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BEREZIN, B.D.

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5(4)

AUTHORS: Vasil'yev, V. P., Korableva, V. D., Yatsimirskiy, K. B. SOV/153-58-3-30/30

TITLE: Conference Discussion on the Methods of Investigating the Complex Formation in Solutions (Soveshchaniye-diskussiya po metodam izucheniya kompleksoobrazovaniya v rastvorakh)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 3, pp 173 - 174 (USSR)

ABSTRACT: From February 18 to 21, 1958 a conference discussion took place at the town of Ivanovo: it dealt with the subjects mentioned in the title. It was called on a decision of the VIIth All-Union Conference on the Chemistry of Complex Formations. More than 200 persons attended the conference, among them 103 delegates from various towns of the USSR. At the conference methods of determining the composition of the complexes in solutions were discussed, as well as the methods of calculating the instability constants according to experimental data and problems concerning the influence of the solvent upon the processes of complex formation. [illegible] In the lecture by A. K. Babko and M. M. Tananayko, "Physical and Chemical Analysis of the Systems With 3 Colored Complexes in the Solution", the results of a systematic investigation in copper-quinoline-salicylate, as well as in copper-pyridine-salicylate systems by means of the optical method were dealt with. In the lecture by Ya. A. Fialkov the idea of a further investigation of the complex formation processes in solutions was developed. Besides the determination of the composition and stability of the complexes also the physical and chemical properties, the chemical nature and the structure of the complex compounds must be investigated . . . . .

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I. I. Alekseyeva and K. B. Yatsimirskiy in their lecture "Investigation of the Polymerization of Iso-Poly Acids in Solutions" mentioned experimental results of the investigation of the polymerization in solutions of molybdic acid. The authors proved that especially the molybdic acid within a certain range of the pH values and the concentrations exists as a number of compounds that can be expressed by an overall formula $MoO_4(HMoO_4)^{n-2}$. In the lecture by N. V. Aksel'rud and V. B. Spivakovskiy investigation results on basic salts taking into account the complex formation in solutions by means of the potentiometric method were mentioned for systems with zinc, cadmium and indium. In the evaluation of their results the authors employed the method of the table difference. The calculation of the consecutive constants was carried out according to the interpolation formula by Newton. M. A. Chepelevtskiy held a lecture on "pH Measurement Method of the Solutions in Combination With the System Analysis of the Solubility Diagram of the System Cu^{2+}-HCl - H_2O in Investigating Complex Copper Compounds in Saturated Solutions". It was found that the substance at the bottom of the liquid is more basic than the solution: furthermore, the increased acidity of the solution from the viewpoint of the formation of hydroxy-chloro complexes in the solution was explained. V. I. Kuznetsov opened the discussion with his lecture; he pointed out the necessity of utilizing the concepts worked out in the investigations of the polymerization in organic chemistry in the chemistry of polynuclear complexes. A. A. Grinberg thinks that the new approach of the hydrolysis

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investigation as developed by the Scandinavian school is of high value. He also pointed to the necessity of studying the kinetics of the polymerization process and a quantitative determination of the strength of the polymers. A. K. Babko pointed out that the study of the polymer structure was necessary. N. P. Komar' mentioned in his lecture that the rather widely spread polymerization type according to the scheme "nucleus + chain members" is not obtained in all cases. The following scientists took part in the discussion: V. N. Tolmachev, A. V. Ablov, I. S. Mustafin, I. V. Tananayev and K. B. Yatsimirskiy. A. K. Babko then discussed in his lecture "Methods of Determining the Dissociation Constant of the Complex Groups in Solutions" the main principles of determining the instability constants. N. P. Komar' discussed in his lecture "Calculation Methods of the Instability Constants of the Complex Compounds According to Experimental Data" the possibilities of using the known calculation methods of the instability constants for various cases of the complex formation in solution. If several mononuclear complexes are formed the displacement method by Abegg and Bodlender (completed by A. K. Babko) cannot be recommended for the calculation of the instability constant. The lecturer discussed the dissolution methods of the polynomials proposed by B'yerrum, Leden, Rossoti, Sketchard, Edsolloy and other authors. The constants calculated in this way are not very accurate. It was proved that the method of successive approximations can lead to wrong conclusions as to the chemical processes taking place in the system investigated. The most probable value of the physical constants can be obtained by the method of the least squares. B. V. Ptitsyn, Ye. N. Tekster and L. I. Vinogradova described the determination methods of the instability constants of the oxalate complexes of niobium, uranium and iron which are based on the investigation of the equilibrium displacement of the complex formation by silver ions. N. K. Bol'shakova, I. V. Tananayev and G. S. Savchenko held a lecture on "The Role of the Time Factor in the Investigation of the Complex Formation". In the discussion on the lectures A. A. Grinberg mentioned that due to the slow adjustment of the equilibria the methods discussed of determining the instability constants (palladium and cobalt complexes) can often not be employed. A. V. Ablov pointed out the necessity of devising direct methods of proving the existence of intermediate forms in a step-wise complex formation. K. B. Yatsimirskiy mentioned that the instability constants of slowly dissociating complexes can be calculated from thermochemical data. L. P. Adamovich, A. M. Golub among others took part in the discussion on the lectures. A. K. Babko requested inclusion in the next conference on the chemistry of complex compounds a lecture in which various calculation methods of the instability constants should be discussed by the example of actual cases. This should clarify to which divergencies of the values of the constants different methods of evaluating the experimental data can lead. N. P. Komar' stressed that in the determination of the instability constants all chemical equilibria should be taken into account that render complex the complex formation process in the solution, especially the hydrolysis processes of the central ion and the addendum. In the lecture delivered by V. M. Peshkova and A. P. Zozulya "Application of the Distribution Method to the Investigation of the Stability Constants

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of Some Thorium Complex Compounds" results obtained from the experimental investigation of the distribution of thorium compounds in the systems: acetylacetone - benzene - water, and 2-oxy-1,4,-naphthoquinone - chloroform - water were given. From these data the instability constants of the thorium complexes with acetyl-acetone and 2-oxy-1,4-naphthoquinone were calculated. I. V. Tananayev, G. S. Savchenko and Ye. V. Gonchorov held a lecture on the application of the solubility method in the determination of the stability of complex compounds in solutions. In this lecture also other methods of investigating complex formation processes in the solution were discussed (pH measurement, measurement of the optical density, as well as of the heat of mixing). B. D. Beregin held a lecture on the "Application of the Solubility Method in Studying the Phthalocyanine Complexes of Metals". He used the determined quantitative characteristics of the reaction of the transition of the phthalocyanides of cobalt, nickel, copper and zinc, as well as of the free phthalocyanine into the sulfuric acid solution for the theoretical reasoning, and as an experimental proof of the existence of

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π-bonds in the complexes investigated. These characteristics also served him as a proof of new electronic formulae of phthalocyanine and its complex derivatives. In the lecture delivered by L. L. Krupatkin on "The Method of the Two Solvents as a Method of Investigating the Formation and Properties of Organic Complexes" it was proved that this method makes it possible to determine the number of complexes formed in the system, their composition and relative stability. V. I. Kuznetsov, A. K. Babko, N. P. Komar', I. S. Mustafin and Ye. I. Tur'yan took part in this discussion. In the lecture delivered by A. A. Grinberg and S. P. Kiseleva on the complex palladium compounds (II) with a coordination number above four it was proved that in the case of a large chlorine and bromine ion excess complexes with the coordination number 5 are formed. The instability constants of these complexes were estimated. L. P. Adamovich mentioned a new manipulation in the spectrophotometric investigation of the complex compounds that can be used in systems with the formation (or predomination) of one single complex. This method makes it

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possible to determine the composition and instability constant of the complex. In the lecture delivered by K. B. Yatsimirskiy and V. P. Kozhablova the application of the theory of crystalline fields for the determination of the composition and structure of the chloride complexes of cobalt, nickel and copper according to the absorption spectra of these complexes was discussed. It was proved that in a hydrochloric acid concentration above 5 mole/liter in the solution there exists an equilibrium between the tetrahedric and octahedric form of the cobalt chloro complexes. Yu. P. Kazarenko proved in his lecture "The Application of Radioactive Isotopes in the Investigation of the Solvation Equilibrium in Solutions of Complex Compounds" the possibility of using data on the isotope exchange to clarify the structure of the complex and mechanism of the hydration processes. V. Klimov mentioned in his lecture the use of radioactive isotopes in the study of tin and antimony complexes in non-aqueous solutions. A. V. Ablov, V. N. Tolmachev, V. I. Kuznetsov and A. M. Golub took part in the discussion of the lectures. The usefulness of employing the theory of the crystalline fields in explaining the results obtained from the absorption spectra of the com-

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plex compounds was stressed. In the lecture delivered by I. A. Shek on "The Investigation of the Complex Formation by the Method of the Dielectric Permeability and the Polarization" the principles of the methods mentioned were presented. This method was employed for investigating the compounds of the type of the "affiliation" products. The lecture delivered by I. A. Shek and Ye. Ye. Kries "Employing the Method of the Dielectric Constant for Investigating Complex Compounds of the Type of Crystal Solvates in Solutions" dealt with the investigation of the solvates of lanthanum and cerium chlorides with ketones, as well as with the study of the compounds formed in heterogeneous systems with tributyl phosphate and nitric acid. V. V. Toropova gave in her lecture "The Polarographic Method of Investigating the Complex Formation in Solutions" a survey of the applications of the polarographic method in the study of the complex compounds, and illustrated several fine characteristic features of this method. In the lecture delivered by T. N. Sumarokova "The Cryoscopic Method of Investigating the Complex Formation Reactions" a survey of the possibilities of the cryoscopic method was given, and its applicability in the study of several complex compounds of stannic chloride with organic substances was proved. A. N. Golub described the results of his investigations of thiocyanate complexes of several metals. A vivid discussion took place on the lectures held. Ya. A. Fialkov and Yu. Ya. Fialkov considered the cryoscopic method of investigating complex compounds to be of considerable value. K. B. Yatsimirskiy pointed out that the publication of the surveys on individual methods of investigating the complex formation reactions would be desired; this concerns especially the polarographic method. The cryoscopic method should be brought to a level that makes the calculation of the equilibrium constants of the processes to be investigated possible. The problem of the method of evaluating the experimental results becomes more and more important. Many scientists use the instability constants without taking into account the way in which they had been obtained. The calculation methods employed by A. N. Golub are one step back, as compared to those employed at present. In his lecture N. P. Komar' pointed out the extremely great importance of the mathematical evaluation of the results obtained, as well as of the plotting of curves. A. K. Babko suggested selecting one or two systems that are experimentally well investigated, and to evaluate the results obtained according to different methods so that it is possible to check and evaluate them. Ya. I. Tur'yan took part in the discussion. Ya. A. Fialkov discussed in his lecture "The Effect of the Solvent on the Complex Formation Process as Well as on the State of Equilibrium in the Solutions of Complex Compounds" the influence exerted by the solvents upon the molecular state, upon the solvation of the system components, upon the stabilization of the complexes formed in the system, upon the step-wise dissociation of the complexes and upon a number of other processes. The influence exercised by the dielectric constant upon the complex formation process was discussed. It was concluded that a direct relation does not exist, and that the chemical nature of the solvent must be taken into account. A. V. Ablov and L. V. Nagarova held a lecture on "The Spectroscopic Investigation of Nickel Cobalt 'Pyridinates' in Various Solvents". The instability constants of the complexes were determined and it was proved that the

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stability of the 'pyridinates' is changed in dependence on the solvent. Ya. I. Tur'yan in his lecture "The Influence of the Solvent Upon the Composition and Stability of Complex Ions" discussed the polarographic investigation method of the chloride and thiocyanate complexes of lead in aqueous ethanol solutions at different content of the non-aqueous solvent and at a constant ionic strength. A step-wise character of the complex formation was found as well as the instability constants of the complexes. The influence of the dielectric constant of the solution on the stability of the investigated complexes was proved. In the lecture by V. P. Vasil'yev on the "Investigation of Aquo Complexes in Mixed Solvents" the main attention was devoted to the necessity of the qualitative recording of the solvation effects in the complex formation. The applicability of the polarographic method in the determination of the composition and stability of the aquo complexes in mixed solvents was proved and experimental material on the thermodynamics of the dissociation of the cadmium-aquo complexes in aqueous ethanol solutions was mentioned. V. N. Kolmachov, V. I. Kuznetsov

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and I. V. Tananayev stressed in their lectures the necessity of a more complete and general investigation of the solvation processes. A. K. Babko and A. M. Golub pointed out the great importance of the investigations of the complex formation equilibria in non-aqueous solutions, and made several critical comments on the lecture by Ya. I. Tur'yan. The following scientists took part in this discussion: L. P. Adamovich, O. I. Khotyanovskiy, A. P. Nemkvin and A. G. Mustakhov. At the final meeting of the conference A. A. Grinberg, Corresponding Member, AS USSR, said in his speech that such a conference was very urgent. A detailed discussion of the determination methods of the composition of the complexes, as well as of the method used in the study of the quantitative characteristics of the stepwise complex formation was extremely useful for all who attended this conference.

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5(2)

AUTHORS: Yatsimirskiy, K. B., Berezin, B. D.

TITLE: Indicators of the Mercurometry (Indikatory merkurimetrii) Communication II: Diphenyl Carbazone (Soobshcheniye II. Difenilkarbazon)

SOV/153-58-4-6/22

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 4, pp 35 - 42 (USSR)

ABSTRACT: Although diphenyl carbazide, according to corresponding publications (Ref 11), is less suitable as indicator for the determination of the chlorides of thallium (Ref 4), silver in the presence of copper (Ref 5), methyl thiouracil (Ref 6), and others, diphenyl carbazone, which is a better mercurometric indicator, has been still insufficiently investigated. Blue-violet compounds are formed by it with Hg^{2+}, the composition of which, however, is unknown. Scientists also disagree as to the optimum pH-value in the determination of halides. It would be necessary to know the solubility product of mercury diphenyl carbazonate and the acid dissociation constant of diphenyl carbazone in order to find the

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Indicators of the Mercurometry. Communication II: Diphenyl Carbazone

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optimum concentrations of the indicator, the possible dilutions of halide solutions and the optimum accuracy of the methods under various conditions. Perchloric acid and mercury perchlorate were used in the experiments. Table 1 presents the solubility of diphenyl carbazone in borate buffer solutions determined at 25°. In an alkaline medium it can be transformed into diphenyl carbodiazone (Ref 2). K_s of diphenyl carbazone was measured by the spectrophotometer (Table 2). The data obtained from the two methods mentioned above were checked (Table 3). The spectrophotometric method of the isomolar series was applied, because the preparative determination of the indication product of mercury ions (II) with diphenyl carbazone is, for various reasons, very difficult. The results are given in table 4. The solubility product of mercury diphenyl carbazonate was determined according to Gorbachev's method, the latter having been modified to a certain extent. The solubility product amounts to (Ref 17) $(6.7 \pm 0.7) \cdot 10^{-26}$. First a calibration curve was plotted. Hg^{2+} is practically

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Indicators of the Mercurometry. Communication II: Diphenyl Carbazone

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completely bound by diphenyl carbazone at a pH of 5 approximately. The composition at pH 2 and 5 corresponds to the ratio of diphenyl carbazone: Hg^{2+} = 2:1. The dissociation constants of diphenyl carbazone after the first step at 25° and at ionic strengths of 0,1 and near zero amounts to $(3,4\pm0,3).10^{-8}$ and $(1,1\pm0,1).10^{-8}$. There are 2 figures, 5 tables, and 18 references, 9 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Chemo-Technological Institute) Kafedra analiticheskoy khimii (Chair of Analytic Chemistry)

SUBMITTED: September 10, 1957

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5(2,3)

AUTHORS: Yatsimirskiy, K. B., Berezin, B. D.

TITLE: Indicators of Mercurimetry (Indikatory merkurimetrii). III. ß-Nitroso-α-naphthol (III. ß-nitrozo-α-naftol)

SOV/153-58-6-5/22

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 6, pp 28-33 (USSR)

ABSTRACT: Among the indicators proposed in the most recent papers (Refs 1-6) and mentioned in the title, the substance mentioned in the subtitle and its monobromine derivative, bromonitrosol (Ref 4), have proved most useful for various applications (Refs 4,7-9) in practical work. However, a number of difficulties still prevent their further introduction into the practical field. There are no systematic quantitative investigations into this matter, and the necessity of appropriate investigations is therefore most obvious. As bromonitrosol is structurally fairly similar to ß-nitroso-α-naphthol, the latter was investigated. The experimental part contains discussions of: (1) Acid properties of ß-nitroso-α-naphthol, (2) the solubility of ß-nitroso-α-mercury-naphtholate in acid solutions (Tables 3,4). Table 2 presents the computed and experimentally obtained values of the dissociation constant

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of ß-nitroso-α-naphthol. Table 1 shows its solubility in borate buffer solutions at 25°. From their results, the authors draw the following conclusions: The qualitative characteristics of the substances mentioned in the subtitle and of the indication product formed by the former with mercury-(II) ions are very close to the corresponding values of diphenyl-carbazonium (Ref 14). Consequently, the two indicators can be regarded as equivalent in this respect. Diphenyl-carbazonium does, however, yield a more vividly colored product with Hg-ions (II), and is therefore more sensitive. The latter reaction appears instantaneously, whereas the reaction product of ß-nitroso-naphthol tends to form oversaturated solutions with the Hg-(II) ions. Thus diphenyl-carbazonium is to be more highly recommended. In the course of work, the acid dissociation constant of ß-nitroso-α-naphthol $(2.15 \pm 0.13) \cdot 10^{-8}$ was established. From the data on the solubility of mercury-ß-nitroso-α-naphtholate in different solvents, the equilibrium constant of the indication reaction of the Hg-(II) ions with ß-nitroso-α-naphthol was obtained (Table 4), and the solubility product $(9.7 \pm 1.2) \cdot 10^{-27}$ as well as the instability constant of mercury-ß-nitroso-α-naphtholate $(1.2 \pm 0.2) \cdot 10^{-20}$ were determined. There are 4

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Indicators of Mercurimetry. III.β-Nitroso-α-naphthol SOV/153-58-6-5/22

tables and 14 references, 11 of which are Soviet.

ASSOCIATION: Kafedra analiticheskoy khimii; Ivanovskiy khimiko-tekhnologicheskiy institut (Chair of Analytical Chemistry; Ivanovo Chemo-technological Institute)

SUBMITTED: September 10, 1957

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5(2,3)

AUTHOR: Berezin, B. D.

SOV/153-2-1-2/25

TITLE: A Study of Metal Phthalocyanines in Solutions (Izucheniye ftalotsianinov metallov v rastvorakh). I. Stability of Phthalocyanines of Some Metals From th Middle of the IV. Period (I. Ustoychivost' ftalotsianinov nekotorykh metallov serediny chetvertogo perioda)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1959, Vol 2, Nr 1, pp 10-14 (USSR)

ABSTRACT: After a survey of publications (Refs 2-18) the author states that the thermodynamic properties of metal phthalocyanines (MPc) apparently have not yet been investigated. Particularly interesting are the determination of the thermodynamic stability mentioned in the subtitle and a study of the kind of the chemical bond in connection with special properties of phthalocyanine as an addendum. Special attention should also be devoted to the close similarity between phthalocyanine and biologically important porphyrine derivatives which play a significant role in the vital action of plant and animal organisms (Refs 22,23). Those phthalocyanines were studied in sulphuric acid solutions. The majority of metal phthalocyanines

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enter an exchange reaction in such solutions, which is accompanied by the formation of a free phthalocyanine (H_2Pc; Pc denotes the phthalocyanine radical). It has remained unknown up till now how far the reaction proceeds according to the equation (I) in the case of the Co-, Ni-, Cu-, and Zn-compounds. In the first part of his article the author tried to determine the relation - $\frac{[M^{2+}]}{[H_3O^+]^2} = K$. It should remain constant even if the bottom phase consists of MPc and H_2Pc. For this purpose the author studied the solubility of CoPc, NiPc, CuPc, and ZnPc by the quantitative method, while that of FePc was ascertained semi-quantitatively. Tables 1 and 2 show the solubility of copper- and cobalt phthalocyanine. The author found approximate values of the equilibrium constant of the reaction of dissolution (see equation) for copper- and cobalt phthalocyanine. At 20-70° they have the order of

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A Study of Metal Phthalocyanines in Solutions. SOV/153-2-1-2/25
I. Stability of Phthalocyanines of Some Metals From the Middle of the
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magnitude of 10^{-6} (approximately). Further, the author proved that in preparing pigment dyes from phthalocyanine with Cu^{2+}, Ni^{2+}, and Co^{2+} by treatment with H_2SO_4 solutions of up to 7-8 mols/l neither losses occur due to dissolution nor a deterioration of the tinge due to the accumulation of free phthalocyanine or of its decomposition products. The subject was recommended by K. B. Yatsimirskiy. There are 2 tables and 26 references, 8 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut; Kafedra analiticheskoy khimii (Ivanovo Institute of Chemical Technology, Chair of Analytical Chemistry)

SUBMITTED: January 9, 1958

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5(2, 3)

SOV/153-2-2-4/31

AUTHOR: Berezin, B. D.

TITLE: Investigation of the Metallic Phthalocyanines in Solutions (Izucheniye ftalotsianinov metallov v rastvorakh). II. Acidic-alkaline Interaction of the Phthalocyanines of Some Metals in Sulphuric-acid Solutions (II. Kislotno-osnovnoye vzaimodeystviye ftalotsianinov nekotorykh metallov v sernokislykh rastvorakh)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1959, Vol 2, Nr 2, pp 165-172 (USSR)

ABSTRACT: Under the presupposition that the dissolution of stable phthalocyanines in a concentrated H_2SO_4 is accompanied by the reaction:

$$(MPc)_{solid} + H_2SO_4 \rightleftarrows MPcH^+ + HSO_4^- \qquad (II)$$

(an intensely green acid phthalocyanine form $MPcH^+$ accumulating in the solution), the author looked for quantitative characteristics of the dissolution process (II) of the phthalocyanines Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and of the nonmetallic phthalocyanine, i.e. of those objects which have the biggest technical importance. These characteristics have a practical value as

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Investigation of the Metallic Phthalocyanines in Solutions. II. Acidic-alkaline Interaction of the Phthalocyanines of Some Metals in Sulphuric-acid Solutions

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they lead to formulas which are useful for the practical computation of the dissolution of phthalocyanine dyes in H_2SO_4 (and other concentrated acids) in their industrial purification. The derivation of the mentioned formulas is based on the fact that 4 peripheral, so-called extracyclic, nitrogen atoms are present in the molecule. They carry free electron pairs which give the phthalocyanines the properties of very weak bases. In the opinion of the author, this is due to the participation of free electron pairs of the extracyclic nitrogen atoms in the composition of a metalline molecule (Ref 2). The author assumes that the metallic phthalocyanines can only absorb one proton in a noticeable degree. This proton considerably weakens the basic properties of the $MPcH^+$ as it intensely deforms the π-electron cloud of the conjugate large ring in the direction of the absorbed proton. This assumption was well confirmed by the experimental results of the present paper. From the data on the solubility, the equilibrium constants K_{MPc} for the reaction (II) for the phthalocyanines of the

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Investigation of the Metallic Phthalocyanines in Solutions. II. Acidic-alkaline Interaction of the Phthalocyanines of Some Metals in Sulphuric-acid Solutions

4 metals mentioned before as well as for H_2Pc were computed (1). Tables 1 and 2 show the indices of these constants (computed by formula 4). The pK_{MPc}-values keep a good constancy over a considerable range of acidity. For a perfect confirmation of his assumptions and computations, the author determined the solubility of CuPc and CoPc in 16.70 m H_2SO_4 and of ZnPc in 17.25 m H_2SO_4. It is in good agreement with the values computed by equation (4). So it can be assumed that equation (4) only applies to H_2SO_4 up to 100% concentrations. This equation is useless for oleum since stronger acids, such as $H_3SO_4^+$ et al (Ref 7), are present in it. From the experimental results of the present paper, one can make theoretical conclusions which are connected with the dependence of the MPc-solubility on the nature of the metal. On the basis of his investigation of the phthalocyanine properties, the author suggests modified structure formulas of the free phthalocyanine and its covalent complex salts (Fig 2). They are in good agreement with the

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SOV/153-2-2-4/31

Investigation of the Metallic Phthalocyanines in Solutions. II. Acidic-alkaline Interaction of the Phthalocyanines of Some Metals in Sulphuric-acid Solutions

X-ray structural data, as well as with the chemical and physico-chemical properties of the phthalocyanines. K. B. Yatsimirskiy read the manuscript. V. F. Borodkin supplied the phthalocyanine preparations. There are 2 figures, 2 tables, and 9 references, 3 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut; Kafedra analiticheskoy khimii
(Ivanovo Chemical-technological Institute; Chair of Analytical Chemistry)

SUBMITTED: January 9, 1958

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BEREZIN, B.D.; POGODINA, L.G.

Phloroglucinol as an indicator in mercurimetry. Zav.lab. 26 no.12: 1347-1351 '60. (MIRA 13:12)

1. Ivanovskiy khimiko-tekhnologicheskiy institut.
(Phloroglucinol) (Mercurimetry)

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21124

S/153/61/004/001/003/009
B110/B203

54500 also 4112

AUTHOR: Berezin, B. D.

TITLE: Study of phthalocyanines of metals in solutions. III. Absorption spectra of phthalocyanines in sulfuric acid solutions

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, v. 4, no. 1, 1961, 45-52

TEXT: To study photosynthetic and biological reaction chemisms in the living organism, the absorption spectra of porphyrine derivatives are very important for their identification. In the present study, the author uses strong sulfuric acid solutions of stable metal phthalocyanines: chemically pure Cu, Zn, Co, Ni salts, $HSO_4 \cdot AlPcCl$ (according to Linstead), $CuPcCl_{15}$, and free H_2Pc. Sulfuric acid solutions with strong H_2SO_4 of known titer were prepared. The absorption spectra in the ultraviolet, visible, and adjacent infrared spectrum ranges were taken at 22-24°C by an СФ-4 (SF-4) spectrophotometer. Table 1 gives maxima and intensities

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of absorption bands. Co, Ni, Cu, and Zn salts dissolved in 8-10 M H_2SO_4 are assumed to have monovalent, basic character: $(MePc)_{dis}$ + + $H_2SO_4 \rightleftharpoons MePcH^+ + HSO_4^-$. Thus, metal salts protonized in H_2SO_4 solution can be studied in the spectrum for rules basing on the exchange of metals and substituents in the complex, on charges in the central ion, etc. The proton bound in H_2SO_4 solution to the conjugate ring system does not change the character of electron transitions but their probability (bathochromic shift = 80-120 mμ, drop in excitation energy: infrared range 5-6 kcal, ultraviolet range = 16 kcal). This, and similar conditions for other MePc (Tables 1 and 2), is explained as follows: $n \rightarrow \pi^*$ (1) and $\pi \rightarrow \pi^*$ (2) transitions are possible in the Pc molecule. In (1), an unbound electron passes from the noncovalent pair of N atoms to the shell of the π-electron cloud of the macrocycle. In (2), a π-electron within the conjugate system passes from the electron shell of one atom to that of another atom. In Pc molecules, probably only (2) exists, since electron spectra of phthalocyanines and porphyrines are very similar. In metal pheophytinates, (2) is no longer possible since

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the intracyclic N atoms have lost the noncovalent electron pairs by complex formation. A $\pi_C \rightarrow \pi_N$ (3), and a $\pi_N \rightarrow \pi_C$ (4) transition are likely to occur in MePc. (3) corresponds to minimum exciting energy and produces the longwave absorption band. In (4), part of the π-cloud passes from the more electronegative N to C, which produces the less intensive, longwave band. The $\pi_C \rightarrow \pi_C^*$ electron transition from the conjugate benzene system to the macrocycle system may produce the absorption band in the adjacent ultraviolet range. Due to the high autonomy of the two systems, nearly 80 kcal are required to this end. Besides, a transition from the macrocycle to the benzene ring, and a $\pi_C \rightarrow \pi_C^*$ transition in the substituted benzene ring are also possible. Protonization does not interfere with conjugation in the macrocycle, but it strongly polarizes the π-electron cloud by positive charge. Thus, this cloud becomes very mobile, and may be even excited by low-energy photons. Colors are deepened, and maxima are bathochromically shifted according to the color theory. On introduction of metals in the Pc molecule, the intensity of maxima drops, probably due to the formation of a perfectly

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symmetric molecule whose π-electron system is stabilized by double p_π-d_π bonds of the central ion with the addendum. New maxima are not formed, the metal ion is not chromophorous, since the weak transitions on the d-electron shells do not appear in the spectrum. Thus, the nature of transitions and the ionic structure are equal, in principle, for protonized H_2Pc and $MePcH^+$. The spectral shift (color change: deep green → yellowish brown) observed in protonized H_2Pc after standing for 48 hr is being studied now. On introduction of the covalent metal ion, 4 σ bonds of the central ion are formed at the expense of the completing of ion levels $3d4s4p^2$ (Co^{2+}, Ni^{2+}, Cu^{2+}); $4d4s4p^2$ (Zn^{2+}); $3d3s3p^2$, or higher levels (Al), by electrons of unbound electron pairs of intracyclic N atoms. Then, two simple oscillating π-bonds are formed with the π-cloud of the addendum by the d_{zx} and d_{zy} electron orbits of the metal ions unless they have been claimed by σ-bonds. The author had already established an increase of the π-electron density in the order: $CuPcCl_{15} < {}^+AlPcCl < CoPc(ZnPc) < CuPc < NiPc < H_2Pc$. The

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values for the bonding strength metal - addendum, and for the position and intensity of maxima, are likely to give similar sequences. Table 1 shows for λ_{max} of the $MePcH^+$ the order: $H_2Pc > {}^+AlPcCl > CuPc > CoPc(ZnPc) > NiPc$, which agrees well with values of the mesoporphyrine complexes: Zn^{2+} (570 mμ) > Cu^{2+} (561 mμ) > Co^{2+} (552 mμ) > Ni^{2+} (550 mμ). Also here, the Ni complex for which maximum stability is assumed shows the minimum value. The irregularity of $ZnPcH^+$ is explained as follows: The order of the $MePcH^+$ with respect to the π-electron density does not agree with the order of the $MePcH^+$ with respect to λ_{max}, since the same π-electron density of the macrocycle may result from different fractions of σ- and π-bonds, which, in turn, have different effects on the λ_{max} shift. Also the transition intensity log ε is not simply dependent on electron density. Polarization of bonds of benzene nuclei and the macrocycle in $CuPcCl_{15}$ (Fig. 5) effects alleviation of transitions in the macrocycle as well as between the conjugate systems macrocycle - benzene nuclei; maxima are bathochromically shifted: $CuPcCl_{15}$ is green,

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$CuPcCl_{15}H^+$ red-brown. Desolvatation of $MePcH^+$ effects a slight change of λ_{max} as well as of the absorption intensities by interaction of the proton with nitrogen, and, thus, a stronger polarization effect on the π-cloud of the macrocycle. This explains the weak bathochromic shift with increasing H_2SO_4 concentration. The latter has, however, no influence on the position of absorption maxima, which excludes the addition of a second proton to the $MePcH^+$, and proves their existence as monovalent bases at any acid concentration. In the aluminum complex (Fig. 4), a dissociation change according to the scheme:

$$\left[HSO_4 \cdot Al \cdot Pc \begin{smallmatrix} Cl \\ H \end{smallmatrix}\right]^+ \rightleftharpoons HSO_4^- + \left[Al \cdot Pc \begin{smallmatrix} Cl \\ H \end{smallmatrix}\right]^{2+}$$

is likely to take place. K. B. Yatsimirskiy is mentioned. There are 5 figures, 2 tables, and 18 references: 8 Soviet-bloc and 10 non-Soviet-bloc. The two references to English-language publications read as follows: R. Williams: Chem. Revs., 56, 299 (1956); W. Caughey, A. Corwin: J. Amer. Chem. Soc. 77, 1509 (1955).

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21124

S/153/61/004/001/003/009
B110/B203

Study of phthalocyanines of ...

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut. Kafedra analiticheskoy khimii (Ivanovo Institute of Chemical Technology, Department of Analytical Chemistry)

SUBMITTED: May 11, 1959

Legend to Table 1: Position of electron transitions λ_{max} and their intensity in sulfuric acid solutions of MePc; (a) phthalocyanine, (b) concentration H_2SO_4 moles/liter; (c) electron transitions.

Фталоцианин	Концентрация H_2SO_4, моль/л	I: λ_{max}, mμ	I: lg ε
CuPc	17,88	794	5,36
	15,75	792	5,38
	13,80	792	5,39
NiPc	17,44	778	4,57
	14,00	774	4,51
	13,40	774	4,42
CoPc	17,88	790	5,12
	15,00	782	5,09
	13,80	780	5,82
ZnPc	17,44	788	5,32
	14,00	784	5,28
HSO_4·AlPcCl	17,88	810	5,29
	15,27	802	5,07
	13,75	794	4,99
$CuPcCl_{15}$	17,44	865	3,96
H_2Pc	17,44	840	—

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Study of phthalocyanines of ...

с Электронные переходы							
II		III		IV			
λ_{max}, mμ	lgε	λ_{max}, mμ	lgε	λ_{max}, mμ	lgε		
700	4,56	440	4,32	305	4,73		
704	4,56	440	4,36	306	4,75		
700	4,49	440	4,28	305	4,72		
690	4,18	—	—	302	4,61		
700	4,10	—	—	300	4,51		
700	3,95	—	—	300	4,50		
700	4,48	427	4,27	291	4,72		
700	4,48	422	4,32	298	4,84		
700	4,37	420	4,37	300	4,81		
700	4,50	440	4,26	310	4,83		
698	4,46	440	4,12	310	4,78		
720	4,52	460	4,36	312	4,95		
размыт	—	435	4,41	315	5,20		
686	4,30	430	4,32	307	4,73		
—	—	350	4,24	245	5,05		
775	—	430	—	305	—		

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V		VI		VII	
λ_{max}, mμ	lgε	λ_{max}, mμ	lgε	λ_{max}, mμ	lgε
290	4,56	225	4,82	—	—
287	4,61	224	4,86	765	4,92
291	4,56	224	4,83	760	4,98
—	—	226	4,77	820	3,93
—	—	224	4,68	690	—
—	—	223	4,66		
—	—	222	4,65		
—	—	222	4,79		
—	—	222	4,81		
—	—	229	4,95		
—	—	230	4,86		
—	—	225	4,76		
—	—	222	4,73		
—	—	221	4,78		
—	—	—	—		
—	—	232	—		

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Study of phthalocyanines of ...

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Legend to Table 2: Position of main electron transitions in solutions of MePc in α-$C_{10}H_7Cl$; (a) electron transitions, (b) phthalocyanine.

a Электронные переходы	I	II	III	IV
b Фталоцианин	λ_{max}, mμ			
H_2Pc	700	665	605	350
CuPc	680	—	614	346
NiPc	676	—	602	—
CoPc	672	—	604	—
ZnPc	680	—	60[illegible]	315
Cl·AlPc	691	—	622	—

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Study of phthalocyanines of ...

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Legend to Fig. 1: Absorption spectra of CuPc and H_2Pc;

(1) CuPc in 18 M H_2SO_4;

(2) CuPc in 15 M H_2SO_4;

(3) CuPc in α-$C_{10}H_7Cl$;

(4) H_2Pc in α-$C_{10}H_7Cl$.

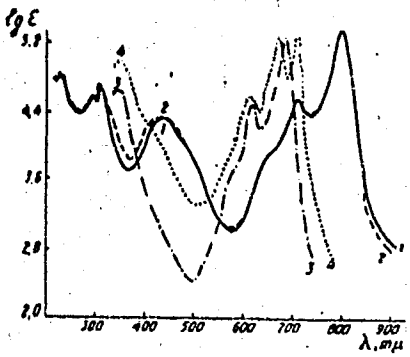

FIG. 1

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Study of phthalocyanines of ...

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Legend to Fig. 4: Absorption spectra of $HSO_4 \cdot AlPcCl$; (1) in 18 M H_2SO_4; (2) in 14 M H_2SO_4.

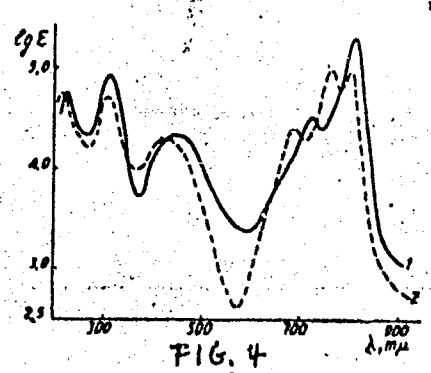

FIG. 4

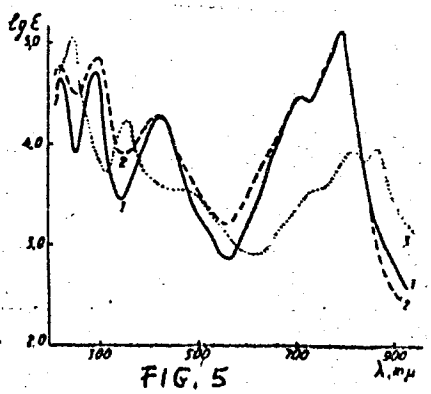

FIG. 5

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21124

Study of phthalocyanines of ...

S/153/61/004/001/003/009
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Legend to Fig. 5: Absorption spectra CoPc and $CuPcCl_{15}$;

(1) CoPc in 18 M H_2SO_4;

(2) CoPc in 15 M H_2SO_4;

(3) $CuPcCl_{15}$ in 18 M H_2SO_4.

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BEREZIN, B.D.

Metal phthalocyanines in solutions. Part 4: Effect of the central ion charge and of substituted derivatives on the properties of phthalocyanines. Izv.vys.ucheb.zav.;khim.i khim.tekh. 4 no.3:379-386 '61. (MIRA 14:10)

1. Ivanovskiy khimiko-tekhnologicheskiy institut, kafedra analiticheskoy khimii.
(Phthalocyanine)

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.

Stability of metal phthalocyanines in solution. Zhur.neorg.khim. 6 no.12:2672-2679 D '61. (MIRA 14:12)

1. Ivanovskiy khimiko-tekhnologicheskiy institut, kafedra analiticheskoy khimii.

(Phthalocyanine)

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S/078/61/006/012/002/011
B110/B147

AUTHOR: Berezin, B. D.

TITLE: Study of the stability of phthalocyanines of metals in solution

PERIODICAL: Zhurnal neorganicheskoy khimii, v. 6, no. 12, 1961, 2672-2679

TEXT: The author studied less stable phthalocyanines of metals by the solubility method, and stable ones by means of isotopic exchange. The decomposition of less stable Pc follows the reaction $MPc_{sol}+2H_3O^+=M^{2+}_{aq}+H_2Pc^{sol}$. An exact MPc addition was shaken with H_2SO_4, HCl, or $HClO_4$ in the thermostat at 25 ± 0.2°C. Next, the Ag^+ content in the filtrate was nephelometrically determined as AgCl. Hg^{2+} was determined with diphenyl carbazone, Fe^{3+} was determined as rhodanide in an HNO_3 medium, Mg^{2+}, Ca^{2+}, Cd^{2+}, and Pb^{2+} were trilonometrically determined by means of eriochrome black. The separation

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of Be^{2+} from MPc proceeded more slowly than that of Mg^{2+} and other ions of less stable Pc except for Fe^{3+}, since the rates of its hydrolysis at 25°C in 17.70 and 15.40 moles of H_2SO_4 are 0.095 ± 0.008 hr^{-1} and 1.40 ± 0.06 hr^{-1}, respectively. To study the stability of stable Pc, $Co^{*}Pc$ and $Zn^{*}Pc$ were formed from an alcoholic anhydrous solution of $CoCl_2$-60, $ZnCl_2$-65, and Li_2Pc in absolute alcohol. They were mixed by shaking with equal amounts of titrated H_2SO_4 (1 - 8 moles/liter), at 25 or 50°C and the activity of the solution was determined after centrifuging. The activity of the deposit was ~20,000 pulses/min. A known volume of a Co^{60} salt dissolved in H_2SO_4 of the same concentration (17.20 moles/liter) was added to sulfuric Pc solutions of Al, Co, Ni, and Zn contained in a bulb. Hydrolysis was conducted according to $MPcH^+ + H_2O \rightarrow H_3O^+ + MPc_{sol}$. Reprecipitated dried MPc was dissolved in concentrated H_2SO_4, and the

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activity of the solution was determined (Table 3). Irreversibility of (1) in acid aqueous solutions may be assumed on the basis of examinations by the usual solubility method of the dissociation of less stable Pc of Mg, Ca, Cd, Hg, Ag, Pb, and Fe. Even with the stable compound ClFePc, complete "washing out" of the metal with 1 mole of acid occurred after 8 - 10 days, with MgPc and PbPc it occurred after 40 - 50 hr, with AgHPc after 120 hr, with HgPc and CdPc after 12 - 15 hr, and with CaPc after 2 - 3 hr. The rate of washing depends on the type of central ion. It increases as the acid concentration increases, but it is quantitatively independent of the H ion concentration. It probably depends on the different rates of rupture of the donor - acceptor bond between metal and addendum. Presumably, it is the higher the lower the covalent character of the metal - addendum bond. It is due to residual basic properties of inner-cyclic N atoms of the macro-ring, since the basic properties of the addendum decrease as the firmness of the σ-bond of metal - nitrogen increases. As regards filling of the hybrid orbit of the metal ion by electron pairs of nitrogen, the following sequences of bond firmness are given: $Fe^{3+} > Ag^{+} > Mg^{2+}$, $Pb^{2+} > Cd^{2+}$, $Hg^{2+} > Ca^{2+}$. The

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author studied the isotopic exchange of Co^{2+}-60 with Pc of Co, Ni, Zn, and Al dissolved in 17.20 moles of H_2SO_4 following the equations $MPcH^+ + 2H^+ = H_2PcH^+ + M^{2+}$ (2a) and $H_2PcH^+ + Co^{*2+} = Co^{*2+} = CoPcH^+$ (2b). Although insoluble H_2Pc and hydrated cations unable to penetrate through the Pc "window", are not formed in (2a) and (2b) as in (1). H_2Pc can separate from (2a) and (2b) due to the slow-rate process. The author thanks N. I. Sosnikova for help with the experiments. There are 3 figures, 3 tables, and 22 references: 12 Soviet and 10 non-Soviet. The three most recent references to English-language publications read as follows: B. West. J. Chem. Soc., 3115 (1957); D. Atkins, C. Garner. J. Amer. Chem. Soc., 74, 3527 (1952); W. Caughey, A. Corwin, J. Amer. Chem. Soc., 77, 1509 (1955)

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut Kafedra analiticheskoy khimii (Ivanovo Institute of Chemical Technology, Department of Analytical Chemistry)

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

S/076/61/035/011/005/013
B140/B147

AUTHOR: Berezin, B. D.

TITLE: A study of metal phthalocyanines in solution. V. The stability of free phthalocyanine in sulfuric acid solutions

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 11, 1961, 2494 - 2499

TEXT: The stability of free phthalocyanine (H_2Pc) in H_2SO_4 solution was studied. Experimental procedure: Free H_2Pc is prepared by treating Na_2Pc with 96% H_2SO_4 and introducing the mixture into an ice-bath prepared from distilled water. To remove impurities, H_2Pc was heated with acetone. The stability of the H_2Pc macroring was studied using weighed portions of H_2Pc and various H_2SO_4 concentrations. The optical density of the solutions was measured at regular intervals on a KM(KM) spectrophotometer (λ = 520 mμ). 12.5 - 17.65 M H_2SO_4 solutions were used for the investiga-

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

tion. The decomposition of H_2Pc in acid solution yields the same products as are obtained by its oxidation (phthalimide and ammonium salts). The influence of atmospheric oxygen and light (using a 1000 w bulb) on the decomposition rate of H_2Pc was also studied. Evaluation of the measurement results showed that the decomposition rate of H_2Pc increases with increasing H_2SO_4 concentration up to a maximum and then decreases rapidly. A 17.65 M H_2SO_4 solution still gave a distinct H_2Pc spectrum. Graphic evaluation yielded the linear function $\log(c_o/c) = f(t)$, (t = time), where c_o denotes the intial H_2Pc concentration, and c the concentration in the course of the reaction. Therefore this function follows the kinetic equation $-(dc/dt) = k_r c_{H_2Pc}$ (2), where k_r = hydrolysis rate constant. The characteristic decomposition reaction of H_2Pc in H_2SO_4 is assumed to involve the participation of H_3O^+, since the H_3O^+ concentration changes in

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the same way as the decomposition of H_2Pc. According to Hammett, the H_3O^+ concentration may be calculated as follows:

H_o = const + log $\frac{HSO_4^-}{H_2SO_4}$ (3), where const = -8.56. It was found experimentally that the H_3O^+ concentration and k_r pass through a maximum at an H_2SO_4 concentration of 14 - 14.5 moles. The author assumes the reaction $H_2PcH^+ + 3H^+ \leftrightharpoons [H_2PcH_4]^{4+}$. Continuous uptake of H^+ leads to rupture of the macroring which in turn results in further hydrolytic decomposition of the H_2Pc: $[(C_8H_4N_2)_4H_6]^{4+} \xrightarrow{8H_2O} 4C_8H_5O_2N + 4NH_4^+ + H_2$ (4). To determine the reaction order of the hydrolytic decomposition of H_2Pc, log k_r was plotted versus log H_3O^+. Thus, the author obtained the linear function log k_r = log k + n log $[H_3O^+]$ (5), where n = 5 for $H_2SO_4 < 16$ moles/liter, and n = 4 for $H_2SO_4 > 16$ moles / liter. From (5), k_r was

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calculated and found to be $1.12 \cdot 10^{-4}$ hr^{-1} which inserted in Eq. (2) yields $-\frac{d[H_2Pc]}{dt} = 1.12 \cdot 10^{-4} c_{H_2Pc} c^4_{H_3O^+}$ (6). Reaction (4), in which 4 protons participate, is assumed to involve the shifting of 2 electrons from the H_2Pc macroring to 2 protons with evolution of H_2 gas. The hydrolytic decomposition of H_2Pc is not affected by O_2 or light. At $H_2SO_4 \leq 16$ moles the rate of solution of H_2Pc is smaller than the rate of hydrolysis so that the reaction does not reach equilibrium state. At $H_2SO_4 \geq 17$ moles the rate of hydrolysis is smaller so that an equilibrium is reached after 1 - 2 hr. It may therefore be assumed that in 17 - 18.8 M $H_2SO_4 \leftrightharpoons H_2PcH^+ + HSO_4^-$ is given by $-\log [H_2Pc]_{H_2SO_4} = 1.67 + H_o + 8.56$. N. I. Sosnikova assisted in the experiments. There are 4 figures, 2 tables, and 11 references: 5 Soviet and 6 non-Soviet. The three most recent references to English-language publications read as follows: P. Barrett, C. Dent, R. Linstead, J. Chem. Soc., 1719, 1936; L. Hammett,

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

A study of metal phthalocyanines ... S/076/61/035/011/005/013
B140/B147

Chem. Revs., 16, 67, 1935; W. Caughey, A. Corvin, J. Amer. Chem. Soc., 77, 1509, 1955.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Institute of Chemical Technology)

SUBMITTED: March 16, 1960

Card 5/5

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D. (Ivanovo)

Metal phthalocyanines in solution. Part 5. Stability of free phthalocyanine in sulfuric acid solutions. Zhur.fiz.khim. 35 no.11:2494-2500 N '61. (MIRA 14:12)

1. Ivanovskiy khimiko-tekhnologicheskih institut.
(Phthalocyanine)

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

30702
S/020/61/141/002/013/027
B103/B110

53700

AUTHOR: Berezin, B. D.

TITLE: Methods of investigating the stability of phthalocyanine complex compounds

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 2, 1961, 353-356

TEXT: The dissociation of metal phthalocyanines which is only noteworthy in proton acid media was studied in this paper: $MPc_s + 2H^+ = M^{2+} + H_2Pc_s$ (2); $MPcH^+ + 2H^+ = H_2PcH^+ + M^{2+}$ (2a), where Pc is the bivalent anion of tetrabenzo tetrazaporphin (phthalocyanine), and M^{2+} is a metal ion. Process (2) takes place in solid phase, and (2a) in H_2SO_4 with a concentration of more than 8 moles/liter. Processes (2) and (2a) were found to be fast and irreversible with unstable phthalocyanines, i. e., with those formed by cations of alkalis, alkaline earths, Hg^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}, Be^{2+}, Ag^+, Fe^{2+}, and those containing Sb^{3+}, Mn^{2+}, and Sn^{2+}. The conversion

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of stable Pc formed by Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pt^{2+}, Pd^{2+}, V^{4+}, $AlCl^{2+}$, and partly $SnCl_2^{2+}$, according to Eqs. (2) and (2a) is hardly noticeable. In aqueous, acid media, stable Pc dissociate irreversibly according to (2) and (2a). Despite a marked ionic dissociation in acid media, Pc cannot be characterized by the equilibrium constant of (2) or (2a). In those cases where it is difficult or impossible to determine the instability constant, or where the binding energy between metal and addenda cannot be measured, it is possible to apply, among others, the method of determining the rate of metal separation under the action of acids (Ref. 10, see below). This method was tested on Pc complexes. The forms of Pc existence in H_2SO_4 at various temperatures, and the properties of H_2SO_4 as solvent were studied in preliminary experiments. In an earlier study (Khim. i khim. tekhnol. 2, 165 (1959); 4, 45, 379 (1961)) the author proved that Pc in concentrated H_2SO_4 at normal temperatures behaved like monoacid bases:

$MPc_s + H_2SO_4 \rightleftarrows MPcH^+ + H_2SO_4^-$ (3). Table 1 gives equilibrium constants of Eq. (3) at 25°C. Those of industrially important Pc are given in Table 2.

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Since the constants remain unchanged at all temperatures, concentrated H_2SO_4 is an ideal solvent. Thus, the ratio of activity coefficients of the reactants in (3) also remains constant, and the reaction product, $(MPcH)HSO_4$, is completely dissociated. $MPcH^+$ predominates in sulfuric acid solutions. The equilibrium constants pK of reaction (3) allow conclusions as to the formation and durability of σ- and π-bonds, the stability of MPc, the existence of an excessive charge on the central ion, and the induction effect of the substituents in the benzene ring. The effect observed is an endothermic one which decreases with increasing solvation ability of Pc, either because of the ability of additional coordination of the central ion (ZnPc, ZnPcCl), or due to a charge of the central ion (^+AlPcCl), or the polarization of bonds in the chlorination of benzene rings ($CuPcCl_{15}$). Pc disintegrates in sulfuric acid solutions and is completely hydrolyzed on the macroring.

$[H_2(C_8H_4N_2)_4H^+] + 8H_2O + 3H^+ \longrightarrow 4C_8H_5O_2N + 4NH_4^+ + H_2$. The coloring of $MPcH^+$ and H_2PcH^+ disappears. All unstable Pc were found to hydrolyze in

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the same manner as free Pc. The hydrolysis of H_2PcH^+ is complicated. The hydrolysis mechanism of stable MPc was studied with the most unstable MPc: $(HSO_4)_2SnPc$. The hydrolysis also follows the equation $MA_n \rightleftharpoons M^{n+} + nA^-$ (1). The limiting stage in unstable Pc, however, is the hydrolysis of the H_2PcH^+ macroring, whereas in stable MPc it is the metal separation (2a). Thus, four coordinate bonds between metal and nitrogen are ruptured. The hydrolysis of stable Pc is only noticeable, at 100 - 120°C. As to the readiness of separation of the central ion in Pc, the metals form the order $V^{4+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Pd^{2+} > Pt^{2+}$. At the same time, the basic properties of the four N atoms of the rings participating in (2) and (2a) are increasingly neutralized. Pt^{2+} has the highest stability, but also (HSO_4) AlPc is very stable. The above order reflects the stability order in porphyrin complexes: $Ba^{2+} > Mg^{2+} > Mn^{2+} > Fe^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Pd^{2+}$. There are 6 tables and 18 references: 12 Soviet and 6 non-Soviet. The three references to English-language publications read as follows:

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

30702

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B103/B110

Methods of investigating...

Ref. 7: R. Williams, Chem. Revs, 56, 299 (1956); Ref. 10: W. Caughey, A. Corwin, J. Am. Chem. Soc., 77, 1509 (1955); Ref. 16: N. Deno, R. Taft, J. Am. Chem. Soc. 76, 244 (1954).

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Institute of Chemical Technology)

PRESENTED: June 23, 1961, by A. N. Terenin, Academician

SUBMITTED: June 22, 1961

Table 1. pK of the equilibrium constants of reaction (3) of stable phthalocyanins at 25°C.

Legend: (1) Phthalocyanin.

Table 2. Temperature dependence of pK of phthalocyanins in H_2SO_4.

Legend: (1) Temperature, °C; (2) pK of phthalocyanins of metals.

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.

Remarks on the article by I.L.Kukhtevich "On chemical stability of α-and β-pheophytins of copper and zinc. Ukr.khim.zhur. 28 no.4:532-534 '62. (MIRA 15:8)

1. Ivanovskiy khimiko-tekhnologicheskiy institut.
(Pheophytins)

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

S/076/62/036/003/003/011
B101/B108

57700

AUTHOR: Berezin, B. D.

TITLE: Study of metal phthalocyanines in solution. VI. Effect of the nature of the central ion on the strength of the phthalocyanine macro-ring in sulfuric acid solutions

PERIODICAL: Zhurnal fizicheskoy khimii, v. 36, no. 3, 1962, 494 - 501

TEXT: The stability of the compounds MPc of phthalocyanine (H_2Pc) with Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Sn^{2+}, Sn^{4+}, Al^{3+}, VO^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}, Ag^{+}, Fe^{3+} as well as of the chlorinated compounds $Cl_{15}PcCu$ in 12 - 17.7 mole/liter H_2SO_4 was investigated at 25 - 65°C. The compounds can be divided into two groups: (1) stable compounds of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, VO^{2+}, which displayed no noticeable dissociation at room temperature, (2) unstable compounds of Mg^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+}, Fe^{3+}, Sn^{2+}, Sn^{4+}. The stable MPc's and $Cl_{15}PcCu$ had very small constants of hydrolyzation rate ($k \sim 10^{-4}$ per

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

hour) at room temperature even in diluted H_2SO_4. The unstable MPc's had constants of hydrolyzation rate different from that of H_2Pc (0.137±0.008 per hour) by one order of magnitude. Unlike the unstable MPc's whose spectra show only the absorption bands of $HePcH^+$, the stable MPc's displayed absorption bands of their own. Hydrolysis proceeds as $MPc_{sd} + H_2SO_4 \rightleftharpoons MPcH^+ + H_2SO_4^-$ (2); $MPcH^+ + 2H_3O^+ \xrightarrow{v_2} M^{2+}_{aq} + H_2PcH^+$ (3); $H_2PcH^+ + 3H_2^+O + 5H_2O \xrightarrow{v_3}$ decomposition products (4). For stable MPc's, the reaction (3) is limiting, which proceeds according to $-dc_{MPc}/dt = k_{MPc}c_{MPc}c^2_{H_3O^+}$, while for the unstable MPc's, the reaction (3) proceeds rapidly and the reaction (4) slowly. For that group the kinetic equation as found for H_2Pc is $-dc_{MPc}/dt = k_{H_2Pc}c_{MPc}c^4_{H_3O^+}$. For the hydrolysis of H_2Pc in 17.7 M H_2SO_4 the activation energy was found to be 19,500 cal, for the reaction $Cl_2SnPcH^+ + 2H^+ \rightarrow H_2PcH^+ + Sn^{IV} + 2Cl^-$ it was found to be 21,700 cal. The assumptions made

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

Study of metal ... S/076/62/036/003/003/011
B101/B108

by W. Caughey, A. Corwin (see below) about the mechanism of decomposition of metallic ethioporphyrine complexes are called erroneous. There are 7 figures, 3 tables, and 9 references: 4Soviet and 5 non-Soviet. The four most recent references to English-language publications read as follows: W. Caughey, A. Corwin, J. Amer. Chem. Soc., 77, 1509, 1955; P. Barrett, D. Frye, R. Linstead, J. Chem. Soc., 1157, 1938; J. Anderson, E. Bradbrook, A. Cook, R. Linstead, J. Chem. Soc., 1151, 1938; P. Barrett, R. Linstead, F. Rundall, G. Tuey, J. Chem. Soc., 1079, 1940.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Institute of Chemical Technology)

SUBMITTED: May 25, 1960

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APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.

Some properties of platinum and palladium phthalocyanines. Zhur.neorg.khim. 7 no.11:2500-2506 N '62. (MIRA 15:12)
(Platinum compounds) (Palladium compounds)
(Phthalocyanine)

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.

Thermodynamic characteristics of phthalocyanines in sulfuric acid solutions. Zhur.neorg.khim. 7 no.11:2507-2513 N '62. (MIRA 15:12)

1. Ivanovskiy khimiko-tekhnologicheskiy institut.
(Phthalocyanine) (Sulfuric acid) (Solubility)

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.; SOSNIKOVA, N.I.

Synthesis and properties of osmium phthalocyanine. Dokl. AN SSSR 146 no.3:604-607 S '62. (MIRA 15:10)

1. Ivanovskiy khimiko-tekhnologicheskiy institut. Predstavleno akademikom A.N.Tereninym.
(Osmium compounds) (Phthalocyanine)

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.

Physicochemical properties of phthalocyanine pigments. Part 1: General characteristics of phthalocyanins. Stability of solid pigments during acid treatment. Izv.vys.ucheb.zav.;khim.i khim.tekh. 6 no.5:841-846 '63. (MIRA 16:12)

1. Ivanovskiy khimiko-tekhnologicheskiy institut, kafedra analiticheskoy khimii.

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L 17907-63 EPF(c)/EPR/EWP(j)/EWT(m)/BDS Ps-4/Pr-4/Pc-4/Pi-4 DE/RM/
MAY/WW/JW

ACCESSION NR: AP3003764 S/0080/63/036/006/1181/1186

AUTHOR: Berezin, B. D.

TITLE: Solubility of phthalocyanines in chlorosulfonic acid and oleum

SOURCE: Zhurnal prikladnoy khimii, v. 36, no. 6, 1963, 1181-1186

TOPIC TAGS: phthalocyanine, oleum, chlorosulfonic acid

ABSTRACT: The application of thermodynamic data obtained from the study of phthalocyanine behavior in sulfuric acid and also the functional properties of the acidity in the concentrated solutions of strong acids, permit the calculations of the solubility equilibrium of phthalocyanines in chlorosulfonic acid and oleum. It also evaluates the magnitude of solubility

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ACCESSION NR: AP3003764

limited by the solubility of proton accepting phthalocyamine salts. This solubility is not possible to determine. However, it must be very large since it has a large dielectric constant and the acidic salts are highly soluble in this media. These systems must be close to the fused systems since their equilibrium apparently can be reached only at high temperatures. Orig. art. has: 3 graphs and 15 equations.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Chemical Engineering Institute)

SUBMITTED: 04Feb62 DATE ACQ: 07Aug63 ENCL: 00

SUB CODE: CH, EL NO REF SOV: 007 OTHER: 012

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

L 12669-63 EWP(q)/EWT(m)/BDS AFFTC/ASD/ESD-3 RM/JD

ACCESSION NR: AP3002573 S/0020/63/150/005/1039/1042

59

58

AUTHOR: Berezin, B. D.

TITLE: Synthesis and properties of rhodium phthalocyanin

SOURCE: AN SSSR. Doklady*, v. 150, no. 5, 1963, 1039-1042

TOPIC TAGS: synthesis, property, rhodium phthalocyanin, acid-stable phthalocyanin, rhodium phthalocyanin, (HSO sub 4) RhPc, dissociation, equilibrium constant, Rh sup plus 3, Os sup plus 4, Pt sub plus 2, Pd sub plus 2

ABSTRACT: Supplementing earlier work of B. Berezin and N. Sosnikova (DAN, 146, 1962, 604) on acid - stable phthalocyanins, anhydrons trivalent rhodium chloride was reacted with a five-fold excess of phthalonitrile, with cooling for 4 hrs, to form rhodium phthalocyanin; purified from acetone and from 96% H sub 2 SO sub 4 the complex (HSO sub 4) Rh Pc was formed

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

[illegible] a five-fold excess of phthalonitrile, with cooling for 4 hrs, to form rhodium phthalocyanin; purified from acetone and from 96% H sub 2 SO sub 4, the complex (HSO sub 4) Rh Pc was formed. Solubility was determined and dissociation and equilibrium constants were calculated for Rh sup plus 3, Os sup plus 4, Pt sup plus 2, Pd sup plus 2, Cu sup plus 2, and Al sup plus 3 phthalocyanins. The effective ion charges and character of the chemical bonds in the Rh and Os complexes are discussed extensively. Absorption spectra of Rh, Os, and Pd phthalocyanin are compared. The article was presented by Academician A. N. [illegible]

Association: Ivanov Inst. of Chemical Technology

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APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

ACCESSION NR: AP4025263 S/0153/63/006/006/1016/1021

AUTHOR: Berezin, B.D.

TITLE: Physico-chemical properties of phthalocyanine pigments
2. Processes of dissolving phthalocyanines in sulfuric acid and its derivatives

SOURCE: IVUZ. Khimiya i khimicheskaya tekhnologiya, v. 6, no. 6, 1963, 1016-1021

TOPIC TAGS: Phthalocyanine pigment, phthalocyanine, sulfuric acid, phthalocyanine dissolution

ABSTRACT: Under industrial and laboratory conditions, phthalocyanine pigments containing metal are mostly obtained using dry methods. For this purpose, the metals and their chlorides or oxides are coalesced with the phthalocyanine or with a mixture containing phthalic anhydride, urea and a catalyst. The reaction product is an extremely complex mixture. The chemical activity and thermodynamics of the reprecipitation processes of industrial fusions of phthalocyanine from solutions of sulfur, chlorosulfonic acid and fuming sulfuric acid are examined. Based on a previously given thermodynamic ration (F. Baumann et al. Angew. Chem. 68, 133,

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

ACCESION NR: AP4025263

1956) a theoretical analysis of the process of reprecipitation of phthalocyanine pigments (primarily in the example of CuPc) was conducted. Optimum conditions for their solution and sulfuric acid consumption required for the full solution of pigments are found. Values for sulfuric acid consumption (kilogram) needed for the total solution of 100 kg. pigment of blue phthalocyanine (calculated for pure CuPc) are given for 10 and 50 C. It follows from the data, that in the process of reprecipitation of pigment from H_2SO_4 solutions with less than 94% concentration only a small part of the pigment is exposed to the solution and consequently is converted into d-form; a basic part of the pigment to microcrystal degree, is in B-form. Orig. art. has: 4 tables.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanov Chemical Engineering Institute); Kafedra analiticheskoy khimii (Department of Analytical Chemistry)

SUBMITTED: 02Oct62 DATE ACQ: 10Apr64 ENCL: 00

SUB CODE: CH No. REF. SOV: 010 OTHER: 002

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APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.

Dissociation kinetics of stable metal phthalocyanins in sulfuric acid solutions. Zhur. fiz. khim. 37 no.11:[illegible] '63. (MIRA 17:2)

1. Ivanovskiy khimiko-tekhnologicheskiy institut.

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.

Physicochemical properties of phthalocyanine pigments. Part 3: Breakdown of pigment molecules in acid solutions. Chromaticity of phthalocyanines. Izv.vys.ucheb.zav.;khim. i khim. tekh. 7 no. 1:111-117 '64. (MIRA 17:5)

1. Ivanovskiy khimiko-tekhnologicheskiy institut, kafedra analiticheskoy khimii.

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

ACCESSION NR: AP4041680 S/0153/64/007/002/0202/0208

TITLE: Electron absorption spectra and stability of monotypic complexes

AUTHOR: Berezin, B. D.

SOURCE: IVUZ. Khimiya i khimicheskaya tekhnologiya, v. 7, no. 2, 1964, 202-208

TOPIC TAGS: electron absorption spectra, spectral band shift, cyclic pi-ligand, phthalocyanine, porphorin, coordination complex, tetraphenyl-porphorin, sigma bond strength, pi bond strength, hypsochromic shift

ABSTRACT: The relationship between the stability of complexes and the position of their absorption bands was investigated by examining in detail the shift in the absorption band in cyclic π-ligands with phthalocyanine and porphorin upon coordination with different metal ions. The shift in the long wave bands of the spectrum of phthalocyanine (Fig. 1) on complexing with Cu in α-chloronaphthalene is attributed to the $\pi \rightarrow \pi^*$ transition. In $\alpha, \beta, \gamma, \delta$-tetraphenylporphin (Fig. 2) bands II and IV arecaused by $n \rightarrow \pi^*$ transitions while the 3

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

ACCESSION NR: AP4041680

remaining bands are caused by $\pi \rightarrow \pi^*$ transitions. In a series of divalent cations the short wave shift increases in proportion to the stability of the complex; the shift with tri- and tetravalent cations is still greater. However the magnitude of the hypsochromic shift does not correspond to the stability of the complex. Thus it was shown the shift of the primary absorption band of the electron spectra of the π-ligands depends not only on the strength of the σ-band but appears to be also a function of the nature and strength of the π-band, of the magnitude of the effective charge of the central ion in the complex, and of the geometric factor of the distortion of the ligand of the π-system upon coordination. All of these electronic and structural factors have a different effect on the strength of the complex and on the electronic equilibrium of the π-ligand. It is therefore indicated that the spectral criterion used in foreign works (i.e., the greater strength of the complexes with organic π-ligands results in the greater hypsochromic shift) has very limited value. The energy equilibria of the complex, cation and cyclic π-ligand are shown schematically in Fig. 3. Orig. art. has: 2 tables and 5 figures.

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APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

ACCESSION NR: AP4041680

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut Laboratoriya termodinamiki khimicheskikh reaktsiy (Ivanovo Chemical Technological Institute Laboratory of the Thermodynamics of Chemical Reactions)

SUBMITTED: 18May63 ENCL: 03

SUB CODE: NP, GC NR REF SOV: 013 OTHER: 013

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APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

ACCESSION NR: AP4041680

ENCLOSURE: 01

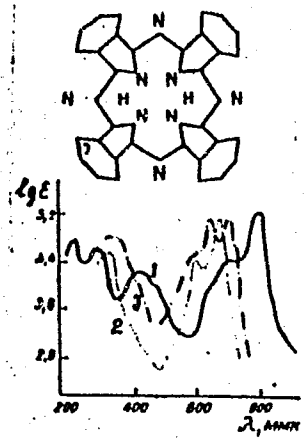

fig. 1

Skeletal formula of phthalocyanine and its absorption spectra. 1--copper phthalocyanine in 18 M H_2SO_4; 2--copper phthalocyanine in -chlornaphthalene; 3--metal-free phthalocyanine in chlornaphthalene

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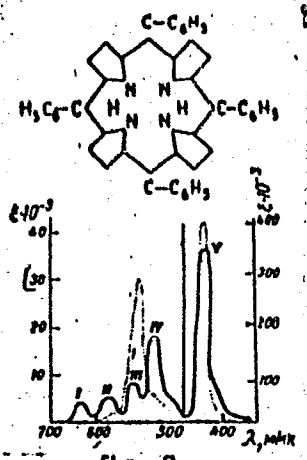

fig 2

Tetraphenylporphorin and its absorption spectra. ---metal-free; . . . . copper complex with benzene (I, II, III, IV, V--absorption band numbers)

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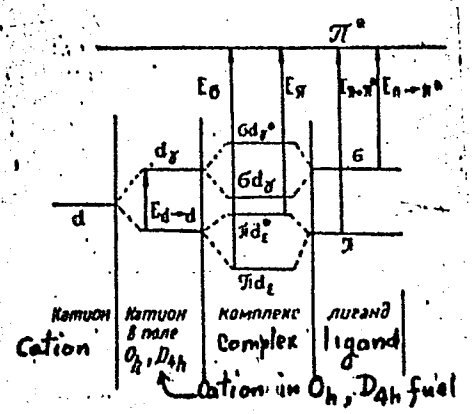

fig. 3

Arrangement of energy equilibria of complexes with cyclic -ligands

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BEREZIN, B.D.

Synthesis and properties of gallium phthalocyanines. Izv.vys.ucheb. zav.; khim.i khim.tekh. 7 no.6:982-988 '64.

(MIRA 18:5)

1. Ivanovskiy khimiko-tekhnologicheskiy institut, kafedra analiticheskoy khimii.

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

ACCESSION NR: AP4034575 S/0076/64/038/004/0850/0857

AUTHOR: Berezin, B. D. (Ivanovo)

TITLE: The mechanism of dissociation of metalphthalocyanines

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 4, 1964, 850-857

TOPIC TAGS: metal phthalocyanine, dissociation, mechanism, dissociation rate, activation energy, activation entropy, metalphthalocyanine hydronium ion complex, trimolecular reaction

ABSTRACT: The dissociation rate of stable Co, Ni, Al, Ga, Os(IV), Rh(III) phthalocyanines in sulfuric acid solutions in the 100-160C range was investigated. The general equation

$$-\frac{dc_{MPcH^+}}{dt} = k_v c_{MPcH^+} c^2_{H_3O^+}$$

(where c_{MPcH^+} is the concentration of the phthalocyanine proton in solution) was found to obtain for the dissociation of the metalphthalocyanines regardless of the

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ACCESSION NR: AP4034575

nature of the central atom. The dissociation of metalphthalocyanines (MPc) in aqueous proton-containing solutions is irreversible: $MPcH^+ + 2H_3O \longrightarrow M^{2+}_{aq} + H_2PcH^+$. The entropy and energy of activation of this dissociation reaction were calculated. It was suggested that in the process of the trimolecular reaction the activated complex $(MPcH^+ \cdot 2H_3O^+)^{++}$ forms from the initial $MPcH^+$ and H_3O^+ because of their strong mutual polarization. The negative values of the entropy of activation are explained by the high charge and strong polarization of the activated complex which makes it more strongly solvated than the initial particles. The special role of the H_3O^+ as a source of H_2O molecules required for the formation of the activated complex and completion of the dissociation is pointed out. "N. I. Sosnikova took part in the experimental work."... "I thank prof. K. B. Yatsimirsk for discussion of the given work." Orig. art. has: 3 tables, 6 figures and 7 equations.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskiy institut (Ivanovo Chemical Technological Institute)

SUBMITTED: 13Feb63

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BEREZIN, B.D.

Interrelation between the stability and kinetic characteristics of phthalocyanine complexes. Zhur. fiz. khim. 38 no.2957-2961 D '64. (MIRA 18:2)

1. Ivanovskiy khimiko-tekhnologicheskiy institut.

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.; SOSNIKOVA, N.I.

Kinetics of the formation of metal pheophytinates, analogs of chlorophyll. Zhur. fiz. khim. 38 no.5:1216-1222 My '64. (MIRA 18:12)

1. Ivanovskiy khimiko-tekhnologicheskiy institut. Submitted June 18, 1963.

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.D.

Structural peculiarities of a phthalocyanine molecule.
Zhur. fiz. khim. 39 no. 2:321-327 F '65. (MIRA 18:4)

1. Ivanovskiy khimiko-tekhnilogicheskiy institut, Ivanovo.

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BEREZIN, B.D.

Calculation from kinetic data of relative equilibrium constants for reactions of phthalocyanine and porphyrin complex formation. Zhur. fiz. khim. 39 no.5:1082-1086 My '65. (MIRA 18:8)

1. Ivanovskiy khimiko-tekhnologicheskiy institut, Ivanovo.

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BEREZIN, B.P., inzh.

Centralization of the repair of machinery. Vest.mashinostr. 45 no.10:76-77 O '65.

(MIRA 18:11)

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BEREZIN, B.D.; SOSNIKOVA, N.I.

Kinetics of the formation of metal pheophytinates, analogs of chlorophyll. Zhur. fiz. khim. 39 no.6:1348-1355 Je '65. (MIRA 18:11)

1. Ivanovskiy khimiko-tekhnologicheskiy institut. Submitted Dec. 14, 1963.

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BEREZIN, B.I., kand. tekhn.nauk

Typewriting school. Nauka i zhizn' 29 no.2:74-78 F '62.
(MIRA 15:3)

(Typewriting)

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Acidol as a solvent for grease paints. B. I. Berezin. *Neft* 8, No. 1, 80(1937).—Acidol, a mixt. of insol. naphthenic acids obtained from petroleum, can be used instead of oleic acid for dissolving indoline. Acidol contg. over 3% Na salts of naphthenic acids or 0.6% of sulfonic acids cannot be used as an indoline solvent. A. A. Podgorny

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Measuring the absorptive power of paper toward printing ink. B. I. Berezin. *Bumazhnaya Prom.* 15, No. 2, 50-2(1937); *Chimie & industrie* 39, 951. The method consists essentially in printing a weighed strip of the paper with a standard ink, removing the excess of ink by repeated contact with clean paper and weighing again, the increase in wt. corresponding to the ink absorbed. A two-roll press is used in carrying out the detn.

A. Paphoean Coutus

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Testing of polygraphic lacquers. B. I. Beregin. *Poligraf. Proizvodstvo* 1938, No. 11, 33-4; *Rev. Current Lit. Paint, Colour, Varnish & Allied Ind.* 12, 350(1939). — Methods for the detn. of consistency, drying rate, impurities, gloss, hardness and elasticity of the film, penetration into the paper, etc., are included. George Ayers

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23

Defective print paper. B. I. Berezin. *Bumazhnaya Prom.* 16, No. 6, 33-7(1938).—The most frequent defects in Soviet print papers are discussed. Chas. Blanc

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C1

Standards for print paper. B. I. Berezin. *Bumashnaya Prom.* 16, No. 9, 37-41(1938). A review of literature on the standard chem., phys. and mech. properties of print paper and methods of testing. Fifteen references.
Chas. Blanc

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The properties of drying oils used in printing. B. I. Beregin and T. N. Malova. *Poligraf. Proizvodstvo* 1939, No. 10, 37-8; *Khim. Referat. Zhur.* 1940, No. 6, 119.—A comparative evaluation is given of drying oils used in printing (linseed, petroleum and rosin). W. R. Henn

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Increasing the resistance of pigments to water in flat printing. B. I. Berezin.—*Poligraf. Proizvodstvo* 1939, No. 11, 42; *Khim. Referat. Zhur.* 1940, No. 6, 119.—To increase the water-resistance of dyes used for lithographic offset printing it is proposed to moisten the printing mold with a soln. of a suitable pptg. agent instead of with water. The method prevents the dyes from dissolving in water in the printing process and has no effect on the quality of the mold. W. R. Henn

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23

Production of metallized paper. B. I. Brizan. *Bumazhnaya Prom.* 18, No. 4, 28-35(1940).—A discussion of the methods of production and uses of metal-coated paper, based on foreign practice and patents. D. I. Belyal. *Ibid.* No. 5, 25-8(1940).—Foreign methods of production and uses are discussed. Chas. Blanc

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Difficulties in three- and four-color printing. B. I. Betezin. *Poligraf. Proizvodstvo* 1941, No. 3, 26-7; *Chem. Zentr.* 1942, II, 2853. To eliminate the difficulties in printing multicolored reproductions on enameled paper, dry pastes are used, such as 65-67 linseed oil, 30 Pb Mn resinate, and 3-5 beeswax or 45-47 linseed oil, 20 Pb Mn resinate, 30 siccative and 3-5 beeswax. The addn. of paste to the printing ink, in an amt. of 10-15%, prevents an excessive absorption of the binder and accelerates the drying of the paper. To avoid a glassy print, it is recommended to add slight amts. of beeswax to the ink directly or in the form of a 50% soln. in pyromaphtha or in linseed varnish. Paraffin or petrolatum could also be used, though the drying of the ink is inhibited by petrolatum.

Sonya G. Macheleson

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Cl

26

Substitute for linseed drying oil. B. I. Berezin and S. V. Rudin. *Poligraf. Proizvodstvo* **1946**, No. 9-10, 22-4. — The possibilities of at least partly replacing linseed oil in printing inks are discussed. Several recipes are given.

M. Hosch

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CA

23

Testing the absorbency of paper by means of photoelectric apparatus. V. I. Mudrik and B. L. Berezin. *Poligraf. Proizvodstvo* 1946, No. 11/12, 21-6. — The photoelec. method of TAPPI for testing paper absorbency is described.

M. Hosch

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BEREZIN, B

I

Poligraficheskiye Materialy. (Polygraphic Materials)...Uchebnik...Moskva, Gizlegprom, 1948.

304 P. Illus., Diagrs.
Bibliographies at end of chapters.

Gives information on designation, quality and working principles of Polygraphic materials, applicable for courses in studying material used for polygraphic production.

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A New Method for Determination of the Absorptive Properties of Paper. (In Russian.) B. V. Deryagin and B. I. Beregin. *Poligraficheskoi Proizvodstvo* (Printing Industry), Oct. 1948, p. 22-26.

A new method and apparatus are described and diagrammed. Typical results are graphed and discussed.

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CA 31

The attaching [or cementing on] of synthetic cliches. B. I. Byrzin. *Poligraf. Proizvodstvo* 1948, No. 2, 19-20; *Chem. Zentr.* 1949, 294-5.—The following adhesives are recommended for cementing on typographic plates of polyvinyl chloride plasticized with diethyl phthalate: (1) leather or bone glue with 10% glycerol, (2) a 10-15% polyvinyl chloride soln. of the type PH-111 in dichloromethane (which is better), (3) carbinol sirup with 0.1-0.25% Edgeright as stabilizer and 2-3% benzoyl peroxide or 1-2% HNO_3 as catalyst (which is still better), (4) a 10-15% soln. of rubber in benzene, and (5) friction tape.

M. G. Moore

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BEREZIN, B I

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Poligraficheskiy retsepturnyy spravochnik
(Polygraphic Prescription Book)
Moskva, Gos. Izd-vo "Iskusstvo", 1953. 311 p. tables.
Bibliographic footnotes.

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BEREZIN, B.I., kandidat tekhnicheskikh nauk (Moscow).

Staining of litho-offset forms and problems concerning the theory of printing element formation. Poligr. proiz. 4:15-16 Ap '53. (MLRA 6:6)
(Lithography--Metal plate processes)

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BERZIN, B.I., kandidat tekhnicheskikh nauk.

Printing properties of paper. Bum.prom. 28 no.8:12-15 Ag '53.
(MLRA 6:7)
(Paper)

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"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BERETIN, Boris Ivanovich; ZAGARINSKAYA, Lyudmila Aleksandrovna; ZARKHINA, M.Ye.; ALEKSANDROV, V.I., tekhn.red.

[Printing materials] Poligraficheskie materialy. Moskva, Gos. izd-vo "Iskusstvo," 1955. 618 p. (MIRA 12:3)
(Printing machinery and supplies)
(Bookbinding—Equipment and supplies)

APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9"

"APPROVED FOR RELEASE: 06/08/2000 CIA-RDP86-00513R000204820006-9

BEREZIN, B.I., kandidat tekhnicheskikh nauk.

Kinds of coated papers for the printing industry. Bum.prom.30 no.10:20-21 O'55. (MLRA 9:1)
(Paper coatings)

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