alkalies, give at great aqueous dilutions identical colors which are some shade of yellow, it follows that the mass influence of water is to yield the azoid form, notwithstanding the presence of acids or of alkalies.

(5) At higher concentrations, aqueous solutions of the two types of helianthine salts differ in degree but not in kind. For high and equal concentrations of helianthine, the "acid solutions" are a deeper yellow-red while the "alkaline solutions" are a lighter red-yellow. Only in the dry condition or in some anhydrous solvents are the acid salts red and the alkaline salts yellow.

(6) Strictly speaking, there is no neutral point in titrations with methyl orange, for all aqueous solutions of helianthine, with equimolecular quantities of acids and alkalies, contain at least some of each chromoisomer. With larger quantities of acids and alkalies, color changes are more evident; at extreme concentrations only, that is at 100% concentration, are pure reds or pure yellows obtained. Since the mass influence of water on all equimolecular acid and alkaline solutions of helianthine yields the same color—the volume of water, that is, the concentrations of the methyl orange, is important with all titrations with this indicator.

(7) Since hydrolysis of its salts conditions the changes of color, the specific nature of such salts is a determining factor in the production of the varied color effects. That the color changes of these salts, however, are not directly proportional to the known affinity constants of the involved acids and bases, indicate that the affinity constants of the two helianthines and the mass influence of water produce a *leveling* effect.

(8) The changes of color of helianthine solutions are not primarily influenced by the concentrations of hydrogen or hydroxyl ions. *The simultaneous and equal influence of both ions* of an acid or of a base, either dissociated or undissociated, influence the color changes, but that the H^+ of "acid solutions" or that the OH^- of "alkaline solutions" independently affect indicators seems improbable. This and other phases of indicator theories will be discussed in a future paper.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

COLORIMETRIC DETERMINATION OF THE SOLUBILITIES OF HELIANTHINE AND ITS SALTS.

BY WILLIAM M. DEHN.

Received February 27, 1917.

Pure helianthine made from the pyridine salt of helianthine, according to the method of Hantzsch,[1] was placed in small glass-stoppered bottles and was treated with sufficient quantities of the respective solvents.

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[1] *Ber.*, 46, 1538 (1913).

The bottles were shaken occasionally during a number of days. When saturation at ordinary temperature was assured, the solutions were filtered and 1 cc. portions were diluted to 250 cc. with *N* HCl. A square 30 cc. bottle was filled with such solution and its color was compared with members of a decimal series of similar 30 cc. bottles containing helianthine diluted with *N* HCl. Readings were made either directly, or, if the solution was too deeply red, after diluting to $^1/_{10}$ or $^1/_{100}$ of this concentration.

Since a 0.00001% solution of helianthine is perceptibly pink and since all the compared solutions were prepared with *N* HCl, it is evident that the final readings involved equal concentrations of red quinoid molecules, though these were only about 13% of the total helianthine concentrations.[1]

Frequently the original solvents were colored yellow, owing to impurities. Usually not being of dye origin, this color, however, did not influence the final red colors observed in the *N* HCl solutions. Since all the readings are made in terms of helianthine, the solubilities of the respective salts formed can readily be calculated, if desired.

GRAMS OF HELIANTHINE SOLUBLE IN ONE LITER OF SOLVENTS.

Acids.	Color.	Sol.	Bases.	Color.	Sol.
Formic (90%)	Deep red	12.500	Pyridine	Deep yellow	7.500
Formic (23%)	Deep red	0.125	Pyridine (85%)	Deep red-brown	250.000
Acetic (99%)	Deep red	0.175	Pyridine (75%)	Deep red-brown	437.000
Dichloroacetic	Deep red	5.000	Pyridine (60%)	Deep red-brown	500.000
Trichloroacetic	Deep red	0.075	Pyridine (50%)	Deep red-brown	625.000
Propionic	Light yellow	0.010	Pyridine (40%)	Deep red-brown	397.000
Butyric (60%)	Red	0.625	Pyridine (25%)	Deep red-brown	310.000
Lactic	Deep red	0.375	Pyridine (15%)	Deep red-brown	310.000
Oleic	Colorless	0.000	Pyridine salt		
HCl (36%)	Deep red	0.750	(H_2O)	Deep red-brown	310.000
HCl (18%)	Deep red	0.375	Collidine	Deep yellow	1.250
HCl (9%)	Deep red	0.075	Quinoline	Deep red	3.750
HCl (4.5%)	Deep red	0.063	Piperidine	Deep yellow	0.063
HCl (*N*)	Deep red	0.038	Nicotine	Yellow	0.075
HBr (25%)	Deep red	0.063	Aniline	Deep yellow	0.750
HBr (10%)	Deep red	0.063	Dimethylaniline	Deep yellow	0.750
H_2SO_3 (6%)	Deep red	0.025	Diamylamine	Deep yellow	0.006
H_2PO_3 (sp. gr.			Phenylhydrazine	Deep yellow	0.750
1.12)	Deep red	0.075	Tripropylamine	Colorless	0.000
Phenols, etc.	Color.	Sol.	Alcohols, etc.	Color.	Sol.
Phenol	Deep red	10.000	Methyl	Deep red	0.500
o-Cresol	Deep red	0.250	Ethyl	Deep yellow	0.100
m-Cresol	Deep red	5.500	*n*-Propyl	Deep yellow	0.080
p-Cresol	Deep red	5.000	*i*-Propyl	Deep yellow	0.200
Guaiacol	Deep red	0.500	*i*-Butyl	Light yellow	0.030
Eugenol	Red-brown	0.160	*i*-Amyl	Light yellow	0.060
Veretrol	Deep yellow	0.125	Caprylic	Light yellow	0.025

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[1] See preceding paper on the helianthines.

GRAMS OF HELIANTHINE SOLUBLE IN ONE LITER OF SOLVENTS (*continued*).

Phenols, etc.	Color.	Sol.
Anethol	Yellow	0.010
Anisol	....	....
Phenetol	....	....
Phenol (90%)	Red	2.500
Phenol (80%)	Red	2.500
Esters.	**Color.**	**Sol.**
Ethyl acetate	Yellow	0.013
Amyl acetate	Yellow	0.015
Amyl formate	Yellow	0.025
Allyl formate	Yellow	0.013
Ethyl oxalate	Yellow	0.050
Ethyl malonate	Yellow	0.000
Amyl nitrate	Light yellow	0.005
Ethyl benzoate	Light yellow	0.010
Triacetin	Light yellow	0.050
Methyl salicylate	Light yellow	0.075
Ethyl salicylate	Light yellow	0.006
Miscellany.	**Color.**	**Sol.**
Sat. sol. NaCl	Red	0.006
Sat. sol. glucose	Red	0.038
Sat. sol. sucrose	Red	0.038
Sat. sol. invert sugar	Red	0.123
Allyl mustard oil	Red	0.025
Phenyl mustard oil	Red	0.150
Acetic anhydride	Light yellow	0.001
Benzoyl chloride	Deep red	0.050
Terebene	Deep yellow	0.075
Anise oil	Light yellow	0.025
Water	Red	0.225 0.055

Alcohols, etc.	Color.	Sol.
Allyl	Deep yellow	0.090
Glycol	Deep red	0.100
Glycerol	Deep red	1.250
Monacetin	Deep red	0.880
Diacetin	Deep yellow	0.320
Benzyl alc.	Deep red	0.125
Aldehydes, ketones.	**Color.**	**Sol.**
Formaldehyde (30%)	Red	0.625
Valeraldehyde	Light yellow	0.075
Paraldehyde	Colorless	0.000
Acetal	Colorless	0.000
Methylal	Colorless	0.000
Benzaldehyde	Deep yellow	0.025
Cinnamaldehyde	Deep yellow	0.125
Acetone	Deep yellow	0.300
Diethylketone	Yellow	0.010
Methylphenylketone	Yellow	0.075
Ethylphenylketone	Yellow	0.019
Insoluble in	**Color.**	
Ether	Colorless	
Carbontetrachloride	Colorless	
Carbondisulfide	Colorless	
Ethyl bromide	Colorless	
Heptane	Colorless	
Amylene	Colorless	
Benzene	Colorless	
Turpentine	Colorless	
Benzyl chloride	Colorless	
Benzal chloride	Colorless	
Nitrobenzene	Colorless	

From a study of the table it becomes evident that helianthine exhibits three types of behavior toward solvents: (1) It is insoluble in certain solvents such as the hydrocarbons, their halogen, nitro and alkyloxy derivatives; (2) it forms soluble salts with certain acids and soluble yellow salts with certain bases; (3) it is soluble in certain "indifferent"[1] solvents.

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[1] *Z. physik. Chem.*, **2**, 176 (1898). Waddell observed that neutral and alkaline solutions of helianthine in acetone, alcohol, ether, benzene and chloroform are yellow and that their acid solutions are red. Addition of water to the latter yields yellow solutions.

Ber., **48**, 169 (1915). Hantzsch states that red helianthine is dissolved to yellow solutions by all non-acid media. These statements must be modified somewhat by the data of the above table.

It forms with then red amd yellow solutions and perhaps forms with them *feeble chemical compounds.*

Evidences for the Existence of Feeble Chemical Compounds.

(1) On the one hand, concentrated solutions of helianthine in water are red, dilute solutions of helianthine in water are yellow; the cause of such isomerizations must be *chemical*, since the temperature and other physical conditions are identical. On the other hand, it is recognized that compounds uniting with the sulfonic acid group of helianthine are red, compounds uniting with its amino group are yellow, therefore changes of color of helianthine solutions chemically involve one or the other of these groups. But at the same concentrations of helianthine in certain "indifferent" solvents, some solutions are red and other solutions are yellow. Since the physical conditions remain the same, the cause of the changes from red helianthine to yellow helianthine must also be chemical. Therefore, *the quality of the color* of helianthine in certain "indifferent" solvents must be indicative of a chemical union[1] between the solute and the solvent, giving one or the other of the tautomeric forms of helianthine.

(2) Solvents not containing chemically active groups do not dissolve helianthine. "Indifferent" solvents that do dissolve helianthine contain labile hydrogen or chemically active groups such as aldehyde or ketone carbonyls. These very groups exhibit tendencies to react with simple sulfonic and amino derivatives, hence they may show some tendencies to unite with the sulfonic and amino groups of helianthine.

(3) According to the principle of continuity, all degrees of stability of salts[2] of helianthine from those on the one hand compounded of strong acids, to those on the other hand compounded of strong bases, must be expected. Therefore, certain intermediate forms may represent feeble chemical unions that can exist only in solutions.

(4) It will be observed that whereas helianthine is difficultly soluble in pure water (0.225 g.) and in pure pyridine (7.5 g.), it is tremendously

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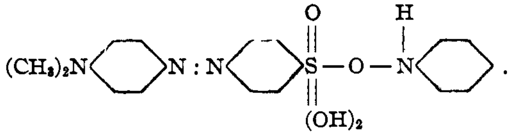
[1] Though denying at one time any isomerizing influence of hydroxide ions, and though recognizing now the primary influence of the solvent, Hantzsch evidently believes that hydrogen and hydroxide ions, at least secondarily, influence the helianthine isomerizations. *Ber.*, 46, 1539, 1555 (1913); 48, 159, 168 (1915).

If the evidences given above in the paper on the chromoisomerism of the helianthines and the data of this paper prove the independence of chromoisomerization of ions, then its true cause, other than the physical effect of heat, must be sought in the solvent itself. How some "indifferent solvents," with the same concentration of helianthine, yield red solutions and how other such solvents yield yellow solutions, can be explained only on the basis of chemical unions of solutes and the solvents. See a discussion of solubility given in a following paper on pyridine solubilities.

[2] A score of new salts of helianthine have been prepared and will be described in an early paper.

soluble in 50% aqueous pyridine (625 g.). In water, structure[1] (II) is involved; in pyridine, structure (III) is involved; and in 50% pyridine, a hydrated form of (III) probably is involved. Indirect evidences for assuming such hydrated form are at hand—pyridine becomes warm on adding water and a pyridine hydrate[2] has been described. The pyridine salt of helianthine containing one molecule of water probably has the structure

(V). 

In other words, the differences in solubility of helianthine in water, pyridine and mixtures of the same can be explained on the basis of involving different forms of the solute such as (II), (III) and (V).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

COLORIMETRIC STUDIES OF PICRATE SOLUTIONS.

BY WILLIAM M. DEHN AND ALICE A. BALL.

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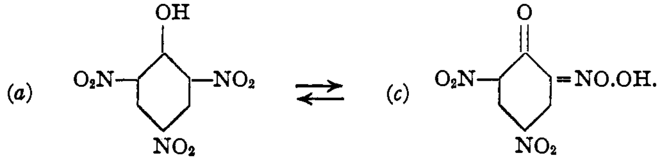
In a recent colorimetric study of chromate solutions by one of us, it was stated[3] that preliminary experiments with picrates in different solvents and under varied conditions of concentration, temperature and alkalinity, in accordance with the conclusion of Hantzsch,[4] indicated equilibria of two isomeric forms of the acid.



Recognition of tautomeric forms of picric acid has been made by various investigators,[5] but perhaps the greatest credit for such recognition should be given to Hantzsch, who in voluminous contributions to the quinones, nitro phenols and the pseudo-acids, has steadfastly maintained[6] a theory

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[1] See preceding paper on methyl orange.

[2] Goldschmidt and Constam, *Ber.*, 16, 2977 (1883). Also see paper following.

[3] THIS JOURNAL, 36, 846 (1914).

[4] *Ber.*, 39, 1077 (1906); 40, 350 (1907). For iso-picric acids see Nietzki and Dietschy, *Ibid.*, 34, 57 (1901).

[5] Draeper, *J. Chem. Soc.*, 99, 2096 (1911)..

[6] *Ber.*, 12, 1803, 1807, 2071 (1879); 32, 575 (1899); 39, 1073, 1084, 3074 (1906); 40, 338, 1533, 1556, 4875 (1907). Compare also Kauffmann, *Ibid.*, 39, 1959 (1906); 40, 843, 4547 (1907); Torrey and Heuter, *Ibid.*, 40, 4332 (1907); Kehrmann, *Ibid.*, 32, 927 (1899); 38, 2577 (1905); 40, 1960 (1907).