalente Mengen in 5 ml 96-proz. Aethanol gelösten Aldehyds (0,42 g 4-Chlor-benzaldehyd bzw. 0,37 g 4-Hydroxy-benzaldehyd, beide 3 mMol) und das Reaktionsgemisch 2 Stunden am Wasserbad erwärmt. Nun wurde es filtriert, in Aethanol gewaschen, bei Raumtemperatur getrocknet und das rohe Produkt aus 96-proz. Aethanol/Essigester (1:1) umkristallisiert.

b) *Durchführung der Kondensation in Gegenwart von* $AlCl_3$. Es wurde mit dengleichen Mengen gearbeitet wie bei der alkalischen Kondensation, aus den Acetophenonen und Aldehyden ein homogenes Gemisch bereitet und dieses mit 0,81 g $AlCl_3$ (VEB Feinchemie, Eisenach) (6 mMol) versetzt. Nach erneuter Homogenisierung wurde das Gemisch 1 Stunde lang bei 145° am Ölbad in geschmolzenem Zustande gehalten. Nach dem Abkühlen der erstarrten Masse erfolgte Zerlegen durch ein Gemisch von 4 ml eiskalten dest. Wasser und 1 ml cc HCl, nach eintägigem Stehen, Filtrieren, Waschen mit Wasser und dann mit Aethanol und Trocknen bei Raumtemperatur. Das Rohprodukt wurde aus Aethanol/Essigester (1:1) umkristallisiert.

3'-Nitro-4'-hydroxy-4-chlor-chalkon (Ia). Es scheiden 0,96 g Chalkon-Natriumsalz aus, dieses wurde bei 50—60° C mit 6 ml 1*n* H_2SO_4 ansäuert. 0,70 g gelbe Substanz, Schmp. 170—175° C. Nach dem Umkristallisieren hellgelbe Nadeln, Schmp. 183—184° C.

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[2] Alle Schmelzpunkte sind unkorrigiert.

[3] Die in dieser Arbeit als Ausgangsmaterial verwendeten Nitro-hydroxy-acetophenone wurden durch Fries'sche Verschiebung aus den entsprechenden Nitro-phenyl-acetaten dargestellt; vgl. hierzu C. F. Brown: J. Amer. Chem. Soc. **68**, 872 (1946); A. Gerecs, T. Széll, H. Windholz: Acta Chim. Hung. **3**, 459 (1953); T. Széll, Frau Gy. Sipos, Gy. Szentgáli: Magyar Kémiai Folyóirat (Ung. Z. Chem) **59**, 148 (1953).

Analyse: $C_{15}H_{10}NO_4Cl$ (303,7)
Berechnet: C 59,30 H 3,30 N 4,61
Gefunden: C 59,52 H 3,07 N 4,71

3'-Nitro-4'-hydroxy-4-chlor-chalkon (Ib). 0,95 g rohes Chalkon wurden erhalten. Bräunlichgelbe Substanz, Schmp. 180—181° C. Nach Umkristallisieren (die Lösung war gelb) blaugrüne Nadeln, Schmp. 183—184° C.

Der Mischschmelzpunkt der Substanzen Ia und Ib gab keine Depression.

Analyse: $C_{15}H_{10}NO_4Cl$ (303,7)
Berechnet: C 59,30 H 3,30 N 4,61
Gefunden: C 59,10 H 3,00 N 4,85

3'-Nitro-4', 4-dihydroxy-chalkon (IIa). Nach der Kondensationszeit schied kein Chalkon-Natriumsalz aus. Nach Ansäuern mit 2 ml cc HCl erhielten wir bräunlichgelbe Substanz, die nach Umkristallisieren aus Aethanol/Essigester (1:1) schmolz bei 214—216° C.

Analyse: $C_{15}H_{11}NO_5$ (285,2)
Berechnet: C 63,15 H 3,88 N 4,91
Gefunden: C 62,91 H 3,62 N 5,22

4'-Nitro-2'-hydroxy-4-chlor-chalkon (IIIa). Auf die gleiche Weise erhalten wie Ib. Nach dem Umkristallisieren lebhaft gelbe Nadeln, Schmp. 192—193° C

Analyse: $C_{15}H_{10}NO_4Cl$ (303,7)
Berechnet: C 59,30 H 3,30 N 4,61
Gefunden: C 59,30 H 3,01 N 4,91

5'-Nitro-2'-hydroxy-4-chlor-chalkon (IVb). 0,5 g rohes Chalkon wurden erhalten. Nach Umkristallisieren gelbe pulverartige Substanz, Schmp. 216—217° C.

Analyse: $C_{15}H_{10}NO_4Cl$ (303,7)
Berechnet: C 59,30 H 3,30 N 4,61
Gefunden: C 59,47 H 3,04 N 4,80

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BEITRÄGE ZUR WASSERABWEISENDEN AUSRÜSTUNG VON GEWEBEN AUS ZELLULOSE MITTELS METALLSEIFEN

Von B. VÁRKONYI
Kolloidchemisches Laboratorium der Universität Szeged
und
T. SZÉLL
Institut für Angewandte Chemie der Universität Szeged

(Eingegangen am 1. April 1959)

Die hydrophobierende Wirkung verschiedener Metallseifen sowie der Einfluß der Reihenfolge und der Konzentration der Imprägnierbäder wurde an Geweben aus Baumwolleleinwand untersucht. Es wurde festgestellt, daß die stärkeste hydrophobierende Wirkung durch Aluminium-, Kupfer-, Zink- und Bleiseifen erreicht werden kann. Imprägniert man die Geweben zuerst mit einer Natriumseifenlösung und sodann in einem nachfolgenden Bade mit einer Metallsalzlösung, so erhält man einen günstigeren Effekt. Es wurde ferner gefunden, daß die Hydrophobierung auch vom Molverhältnis der metallseifenbildenden Komponenten abhängt, und daß die Hydrophobität der Geweben je höher sein wird, desto mehr man die Bildung von Metallseifen höherer Basizität sichert.

Es ist bekannt, daß die Benetzungsfähigkeit der Oberflächen von festen Körpern mit dem Randwinkel (α) gekennzeichnet werden kann, den die am Rande des die Oberfläche des festen Körpers benetzenden Flüssigkeitstropfens gelegte Tangente mit der festen Oberfläche bildet [1].

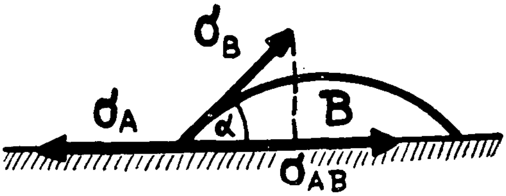

Fig. 1.

Der Wert dieses Randwinkels wird durch die zwischen dem festen Körper und dem Gas bestehende Oberflächenspannung (σ_A), durch die zwischen der Flüssigkeit und dem Gas bestehende Oberflächenspannung (σ_B), sowie durch die zwischen dem festen Körper und der Flüssigkeit bestehende Grenzflächenspannung (σ_{AB}) bestimmt.

Aus der Fig. 1 geht hervor, daß im Falle eines Gleichgewichtes

$$\sigma_A = \sigma_{AB} + \sigma_B \cos\alpha \quad \text{und} \quad \cos\alpha = \frac{\sigma_A - \sigma_{AB}}{\sigma_B}.$$

Die Differenz $\sigma_A - \sigma_{AB}$ gibt die Benetzungsspannung (Adhäsionsspannung) an. Handelt es sich um eine lyophile Oberfläche, so ist $\sigma_A - \sigma_{AB} > 0$ bzw. bleibt der Randwinkel α kleiner als 90°, während im Falle einer lyophoben Oberfläche $\sigma_A - \sigma_{AB} < 0$ ist, bzw. bewegt sich der Wert des Randwinkels über 90°.

Die Benetzungsfähigkeit von festen Körpern kann man durch Änderung der Oberflächenspannung des Netzmittels bzw. der Benetzungsspannung beeinflussen. Nachdem aber reines Wasser eine konstante Oberflächenspannung besitzt, hat man bei der wasserabweisenden Ausrüstung der Geweben ausschließlich die einzige Aufgabe, die Benetzungsspannung in solchen Maße herabzusetzen, daß $\sigma_A - \sigma_{AB} < 0$ sei.

Zu diesem Zweck werden die hydrophilen Gewebenoberflächen mittels Behandlung mit apolaren Substanzen (wie Paraffin, Wachse, Metallseifen, usw.) oder durch chemische Wechselwirkungen (wie Veresterung bzw. Verätherung) hydrophobiert [2]—[5].

In der vorliegenden Mitteilung beschäftigen wir uns mit einigen Problemen des Zweibadverfahrens mit Metallseifen.

Obwohl diese Methode schon seit langer Zeit angewendet wird, blieben einige Probleme noch ungenügend aufgeklärt.

Es schien interessant die folgenden Fragen näher zu untersuchen:

1. Welche Unterschiede zeigen sich in der Hydrophobität der bei der Gegenwirkung der verschiedenen Natriumseifen und Metallsalze entwickelten Metallseifenschichten?

2. Was für ein Zusammenhang besteht zwischen die Hydrophobität der imprägnierten Geweben und der Reihenfolge der Imprägnierung mit den verschiedenen metallseifenbildenden Komponenten?

3. In welchem Maße sich die Hydrophobität der Geweben mit der Konzentration der angewandten Lösungen der metallseifenbildenden Komponenten erhöht?

1. Hydrophobität der mit verschiedenen Metallseifen ausgerüsteten Geweben

Bei der Darstellung von wasserunlöslichen hydrophoben Metallseifen benötigt man einerseits ein im Wasser gut lösliches Salz irgendeiner seifenbildenden organischen Säure, andererseits aber auch ein mehrwertiges Metallion.

Im Laufe unserer Versuche wurden an der Oberfläche des Gewebes[1] die Stearate, Naphthenate bzw. Resinate einiger mehrwertigen Metalle auf solche Weise hergestellt, daß die Geweben nach einem Imprägnieren mit Lösungen von Natriumstearat, Natriumnaphthenat bzw. Natriumresinat von 2,5% Konzentration 20 Minuten lang bei 80—85° C getrocknet, sodann mit einer 2,5%-igen Metallsalzlösung behandelt wurden. Die Geweben wurden in jedem Versuch mit der Hand, auf gleiche Weise, für je 10 Sekunden in die Imprägnierbäder von 20—22° C eingetaucht. Dann ließ man die überschüssige Flüssigkeit abtropfen und trocknete die Gewebemuster in einem Trocken-

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[1] Bei den vorliegenden Versuchen wurden immer Muster aus gefärbtem Baumwolleleinwandgewebe gleicher Qualität, mit einem Bedeckungsfaktor von 105,8% angewandt.

schrank von 110° C. Nachdem wurde die Wasserdichtheit der imprägnierten Gewebemuster mit einem SCHOPPERschen Apparat gemessen. Die Höhe der angewandten Wassersäule wurde in jedem Fall mit einer Geschwindigkeit von 10 cm/min vergrößert. Die gefundenen Werte (als Höhen der Wassersäule) sind für die mit verschiedenen Metallseifen ausgerüsteten Gewebemuster in der Tabelle I zusammengefaßt.

Tabelle I

Wasserdichtheiten der mit verschiedenen Metallseifen ausgerüsteten Geweben
(ausgedrückt in cm der Wassersäulen)

Angewandtes Metallsalz	Angewandte Seife		
	Natriumstearat	Natriumnaphthenat	Natriumresinat
Aluminiumazetat	63	50	58
Aluminiumformiat	56	50	55
Aluminiumchlorid	45	35	43
Zinksulfat	46	33	44
Kupfersulfat	43	42	53
Bleinitrat	42	35	48
Kalziumchlorid	46	20	24
Bariumchlorid	40	24	23
Mangan(II)sulfat	40	30	38
Nickelsulfat	40	30	39
Kadmiumsulfat	37	22	39
Kobalt(II)nitrat	37	29	35
Eisen(III)chlorid	36	33	41
Chrom(III)chlorid	35	31	37
Strontiumchlorid	30	14	38
Zinn(II)chlorid	20	18	24
Titan(III)chlorid	17	16	38
Wismutnitrat	15	13	3
Antimon(III)chlorid	15	16	25

Aus den Angaben der Tab. I geht hervor, daß die Hydrophobität der entwickelten Metallseifenschicht sowohl von der Qualität der metallseifenbildenden organischen Säuren wie auch von der Qualität der angewandten mehrwertigen Metallionen beeinflußt wird. Die höchsten Wasserdichtheiten (Wassersäulenwerte) wurde mit jenen Gewebemustern erhalten, die wir mit Aluminium-, Kupfer-, Blei- bzw. Zinkseifen imprägnierten.

Überdies beeinflußt die Qualität der metallseifenbildenden Komponenten noch verschiedene, praktisch wichtige Eigenschaften der Oberflächenschicht, wie z. B. die Adhäsion zur Zelluloseoberfläche, die mechanischen Eigenschaften (Festigkeit, Biegsamkeit, Elastizität, usw.), die Waschechtheit, die durch Einwirkung von Licht und Wärme hervorgerufene Alterung und nicht allzuletzt die Schutzwirkung gegen Verschimmeln und Fäulnis.

2. *Hydrophobität von Geweben, die durch in verschiedener Reihenfolge angewandten Bäder ausgerüstet wurden*

Es ist eine schon längst bekannte Erfahrung, daß die Reihenfolge der Imprägnierbäder das Maß der Hydrophobität der Geweben stark beeinflußt. Wird nämlich ein Gewebe zuerst in einer Seifenlösung und nachfolgend in einem zweiten Bad mit einer Metallsalzlösung imprägniert (gerade Reihenfolge), so erhält man ein Produkt von wesentlich besserer Hydrophobität als im entgegengesetzten Falle (umgekehrte Reihenfolge).

Es wurden Versuche mit der Zielsetzung durchgeführt, das Maß zu bestimmen, mit welchem die Hydrophobität der Geweben bei Anwendung der umgekehrten Reihenfolge herabgesetzt wird. Die diesbezüglichen Versuchsangaben sind in der Tabelle II angeführt.

Tabelle II

Wasserdichtheiten der mit verschiedenen Reihenfolgen angewandten Bädern ausgerüsteten Geweben (ausgedrückt in cm der Wassersäulen)

Metallseifenbildende Komponenten				Gerade Reihenfolge	Umgekehrte Reihenfolge
2,5%	Natriumstearat	+ 2,5%	Aluminiumchlorid	45	31
5%	Natriumstearat	+ 5%	Aluminiumchlorid	65	43
5%	Natriumstearat	+ 5%	Aluminiumazetat	68	44
5%	Natriumstearat	+ 5%	Aluminiumformiat	58	40
2,5%	„gemischte Natriumseife“[2]	+ 5%	Aluminiumformiat	53	33
5%	„gemischte Natriumseife“	+ 10%	„gemischtes Metallsalz“[3]	47	30
20%	„gemischte Natriumseife“	+ 20%	„gemischtes Metallsalz“	37	25
30%	„gemischte Natriumseife“	+ 30%	„gemischtes Metallsalz“	37	25

Wie aus den Ergebnissen der Tab. II ersichtlich, sind die Wasserdichtheiten (Wassersäulenwerte) beim Imprägnieren in umgekehrter Reihenfolge stets mit ungefähr 30—40% niedriger. Das ist offenbar dadurch herforgerufen, daß die Hydrophobität der Oberfläche durch den im zweiten Bade auf die Oberfläche angeführten Seifenüberschuß vermindert wird.

Durch Änderung der Reihenfolge der Imprägnierung verändert sich nicht nur die Hydrophobität sondern auch der Griff des Gewebes, es wird nämlich etwas härter, wenn man die Imprägnierung in umgekehrter Reihenfolge durchführt. Dies ist offenbar mit der Entwicklung von wasserunlöslichen basischen Metallsalzen verbunden.

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[2] Die „gemischte Natriumseife“ bestand aus einem Gemisch von Natriumstearat, Natriumnaphthenat und Natriumresinat in Verhältnis von 1:1:1 (g), mit einem durchschnittlichen Molekulargewicht von 260.

[3] Das „gemischte Metallsalz“ bestand aus einem Gemisch von Aluminiumazetat, Kupfersulfat und Zinksulfat in Verhältnis von 1:1:1 (g), mit einem durchschnittlichen Molekulargewicht von 242.

Es wurden Waschversuche vorgenommen, um den Einfluß der Reihenfolge der Imprägnierbäder auf das Maß der Dauer der Ausrüstung zu bestimmen. Bei diesen Versuchen wurden Gewebemuster angewandt, die wir vorangehend mit einer 5%-igen „gemischten Natriumseifenlösung” und mit einer 10%-igen „gemischten Metallsalzlösung” imprägnierten. Nach Ausrüstung wurden die Probestücke in einer 0,5%-igen Seifenlösung eine Minute lang bei 45° C gewaschen. Die Versuchsergebnisse sind in der Tabelle III zusammengefaßt und auf Fig. 2 graphisch dargestellt.

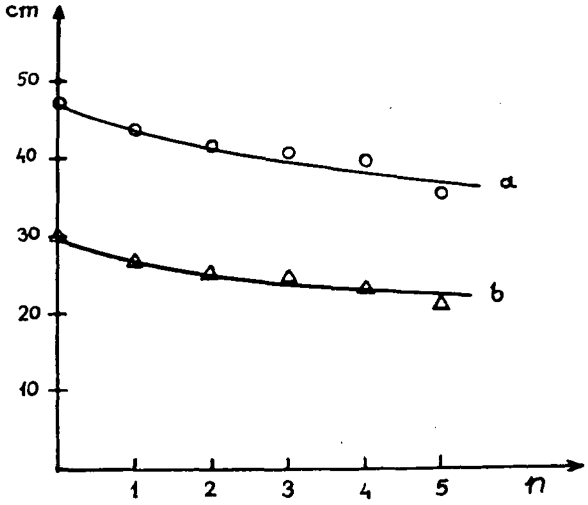


Fig. 2. Änderung der (in cm Wassersäule ausgedrückten) Wasserdichtheitswerte mit der Zahl der Waschungen (*n*). a: Bäder in gerader Reihenfolge angewandt; b: Bäder in umgekehrter Reihenfolge angewandt

Die angeführten Versuchsergebnisse zeigen an, daß auf Einwirkung des Waschprozesses die auf zwei verschiedenen Wegen hergestellten Metallseifenschichten eine Peptisierung in demselben Maße erleiden, und daß Unterschiede nur in den Hydrophobität der Oberfläche vorliegen.

Tabelle III

Änderung der Wasserdichtheitswerte der durch in verschiedener Reihenfolge angewandten Bäder ausgerüsteten Geweben mit der Zahl der Waschungen

Anzahl der Waschungen	Wasserdichtheit ausgedrückt in cm Wassersäule	
	Gerade Reihenfolge	Umgekehrte Reihenfolge
0	47	30
1	44	27
2	42	26
3	41	25
4	40	24
5	36	22

3. *Änderung der Hydrophobität der Geweben mit der Konzentration der Imprägnierlösungen*

In unseren weiteren Versuchen untersuchten wir, wie die durch die Höhe der Wassersäule ausgedrückte Wasserdichtheit mit der Konzentration der metallseifenbildenden Komponenten abhängig ist. Für diesen Zweck imprägnierten wir die Gewebemuster zuerst mit einer „gemischten Natriumseifenlösung" geeigneter Konzentration, sodann in einem zweiten Bad mit einer „gemischten Metallsalzlösung". Die erhaltenen Resultate sind in der Tabelle IV bzw. Fig. 3 dargestellt.

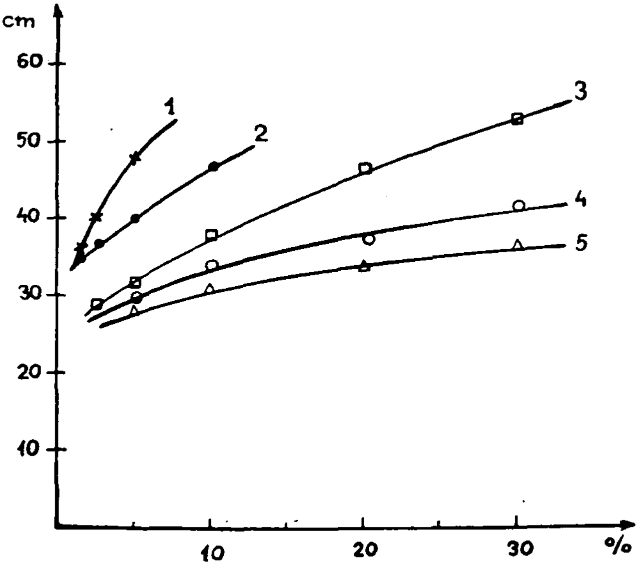


Fig. 3. Änderung der (in cm Wassersäule ausgedrückten) Wasserdichtheitswerte mit der Konzentration der seifenbildenden Komponenten

Wie die angeführten Versuchsergebnisse zeigen, erhöht sich die durch die Höhe der Wassersäule ausgedrückte Wasserdichtheit mit der Konzentration der Metallsalzlösungen in jedem Fall bei konstanter Seifenkonzentration, während eine Verminderung mit der Erhöhung der Konzentration der Seifenlösungen bei einer konstanten Metallsalzkonzentration beobachtbar ist.

Nachdem in unseren vorliegenden Versuchen die durchschnittlichen Molekulargewichte der in der Reaktion teilnehmenden Natriumseifen und Metallsalzen beinahe dieselben waren, ist das Verhältnis der Konzentrationen an Natriumseifen und Metallsalzen dem Molverhältnis annähernd gleich. So kann aus Fig. 3 unmittelbar abgelesen werden, daß z. B. bei einem Molverhältnis 1 : 1 von Seife zu Metallsalz ungefähr die gleichen Werte für Wassersäulen erhalten werden, unabhängig von der Menge der entstandenen Metallseifen, d. h. von der Dicke der hydrophoben Metallseifenschicht. Zahlenmäßig ausgedrückt: gibt es z. B. bei 2,5% „gemischter Natriumseifenlösung" und 2,5%

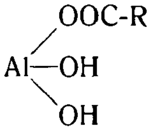
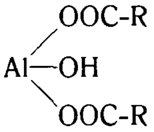
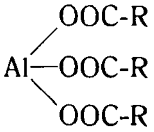
„gemischter Metallsalzlösung” eine Wassersäule von 40 cm, während bei 30% Natriumseife und 30% Metallsalz die Höhe der Wassersäule 37 cm betrug. Wenn jedoch das Molverhältnis der Seife zu Metallsalz unter 1 bleibt, so erhöhen sich die erhaltenen Werte der Wassersäulen, gleichfalls unabhängig von der Menge der entstandenen Metallseife. Bei 10% Seife und 20% Metallsalz ergab sich z. B. eine Wassersäule von 47 cm Höhe, bei 2,5% Seife und 5% Metallsalz dagegen eine Wassersäule von 48 cm Höhe.

Tabelle IV

Änderung der (in cm Wassersäule ausgedrückten) Wasserdichtheitswerte der durch in gerader Reihenfolge angewandten Bäder ausgerüsteten Geweben bei erhöhender Konzentration der seifenbildenden Komponenten

Nr	Konzentration der „gemischten Natriumseifenlösung“	Konzentration der „gemischten Metallsalzlösung“					
		1,5%	2,5%	5%	10%	20%	30%
1	2,5%	36	40	48	–	—	—
2	5%	35	37	40	47	-	—
3	10%	—	29	32	38	47	53
4	20%	—	—	30	34	37	42
5	30%	—	—	28	31	34	37

Mehrwertige Metallionen sind fähig, in einem wäßrigen Medium mit den seifenbildenden organischen Säureradikalen Metallseifen verschiedener Basizität und verschiedener Assoziationsstruktur zu bilden. Im Falle von Aluminiumsalzen und Natriumstearat können z. B. — in Abhängigkeit von dem angewandten Molverhältnis — die folgenden Aluminiumseifen entstehen (es ist jedoch fraglich, ob die „Triseife” wirklich darstellbar sei):

wo $R = C_{17}H_{35}$ ist.

Unsere Versuchsergebnisse bestätigen, daß die Geweben über je höheren Hydrophobitäten verfügen, desto stärker die Entwicklung von Metallseifen höherer Basizität gesichert wird.

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