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KIADJA:
A SZEGEDI TUDOMÁNYEGYETEM
Felelős szerkesztő: Dr. Kiss Árpád

Institut de Chimie-Physique de L'université de Szeged.
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Sur les méthodes d'analyse des courbes d'absorption

par MM. Á. Kiss et C. Sándorfy

(Arrivée VI. 1945.)

Introduction.

Les courbes d'extinction des corps dissolus sont des courbes continues ayant une structure plus ou moins articulée. Elles se composent d'un certain nombre de bandes d'absorption produites par les différentes chromophores de la molécule en question et par des divers phénomènes d'excitation.

Il est nécessaire à l'interprétation du mécanisme de l'absorption de la lumière que les courbes d'extinction soient analysées, c'est-à-dire que les bandes dont elles se composent, soient retrouvées.

Etant donné que de tels travaux ont été effectués dans cet Institut (1) et que d'autres sont actuellement en cours, il nous paraît utile d'en donner une vue d'ensemble.

La forme des bandes d'absorption.

Pour analyser les courbes, on a généralement recours aux courbes d'extinction définies par le coefficients d'extinction moléculaires ε (ou, plus fréquemment par leurs logarythmes) et par les nombres d'onde $\nu = 1/\lambda$.

Afin de pouvoir faire l'analyse de ces courbes, il est nécessaire que nous soyons renseignés sur la forme des bandes d'absorption, autrement dit que nous soyons en possession des formules propres à les représenter d'une façon adéquate.

Les bandes d'absorption sont des courbes de répartition typiques qui décroissent aux deux côtés plus ou moins symétriquement. Leur hauteur est définie par ε max. et leur position par λ et ν.

D'après la physique classique, ε peut être représenté par la formule suivante (2)

$$\varepsilon = \varepsilon_{\max.}/[1 + (\Delta\nu/\mathrm{h})^2] \qquad 1$$

Ici h est une constante et $\Delta\nu$ représente l'écart des valeurs de ν correspondant respectivement à un ε quelconque et a $\varepsilon_{\max.}$ en unités $\nu = 1/\lambda$.

La formule 1 n'est valable que dans le cas où les extinctions ne sont pas trop élevées et où l'indice de réfraction (n) du corps absorbant ne varie pas d'une façon considérable avec le changement de la longueur d'onde (2, 3). Dans le cas d'une extinction forte, on a

$$2\,\mathrm{n}\,\varepsilon/\varepsilon^2_{\max.} = 1/[1 + (\Delta\nu/\mathrm{h})^2] \qquad 2$$

D'après la mécanique ondulatoire, on est conduit à la formule suivante (4)

$$\varepsilon = \varepsilon_{\max.}\, e^{-\left(\frac{\Delta\nu}{h}\right)^2} \qquad 3$$

Ici h, le paramètre de répartition définit la demi-largeur des bandes (ν'), à savoir

$$\Delta\nu' = 1{,}6651\,h = 2\sqrt{\ln 2}\,h. \qquad 4$$

$\Delta\nu'$ est égal à la distance entre le ν corresppondant à $\varepsilon_{\max.}$ et entre le ν correspondant à $\varepsilon = \frac{\varepsilon_{\max.}}{2}$

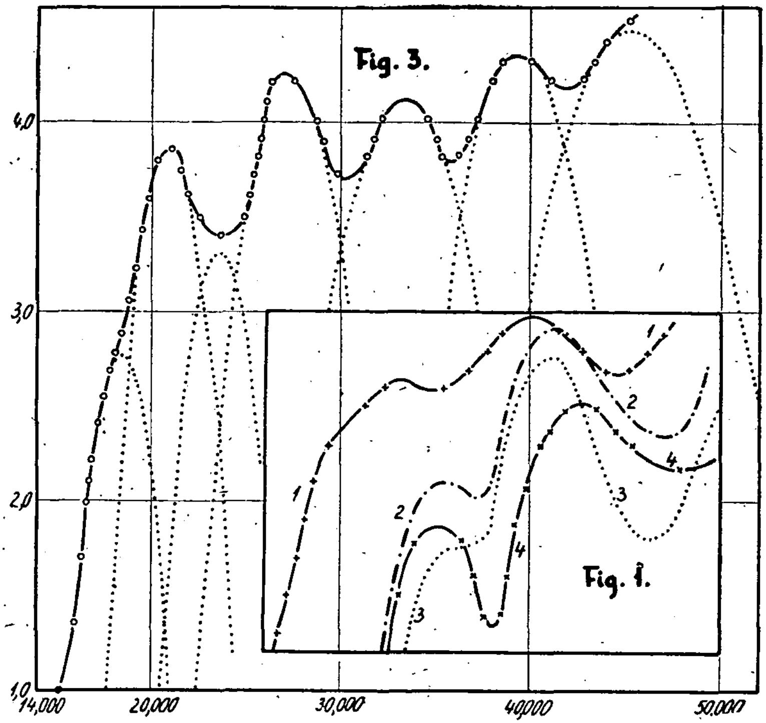

Fig. 1. Courbe d'extinction observée de la benzalaniline (courbe 1). La même calculée (courbe 2) à partir des courbes du benzaldéhyde (courbe 3) et de l'aniline (courbe 4).

Fig. 3. Analyse univoque de la courbe d'extinction du salicylaldéhyde-ortho-phénylène-diimine-nickel.

Fromherz et Menschik (4) ont démontré que les formules 1 et 3 sont identiques. Développons en série la formule 3 et interrompons le développement au deuxième membre ; nous obtenons alors :

$$\varepsilon = \varepsilon_{\max.}\, e^{-\left(\frac{\Delta\nu}{h}\right)^2} = \varepsilon_{\max.}/e^{\left(\frac{\Delta\nu}{h}\right)^2} = \varepsilon_{\max.}\, 1/1 + (\Delta\nu/h)^2 \qquad 5$$

ce qui est équivalent avec la formule 1.

Lowry et Hudson (5a) puis Mead (5b) ont fait usage d'une formule analogue à la formule 3 :

$$\varepsilon = \varepsilon_{\max.}\, e^{-[\nu_{\max.}/\nu(\Delta\nu/h)]^2} \qquad 6$$

Les bandes calculées à partir des formules 1 et 3 sont des bandes symétriques tandis que celles calculées d'après la formule 6 descendent avec une pente moins forte vers les longueurs d'ondes plus courtes. Les bandes mesurées expérimentalement (1, 2, 6) descendent aussi avec une pente moins forte en général vers les ondes plus courtes, mais pas exactement dans la mesure prévus par la formule 6.

D'après la théorie de Condon — Franck (7), la forme d'une bande d'absorption dépend de la forme et de la position relative des courbes de potentiel dans l'état de base et dans l'état excité (6, 8). Suivant que l'excitation laisse la force de la liaison inchangés, la diminue ou l'augmente, trois types principaux de courbes de potentiel sont possibles. Dans le premier cas, on obtient des bandes symétriques ; dans le deuxième et dans le troisième cas, elles descendent respectivement vers les longueurs d'onde plus courtes avec une pente moins forte ou plus forte.

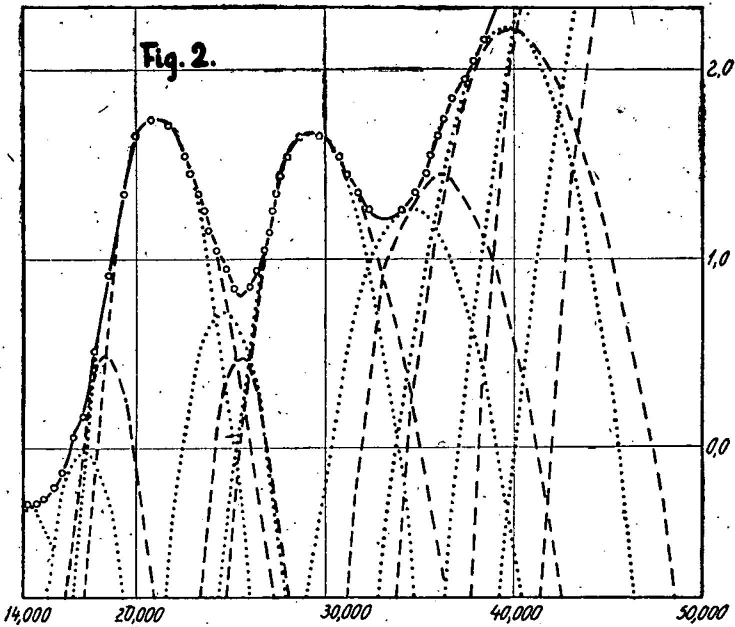

Fig. 2. Courbe d'extinction de l'ion $[Co\,(NH_3)_6]^{3+}$ analysé d'après la formule 3 (ligne pointillée) et 6 (ligne de tirets).

Mais jusqu'à présent, la théorie de Franck — Condon n'était applicable qu'aux molécules di- et triatomiques. Aussi, nous nous contentons d'exécuter nos analyses d'après la formule 3 qui donne des bandes symétriques (9).

Surface renfermée par les bandes.

La surface des bandes peut être représentés par la formule (4)

$$F = \int_0^\infty \varepsilon \, d\nu = \varepsilon_{max.} \int_0^\infty \varepsilon^{-\left(\frac{\Delta\nu}{h}\right)^2} = \varepsilon_{max.} \, h \sqrt{\pi} = \varepsilon_{max.} \, \nu' \, 1{\cdot}0645 \qquad 7$$

Etant donné qu'afin de faire des études comparatives, il suffit de connaître les valeurs relatives des F, il n'est pas nécessaire de calculer le nombre des résonateurs qui figurent dans le domaine d'absorption (4, 10).

La valeur de F dépend du nombre des molécules absorbantes et des probabilités de transition. Au cas où ily aurait un nombre constant de molécules absorbantes, le changement de F peut être considéré comme la mesure du changement des probabilités de transition.

L'exécution de l'analyse des courbes.

Afin de rendre l'analyse aussi peu arbitraire que possible, on calcule d'abord les bandes „libres“. On choisit les valeurs de $\varepsilon_{\max.}$ et de ν' de façon que la bande calculée épouse la forme la plus rapprochée possible de la bande expérimentale. Ensuite, on passe aux parties moins articulées de la courbe d'absorption. Finalement, on attribue les extinctions qui restent à des bandes de moindre intensité. En pratique, on adopte le principe qu'aucun point des courbes d'extinction ne doit appartenir aux champs de plus de trois bandes. Le travail peut être facilité d'une façon considérable si l'on recueille dans des tables les valeurs de $e^{-\left(\frac{\Delta\nu}{h}\right)^2}$ qui correspondent aux valeurs des h et des $\Delta\nu$ les plus fréquents.

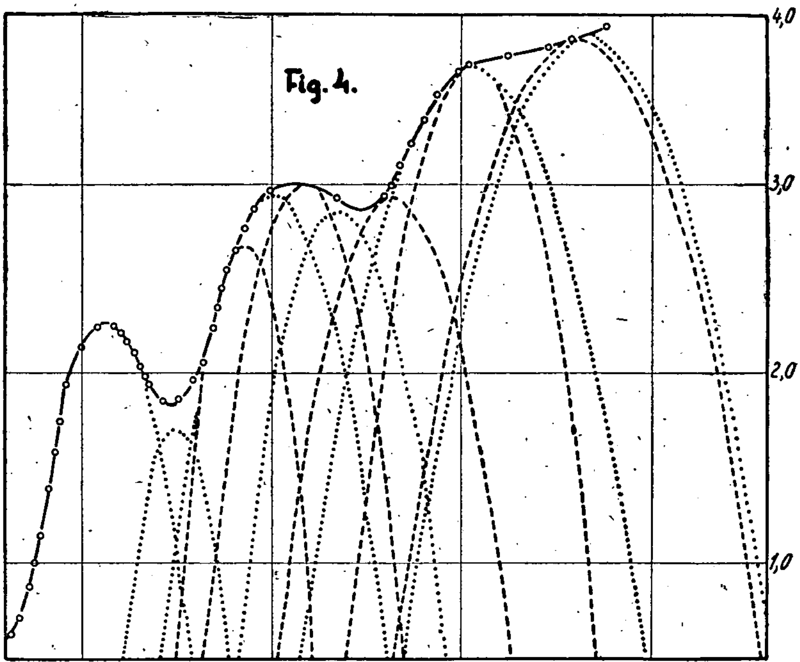

Fig. 4. Analyse non univoque de la courbe d'extinction de l'ion Cis $[Co.SCN.No_2.En_2]^+$ (Lignes pointillées et lignes de tirets.) (En = diamine de l'éthylène.)

Si l'on veut répondre à la question : dans quelle mesure la formation des composés plus compliqués change l'absorption propre des composants, il est utile de recourir à la synthèse des courbes d'extinction (1 a, 1 b, 1 c). Les courbes peuvent en effet s'écrire selon la relation :

$$\varepsilon = n_1 \varepsilon_1 + n_2 \varepsilon_2 + \qquad 8$$

où ε_1 et ε_2 représentent les coefficients d'extinction des composants, n_1 et n_2 le nombre respectif des molécules de ces composants qui figurent dans la molécule résultante.

La différence qui se manifeste entre les courbes observées et ainsi synthétisées prouve qu'en général, l'extinction n'est pas une propriété additive. (Fig. 1). Comme mesure du défaut d'addivité, on peut se servir de la formule

$$F = F_{exp.} - F_{synt.} \qquad 9$$

qui peut être établie par intégration graphique,

La méthode inverse consiste à décomposer les courbes d'extinction observées. Selon cette méthode appliquée par Hertel (10) on soustrait l'extinction des composants de la courbe de la molécule qu'ils composent et on attribue le reste d'extinction aux nouveaux phénomènes d'absorption causés par la formation de la molécule résultante. Selon que la molécule contient ou non des composants doivent être pris en considération avec des valeurs modifiées ou inchangées. Mais ceci implique une incertitude.

Critique de la méthode.

Dans le cas des bandes qui descendent avec une pente moins forte vers les longueurs d'onde plus courtes, nous obtenons, d'après la formule 3, plus de bandes qu'il n'y en a en réalité. Dans ces cas, la formule 6 conduit à de meilleurs résultats. Son application générale se heurte tout de même à l'existence des bandes symétriques et différemment assymétriques. L'usage alternatif dés deux formules donnerait des résultats difficiles à comparer, sans parler de ce que le juste forme des bandes n'est en général pas connue.

Ainsi, nous voulons la préférence à la formule 3 pour négliger les bandes de moindre intensité qui apparaîtraient aux côtés des bandes qui descendent vers les longueurs d'onde plus courtes. Les analyses selon les formules 3 et 6 donnent en général un même nombre de bandes et les différences dans la hauteur et la position de celles-ci ne sont pas assez importantes pour rendre l'analyse illusoire (Fig. 2).

L'analyse des courbes d'extinction qui se composent des bandes bien articulées conduit à des résultats univoques (Fig. 3).

L'analyse devient équivoque quand la courbe ne donne pas de points d'appui pour la fixation des demi- largeurs des bandes. Ainsi l'analyse des parties stagnantes est tout à fait incertaine. En outre, toutes les bandes dont les positions sont à moins d'une largeur de distance sont inséparables (Fig. 4).

Ici se manifestent des lacunes importantes à l'analyse des courbes.

Résumé.

Les méthodes usuelles de l'analyse des courbes sont discutées. L'efficacité et les insuffisances de ces méthodes sont démontrées sur des exemples proprement choisis.

Szeged, (Hongrie) VI. 1945.

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Zur Lichtabsorption der Nitroderivate des Benzols

Von Á. KISS und J. HYROSS.

(Eingegangen am. 10 Juli 1948).

Einleitung.

Die Lichtabsorption der aromatischen Nitroderivate wurde wiederholt eingehend behandelt (1). Da die Erklärung der Versuchsdaten nach einer umfassenden Theorie noch aussteht, so wurde die systematische Untersuchung dieser Frage in Begriff genommen. Die Extinktionskurven hat Hyross (2) in Aethanol bei Zimmertemperatur ausgemessen. Dabei wurden alle uns zur Verfügung stehenden Literaturdaten berücksichtigt. Wegen der starken Mediumwirkung sollen alle Extinktionskurven in gleichem Lösungsmittel (in Hexan) ausgemessen werden. Dies wurde durch die schwache Löslichkeit einiger Verbindungen verhindert. Durch die Mediumwirkung wird aber die Möglichkeit einer richtigen Interpretation der Versuchsdaten nicht gefährdet. Die Experimentelle Einrichtung und die Messmethode betreffend verweisen wir auf eine frühere Arbeit (3). Die verwendeten Verbindungen waren teils reinsste Handelspräparate, teils wurden sie nach Literaturangaben hergestellt. Sie wurden gründlichst gereinigt und ihre Reinheit durch Schmelzpunktsbestimungen geprüft.

Struktur der Extinktionskurven von Nitroderivaten.

Die Nitroderivate des Benzols besitzen anders strukturierte Extinktionskurven, als die übrigen Benzolderivate. Einige monohaloid Nitroderivate ausgenommen (4) fehlt die Schwingungsstruktur der Benzolbande, bedingt durch die elektrische Assymmetrie der Nitrogruppe (5).

Die Entstehung der Banden der Nitroderivate wurde verschiedener Weise erklärt. Nach Förster und Wagner (4) gehört die Vor-und zweite Hauptbande des Nitrobenzols (I) dem Benzol, die erste Hauptbande der Nitrogruppe zu (Abb. 1, Kurve 2a, nachher gek. 1/2a). Dafür können die folgenden Beweise angefürt werden.

Bei Nitromethan liegt die Absorption der unbeeinflussten NO_2-Gruppe bei 276 mμ (6), bei Nitroaethan bei 280 mμ (7). Bei den p-Derivaten der Halogennitrobenzole ist die Lage der ersten Hauptbande nicht feststellbar (5). Bei allen untersuchten o-und m-Derivaten liegt sie bei 280 mμ, also wegen der Konjugation von zwei Chromophoren etwas nach den langen Wellen verschoben (5). Die entsprechende Ausbuchtung der Kurve von I (1/2a) sollte der Bande der Nitrogruppe entsprechen. Die m-Halogenderivate, z. B. m-Chlornitrobenzol (2/3) zeigen in Hexan eine ausgeprägte Schwingungsstruktur (4). Der Abstand der Teilbanden von 1200 cm^{-1} entspricht der aus Raman-Spektren bekannten intensiven Nitrofrequenz von 1340 cm^{-1}. Bei mehreren nitrofreien Benzolderivaten kommt in der Gegend von 350 mμ eine schwache Vorbande vor (5, 15). Nach dem Dipolmoment von I sollte die Vorbande des Benzols bei 357 mμ liegen (8). Dies entspricht wohl ihrer Lage nach der Vorbande von I. Das Maximum der Benzolbandengruppe liegt bei Benzol bei 255 mμ (1/1). Die zweite Hauptbande von I liegt bei 250 mμ. Dies entspricht der etwas nach den kurzen Wellen verschobenen Benzolbande. So ist es zweifellos, das die erste Hauptbande von I der Nitrogruppe zukomt (4). Kortüm (9) ordnet auch die Vorbande von I der Nitrogruppe zu.

Auffallend ist der starke Unterschied der Kurven der o-, m-und p-Nitroderivate So liegt bei den o-und m-Chlornitrobenzolen die erste und zweite Bande sehr dicht zueinander (2/2 und 3). Bei p-Chlornitrobenzol (2/4) sind sie zu einer Bande verschmolzen (5). Auch bei anderen o-, m-und p-Nitroderivaten weist die Struktur der Kurven ähnliche Unterschiede auf. Methanol bewirckt eine starke Verschiebung der Hauptbanden nach den langen Wellen, so dass die Vorbande weniger ausgeprägt ist (5).

Besprechung der Versuchsdaten.

Die Elektronenverteilung des Benzols, die mesomere und induktive Wirkung der Substituenten, weiterhin den Mechanismus der Lichtabsorption betreffend verweisen wir auf eine frühere Arbeit (10). Die Abschätzung der möglichen elektromeren Grenzstrukturen des Grund-und Anregungszustandes gestatten eine Erklärung der Struktur der Extinktionskurven (10, 15, 19), so versuchen wir diese Frage auch bei den Nitroderivaten des Benzols gleicher Weise beantworten.

Das N-Atom und die beiden O-Atome der NO_2-Gruppe haben je zwei π-Elektronen zur Mesomerie zur Verfügung. Im Grundzustand des Nitrobenzols (I) haben Benzolring (10) und NO_2-Gruppe (11) eigene Mesomerie (Abb. 1; Form. Ia-b, nachher gek. 1/Ia-b). Wegen der kleineren Anzahl von Doppelbindungen spielt nämlich die Grenzform Ic erst in dem Anregungszustand eine grössere Rolle. Somit beeinflussen beide Gruppen im Grundzustand die Verteilung der π-Elektronen des Benzols vorwiegend induktiver, in dem Anregungszustand induktiver und mesomerer Art. Dies ist so weit richtig, als die Elektronenverteilung durch elekromeren Grenzformen anzugeben ist, d. h. keine Molekularbahnen sich ausbilden (10). Gemäss der Mesomerie des Grundzustandes besteht die Lichtabsorption in der separaten Anregung der π-Elektronen des Benzolringes und der NO_2-Gruppe. D. h. die miteinander direkt verbunden Chromophore behalten ihre selektive Lichtabsorption in geänderter Form. (1/2a und b).

Das Cl-Atom bindet die π-Elektronen fester, als das C-Atom, somit ist die mit Elektronenabgabe vor sich gehende Mesomerie (2/IIa) des Cl-Atoms bei Chlorbenzol (II) praktisch Null (12). Der beinahe gleicher Verlauf der Extinktionskurven von Benzol (1/1) und von II (2/1) bestätigt dies und weist auf die schwache induktive Wirkung des Cl-Atoms hin. Bei Toluol (III) beeinflusst die nicht mesomeriefähige H_3C-Gruppe nur schwach induktiver Art die π-Elektronenverteilung des Benzols. In heptan sind bei III die drei Schwingungsbanden (2/5) gut sichtbar. Aethanol verwischt die Schwingungsstruktur (8).

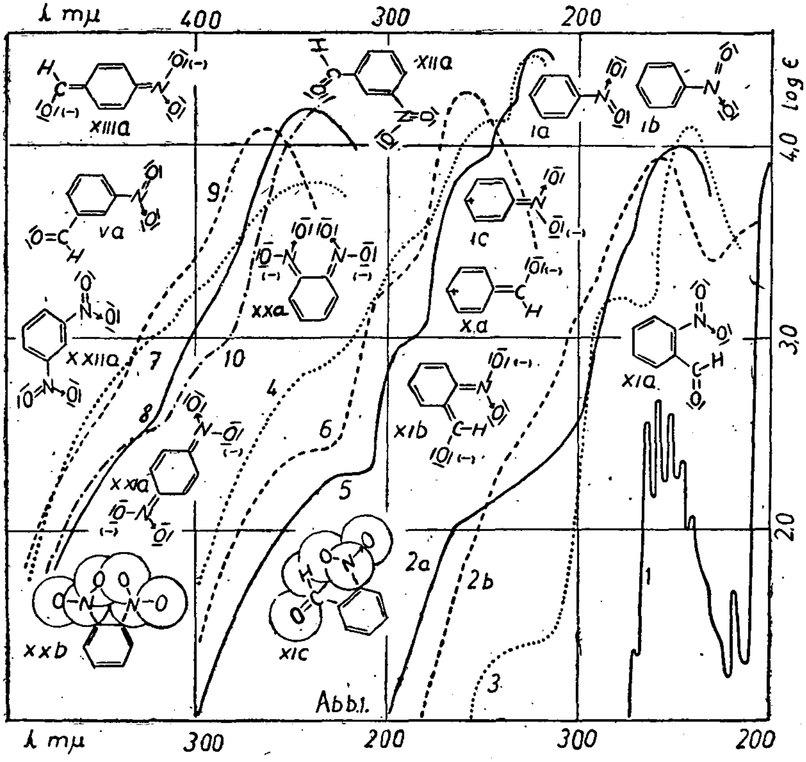

Abb. 1. Kurven: 1: Benzol in Hexan. 2a: Nitrobenzol in Heptan (5). 2b: Nitrob. in Aethanol. 3: Benzaldehyd in Aethanol. 4, 5 und 6: o-, m- und p-Nitrobenzaldehyd in Hexan (18). 7, 8 und 9: o-, m- und p-Dinitrobenzol in Wasser (9). 10: Symm. Trinitrobenzol in 0,001 m HCl (9).

Bei o-, m-und p-Chlorbenzolen (IV, V und VI), bzw. bei o-, m-und p-Chlornitrotoluolen (VII, VIII und IX) werden wegen der sehr schwachen mesomeren Wirkung des Cl-Atoms und wegen der mesomerieunfähigkeit der H_3C-Gruppe die üblichen (der Kürze wegen nicht angegebenen) Strukturformeln die Grenzstrukturen des Grundzustandes beherrschen. Bei den o-und m, bzw. p-Derivaten verstärken, bzw. schwächen sich die induktiven Wirkungen beider Gruppen. Die Kurven von IV und V (2/2 und 3) bzw. bei VII und VIII (2/6 und 7) sind zu dieser von I (1/2a und 2b) ähnlich. Bei VI (2/4) bzw. bei IX (2/8) sind die zwei Hauptbanden zu einer Bande verschmolzen. Methanol verwischt die Bandenstruktur bei den erwähnten Derivaten (5, 18).

Die in p-Stellung zur NO_2-Gruppe befindlichen Methyl-, Propyl-, Isopropyl-und t-Butylgruppen verursachen eine beinahe gleiche Extinktionszunahme bezogen auf die Kurve von I. In m-Stellung üben sie nur eine schwache Wirkung aus. In o-Stellung wird die Extinktion der NO_2-Gruppe durch die Substituenten in der angegebenen Reihe aus sterischen Gründen geschwächt (13). Bei den o-Derivaten weist auch das Raman-Spektrum eine sterische Hinderung auf (14).

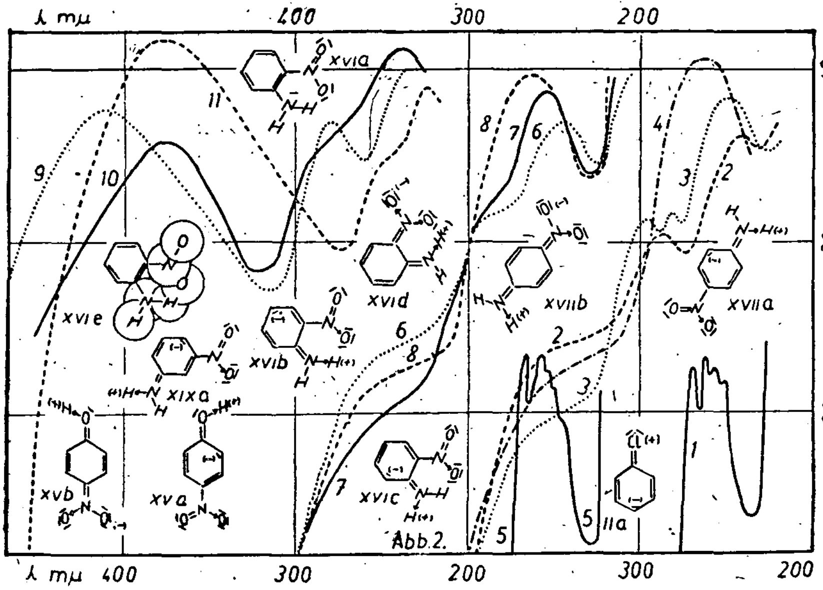

Abb. 2. Kurven: 1: Chlorbenzol in Heptan (5). 2, 3 und 4: o-, m- und p-Chlornitrobenzol in Heptan (5). 5: Toluol in Hexan (5). 6, 7 und 8: o-, m- und p-Nitrotoluol in Heptan (18). 9, 10 und 11: o-, m- und p-Nitroanilin in Aethanol.

Bei Benzaldehyd (X) beteiligt sich die Aldehydgruppe wegen der kleineren Anzahl von Doppelbindungen (1/Xa) nur in kleinerem Masse im Grundzustand in der Mesomerie des Benzolringes. So übt sie im Grundzustand vorwiegend eine induktive, in der Anregungszustand dagegen eine induktive und eine elektromere Wirkung aus, Somit ist die Kurve von X (1/3) aus dem Eigenabsorption des Benzolringes und der Aldehydgruppe aufgebaut. Ahnlich sind die Verhältnisse bei den o-,m- und p-Benzaldehyden (XI, XII und XIII). So sind die, die mesomerie beider Gruppen ausdrückenden Grenzformen (1/XIb und XIIIa) wegen der kleineren Anzahl von Doppelbindungen im Grundzustand von XI und XII kaum vertreten. Bei XII ist sie wegen der m-Stellung beider Gruppen nicht möglich (1/XIIa). Bei XI kann die H-Brüche (1/XIa) vorkommen. bzw. die sterische Hinderung stören (1/XIc). Somit sollen sich die Kurven von XI, XII und XIII (1/4-6) aus den modifizierten Eigenabsorptionen des Benzolringes, der Aldehyd und der NO_2-Gruppe aufbauen, worauf der ähnliche Verlauf der Kurven von XI, XII und XIII (1/4-6) zu dieser von I (1/2a) hinweist.

Die o- und p-stellingen HO-, bzw. H_2N-Gruppen ermöglichen bei o-und p-Nitrophenol (XIV und XV), bzw. bei o-und p-Nitroanilin (XVI und XVII) die Beteiligung sowohl der HO-und H_2N-als der NO_2-Gruppen in der Mesomerie des Benzolringes. Von diesen ist die, das ganze

Molekül durchlaufende Mesomerie (3/XIVb und 2/XVb, bzw. 2/XVId und XVIIb) gegenüber der alleinigen Mesomerie der HO-und H_2N-Gruppen (3/XIVa, XIVc und 2/XVa, bzw. 2/XVIb und XVIIa) energetisch bevorzugt. Bei den o-Derivaten kann die Mesomerie aus sterischen Gründen gehindert werden. (3/XIVd, bzw. 2/XVIe), bzw. kann die H-Bindung (3/XIVa, bzw. 2/XVIa) wegen des Mesomeriekurzschlusses die Ausbildung der übrigen Grenzstrukturen stören. Die Resonanz und Überlagerung der Grenzformen des Grund-und Anregungszustandes und die Ausbreitung des π-Elektronensystems bedingen die Herabsetzung der Anregungsenergie und somit die Verschiebung der Extinktionskurven von XIV und XV (3/1 und 3), bzw. von XVI und XVII (2/9 und 11) zu dieser von I (1/2) nach den langen Wellen. Die Beteiligung der polaren Grenzformen schon im Grundzustand bedeutet, dass die Anregung mit Ladungsverschiebungen vor sich geht, wodurch die Exinktion in langwelligem Spektralgebiet stark zunimmt (10). Bei XVI verursacht die H-Bindung (2/XVIa) wegen Mesomeriekurzschlusses eine Extinktionsabnahme (2/9) verglichen mit der Kurve von XVII (2/11). Die H-Bindung ist so stark. dass sie sogar durch polare Lösungsmitteln nicht zerstört wird (16). Es kann nicht mehr, wie bei I von der selektiven Absorption der NO_2-Gruppe die Rede sein. Somit sind keine Nitro-und-Benzolbanden mehr vorhanden.

Bei den o-und p-Oxyderivaten des Benzalanilins erhält man an der Grenze des Sichtbaren eine langwelligere Vorbande (15). Die erste breite Bande von XIV und XV (3/1 und 3) enthält diese Bande.

Bei m-Nitrophenol (XVIII) und m-Nitroanilin (XIX) beteiligt sich die NO_2-Gruppe wegen der m-Stellung der HO-, bzw. H_2N-gruppen im Grundzustand nicht in der Mesomerie des Benzolringes. Es besteht praktisch nur die Mesomerie der HO-und H_2N-Gruppen (3/XVIIIa, bzw. 2/XIXa). Somit liegt die erste Bande der Verbindungen XVIII (3/2), bzw. XIX (2/10) bei kürzeren Wellenlängen und läuft tiefer als bei XIV (3/1), bzw. XVI (2/9).

Bei o-und p-Dinitrobenzol (XX und XXI)ist die, das ganze Molekül-umfassende Mesomerie (1/XXa und XXIa) wegen der kleineren Anzahl von Doppelbindungen im Grundzustand energetisch ungünstig. Ein Vergleich der Kurven von I (1/2a), bzw. von XX und XXI (1/7 und 9) weist auf die schwache Mesomerie nach XXa und XXIa hin. Die eiwandfreie Interpretierung der Versuchsdaten ist durch den Lösungsmitteleinfluss gestört. Bei m-Dinitrobenzol (XXII) kann wegen der m-Stellung beider NO_2-Gruppen von der gemeinsamen Mesomerie derselben nicht die Rede sein (1/XXIIa). Im Sinne des Gesagten beeinflussen die NO_2-Gruppen bei XX und XXI, eher noch bei XXII die π-Elektronenverteilung des Benzols im Gzundzustand vorwiegend induktiver Art. Bei XX und XXI wirken die induktiven Wirkungen beider NO_2-Gruppen einander entgegen, bei XXII verstärken sie sich gegenseitig. Die Intensitätsabnahme der Kurve von XX kann es verursachen, dass die zwei NO_2-Gruppen in die Ebene des Benzolringes (1/XXb) sich genau nicht einstellen können.

Im Grundzustand des 3, 5-Dinitrophenols (XXIII) spielt wegen der m-Stellung beider NO_2-Gruppen, nur die Mesomerie der HO-Gruppe, im Sinne des bei XVIII und XXII Gesagten, eine Rolle (3/XXIIIa). Die abweichende Struktur seiner Extinktionskurve (3/7) von dieser von I (1/2a), bzw. von XX, XXI und XXII (1/7-9) verursacht die starke Mesomerie der HO Gruppe und die induktive Wirkung beider NO_2 Gruppen.

Im Grunzustand des 2, 6-Dinitrophenols (XXIV) beteiligen sich alle drei Gruppen im Grundzustand in der Mesomerie des Benzolringes. So entsteht ein einheitliches System von π-Elektronen. Auf einmal mesomerisiert die HO-Gruppe nur mit einer der beiden NO_2-Gruppen (3/XXIVa). Durch die Resonanz werden aber beide NO_2-Gruppen in die Mesomerie mit einbezogen. Im Sinne des bei XIV gesagten wird die Kurve von XXIV (3/6) zu dieser von XXII (1/8) nach den langen Wellen mit starker Extinktionszunahme verschoben. Die H-Bindung kann wegen Mesomeriekurzschlusses die Mesomerie stören. Wegen der Hinderung der genauen Einstellung der Substituenten in die Ebene des Benzolringes nimmt die Extinktion ab (3/XXIVb).

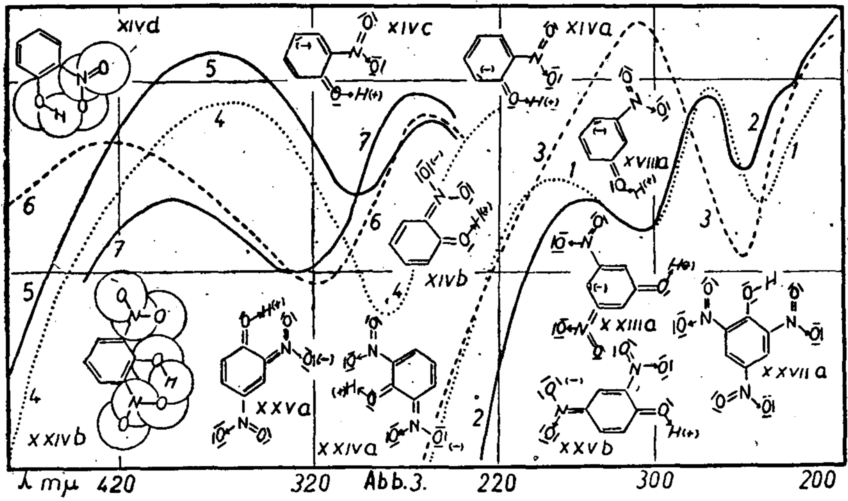

Abb. 3. Kurven: 1, 2 und 3: o-, m- und p-Nitrophenol in Aethanol. 4: Pikrinsäure in Aethanol. 5: 2,4-Dinitrophenol in Wasser (9). 6: 2,6-Dinitroph. in Wasser (9). 7: 3,5-Dinitroph. in Wasser (9).

Bei 2, 4-Dinitrophenol (XXV) ist die Mesomerie noch verwickelter, als bei XXIV, da die o-und p-stelligen NO_2-Gruppen in der Mesomerie des Benzolringes durch Ausbildung der o-, bzw. p-Chinon-Imid-Grenzstrukturen sich beteiligen können. (3/XXIVa und b) Im Sinne des bei XXIV Gesagten wird die Kurve von XXV (3/5) zu dieser von XXII (1/8) mit Extinktionszunahme nach den langen Wellen verschoben. Die Strukturunterschiede der Kurven von XXIV und XXV (3/6 und 3/5) verursachen, dass bei XXV die p-Chinon-Imid-Grenzform beherrscht den Grundzustand des Moleküls. Die schwächere Absorption von XXIV (3/6) gegenüber dieser von XXV (3/5) verursacht, dass die mesomeriesierenden Gruppen aus sterischen Gründen in der Ebene des Benzolringes sich nicht genau einstellen können (3/XXIVb).

Bei symm. Trinitrobenzol (XXVI) kann wegen der m-Stellung der drei NO_2-Gruppen von der Mesomerie derselben nicht die Rede sein, somit beeinflussen sie die π-Elektronenverteilung des Benzolringes vorwiegend induktiver Art. Die Induktiven Wirkungen der NO_2-Gruppen verstärken sich gegenseitig. Im Sinne des Gesagten ist die Kurve von XXVI (1/10) zu dieser von XII (1/8) ähnlich.

Bei der Pikrinsäure (XXVII) vermehrt die Beteiligung der drei NO_2-

Gruppen und der HO-Gruppe in der Mesomerie des Benzolringes die Anzahl der möglichen Grenzstrukturen des Grund- und Anregungszustandes. Ihre Mesomerie setzt sich zusammen aus dieser von XXIV und XXV (3/XXIVa und XXVa-b). Im Sinne des bei Nitrophenolen Gesagten wird die Kurve von XXVII (3/4) zu dieser von XXVI (1/10) mit Intensitätszunahme nach den langen Wellen verschoben.

Zusammenfassung.

Die kritische Durchmusterung der Grenzformen des Grund und Anregungszustandes ermöglicht die einheitliche Erklärung der Struktur der Extinktionskurven der Nitroderivate des Benzols.

Es hat sich einstimmig gezeigt, dass die elektromere Wirkung der Substituenten viel stärker ist, als ihre induktive Wirkung.

Bei Nitrobenzolen, weniger bei Nitrobenzaldehyden, wo der Benzolring und die Substituenten (Nitro-und Aldehydgruppe) noch eigene Mesomeriesysteme besitzen, kann man noch von eigenen Absorptionsgebiete des Benzols und der Nitrogruppe sprechen.

Bei Nitroanilinen und Nitrophenolen kann wegen der, das ganze Molekül umfassenden Mesomerie von der separaten Anregung der einzelnen Chromophore nicht die Rede sein.

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On the Absorption of Light of Isomeric Derivatives of Benzalaniline

By Á Kiss and R. Pauncz.

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1. *Introduction.*

In an earlier communication (1) we have shown that the benzene rings A and B (fig. 1, form. I) which are bound to the C and N atom of the azomethine group, respectively behave differently. So the extinction curves of the isomeric pairs which are substituted in the same places relating to the azomethine groups show great differences. The task of this work is to approach to this problem.

Concerning the experimental apparatus and the method we refer to earlier papers (2). The compounds were prepared by procedures described in the literature by Pauncz (3). The compounds were purified thoroughly and their purity was controlled by determining the melting point. The solvent was ethanol the purity of which was controlled spectrogaphically (4).

2. *General Remarks.*

By benzalaniline (1) in the ground state prevails the Ia structure (fig. 1) on account of the greatest number of double bonds. So the azomethine group can only participate in the excited state in the mesomerism of the phenyl nucleus. The resonance and superposition of many structures (which for the sake of brevity are not formulated) diminish the energy of excitation. Therefore its extinction curve (fig. 1, curv. 1, = 1/1) is shifted compared with that of benzene (1/1a, shifted with log $\varepsilon = 1{,}0$ upwards) toward longer wave lengths and the extinction increases strongly.

When the structure Ia prevails the absorption of light consists in the excitation of the π-electrons ot the benzene ring and that of the azomethine group (1, 5, 6, 7). This assertion is only true as far as we can give the electron arrangement in the benzalaniline by electromeric structures. When π-electrons of the benzene ring and of the azomethine group form molecular orbitals which seems to be probable from the form of the extinction curves then this explanation is not satisfactory (5). The question was not to answer by curve analysis because of the overlapping of the absorption regions of the phenyl nucleus and of the azomethine group (5). To solve this problem absorption measurements are carried on by some benzalaniline derivatives.

By the derivatives of the benzalaniline the trans form is more advantageous from energetic reasons. This seems to be justified by the below discussed mesomeric cases, the hydrogen-bond formation (cf. fig. 1, IIa) by the o-hydroxy derivatives (which cannot develop in the case of cis form IIa), verified by the infrared absorption (8), by the Raman spectra (9) and by the measurement of electric moments (13, 14).

The two benzene rings A and B which are connected directly by the mesomeric capable azomethine group influence one another in different manners (electromerically or inductively) depending on their substituents. These effects are not independent from each other and they are not additive but they mix in a complicated way. Generally the electromeric and the inductive effect operate one against the other. The π-electrons of the A and B benzene rings can enter into mesomerism with the π-electrons of the substituent in different manners depending on the mesomerism ability of the substituent (1).

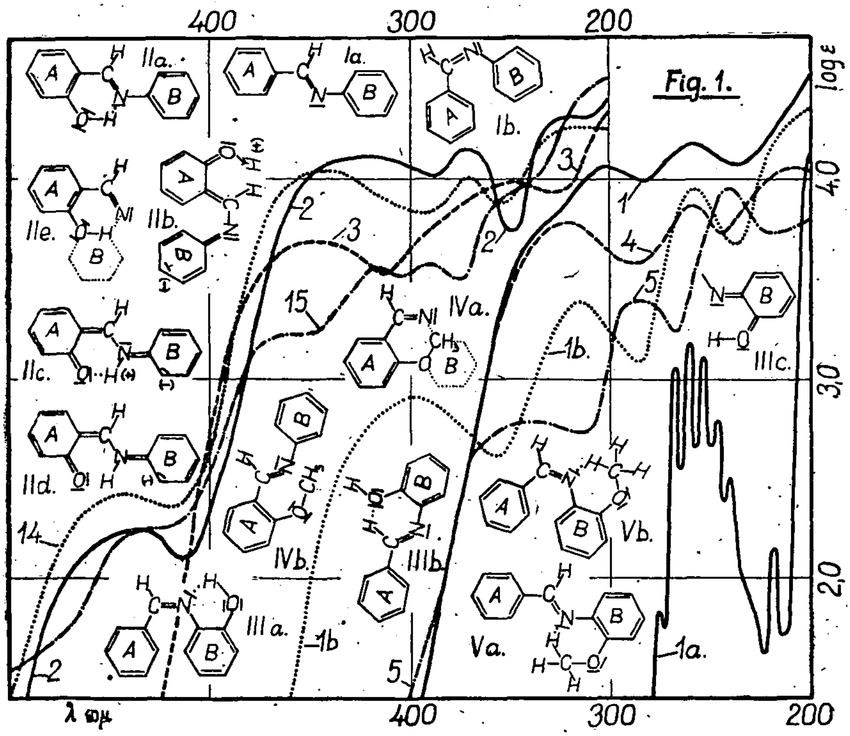

Fig. 1. Curves. 1a: benzene, shifted with logε = 10 upwards. 1b: 2-hydroxybenzalaethylamine, shifted with logε = 0,4 downwards. 1: benzalaniline. 2: 2-hydrobenzalaniline. 3: benzal-2-hydroxyaniline. 4: 2-methoxybenzalaniline. 5: benzal-2-methoxyaniline. 14: 2-hydroxbenzal-2-hydroxyaniline. 15: 3-hydroxybenzal-2-hydroxyaniline.

From the three not sharp bands of benzalaniline (1/1) the first should belong to the azomethine group, the second and the third to the phenyl nucleus (1, 5). To prove this assertion we can mention that by azobenzene and by stilbene the first band belongs to the azo-and to the ethylene group, respectively (10, 11). The above mentioned three bands are present in the spectra of all derivatives of benzalaniline. By the derivatives containing an HO-group in the ortho or para position, appears furthera fourth band at longer waves (1). The position and the intensity of the bands by the singular derivatives varies strongly depending on the energy of excitation and the probability of transition. This influences to a high degree the shape of the extinction curve. When the π-electrons of the A or of the B benzene ring are influenced by the inductive effect differently or if the π-electrons of these benzene rings are in other mesomeric structures in consequence of the electromeric effect of the substituent, then we receive the shifting or the splitting of the bands. Therefore the number of bands changes by the investigated derivatives of benzalaniline.

Because of the strong solvent effect, the following differences of the extinctions curves are only valid in ethanol solvent. In an other solvent the situation is different and this will be the subject of a later paper.

We give a survey of the mesomerism of hydroxy derivatives of benzalaniline. By the meta derivatives the hydroxy group is in mesomerism only with the substituted A and B ring, respectively (cf. fig. 2, form. VIa to VId). By the ortho and para derivatives, the mesomerism starting from the substituted A and B rings, respectively spreads through the whole molecule (cf. fig. 1, form. IIa-IId, resp. IIIc, and fig. II, VIIIa-VIIIc, resp. IXa).

3. *Discussion of the Experimental Data.*

By 2-hydroxybenzalaniline (II) the HO-group in the ortho position increases the possible mesomeric structures in the ground (1/IIa-d) and in the excited state. In the ground state both the quinoidal (1/IIb-c) and the benzenoidal (1/IIa) structures are possible moreover the hydrogen bond (1/IIa) which can hinder the development of other mesomeric structures because of mesomerism short closing (1). The resonance of the structures diminishes the energy of excitation and therefore the extinction curve (1/2) is shifted toward longer wave lengths, compared with that of benzalaniline (1/1). The participation of ionic structures already in the ground state causes the transfer of electronic charge by the excitation whereby the extinction increases (1, 15) The appearance of the first band shows that the quinoidal mesomeric structure (1/IIb-d) participates in the groud state. This question will be discussed more detailed in a later paper in connection with the solvent effect.

As we pointed out the hydrogen bond (1/IIa) can only develop in the case of trans form. It is omitted by the cis form (1/IIe). By IIe the HO-group and the B-ring, respectively is driven out from the plain of the molecule. In the first case the mesomerism of the HO-group is repressed. So we must regain the extinction curve of the benzalaniline (1/1). In the second case we expect the extinction curve of the 2-hydroxybenzalethylamine (1/1b). To both cases contradicts the extinction curve of the 2-hydroxybenzalaniline (1/2), thus this compound must be in the trans form. As we shall see from the followings the steric relation cannot be surely decided alone from the extinction curve. Comparing the extinction curves of the investigated derivatives of benzalaniline with those of cis and trans stilbene (11) we may assume that by the derivatives of benzalaniline the trans form is prevailing.

In the ground state of benzal-2-hydroxyaniline (III) the mesomeric structures (1/IIIa-b) are similar to those of II (1/IIa-d) with the difference that the mesomerism starts from the B-ring. But since the first band is not present (1/3) the quinoidal structure parcipates in the ground state only scarcerly. This should mean that the quinone-imine structure (1/IIIc) owing to its greater energy is much less favourable than the quinone-methine (1/IId) structure. It is remarkable that by III compared to II, all the mesomeric structures are possible in the cis form (1/IIIa) too. By IIIa we can imagine a hydrogen bond with a six-membered ring.

By 2-methoxybenzalaniline (IV) the methoxy group interrupts the

H-bonds in both cases (1/IVa-b). Neither in the in the cis (1/IVa) nor in the trans (1/IVb) form can the methoxy group be placed in the plain of the molecule, whereby its mesomerism will be tied up from steric reasons. So the mesomerism of IV will be analogous to that of I and in accordance with this the extinction curve of both compounds will be similar (1/4 and 1/1, resp.). The little differences are caused by the inductive effect of the methoxy group. The steric hindrance is underlined by the fact that by anisol the etherification does not hinder the mesomerism of the oxygen atom (12).

Bv benzal-2-methoxyaniline (V) the mesomerism in similar to that of IV. Therc is possible a H-bond with a six-membered ring both in the cis (2/Va) and in the trans (2/Vb) form, and this may be the cause by mesomerism short closing of the different shape of the extinction curve of V (1/5) and of IV (1/4), respectively.

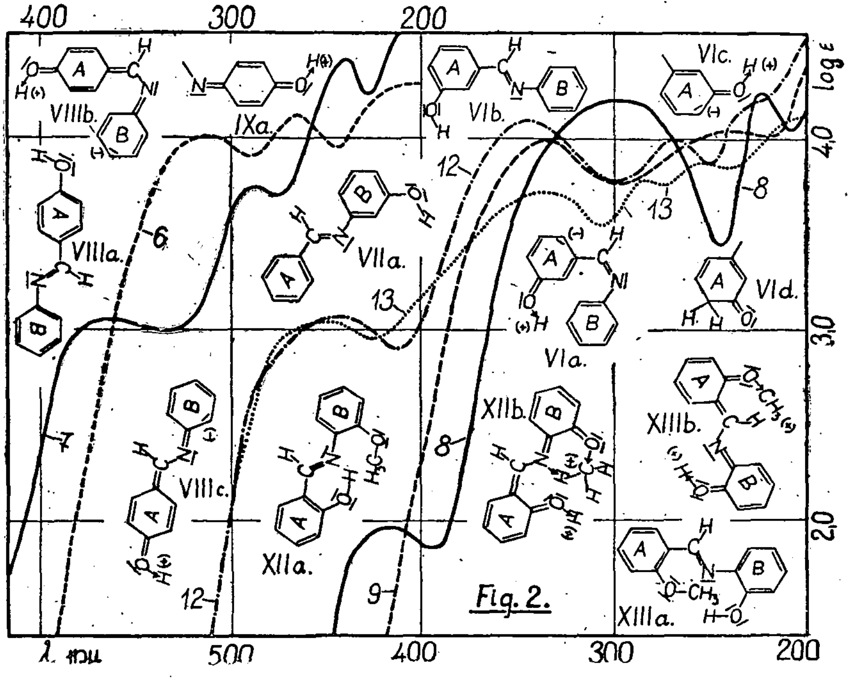

Fig. 2. Curves: 6: 3-hydroxybenzalaniline. 7: benzal-3-hydroxyaniline. 8: 4-hydroxybenzalaniline. 9: benzal-4-hydroxyaniline. 12: 2-hydroxybenzal-2-methoxyaniline. 13: 2-methoxybenzal-2-hydroxyaniline.

In the ground state of 3-hydroxybenzalaniline (VI) the VIa-b mesomeric structures are possible both in the cis (2/VIa) and in the trans (2/VIb) form. Because of the meta position of the HO-group, the quinoidal structure cannot develop by the A-ring in the ground state (2/VIa and VIc). Since its extinction curve (2/6) is very similar to that of I (1/1), the VIb structure can hardly participate in the ground state. The little differences are due to the inductive effect of the HO-group in the meta position.

By benzal-3-hydroxyaniline (VII) the mesomerism is analogous to that of VI (2/VIa-d) with the difference that here the B-ring is in the mesomerism (2/VIIa). We cannot explain satisfactorily the fact that the whole extinction curve is shifted toward the longer waves and the intensity of the first two bands diminishes (2/7).

In the ground state of 4-hydroxybenzalaniline (VIII) both in the cis (2/VIIIb) and in the trans (2/VIIIa) form are quinoidal and benzenoidal structures (2/VIIIa-VIIIc) which is shown by the appearance of the first band (2/8). The stronger appearance by II (1/2) would mean, that the H-bond influences the intensity of this band in some way.

In the ground state of benzal-4-hydroxyaniline (IX) the same mesomeric structures are possible both in the cis and in the trans form as by VIII, with the difference that here the mesomerism starts form the B-ring (2/IXa). The missing of the first band (2/9) shows that the quinoidal form hardly participate in the ground state. This should mean, as we mentioned by III, that the quinone-methine structure because of its lower energy is more probable than the quinon-imine structure.

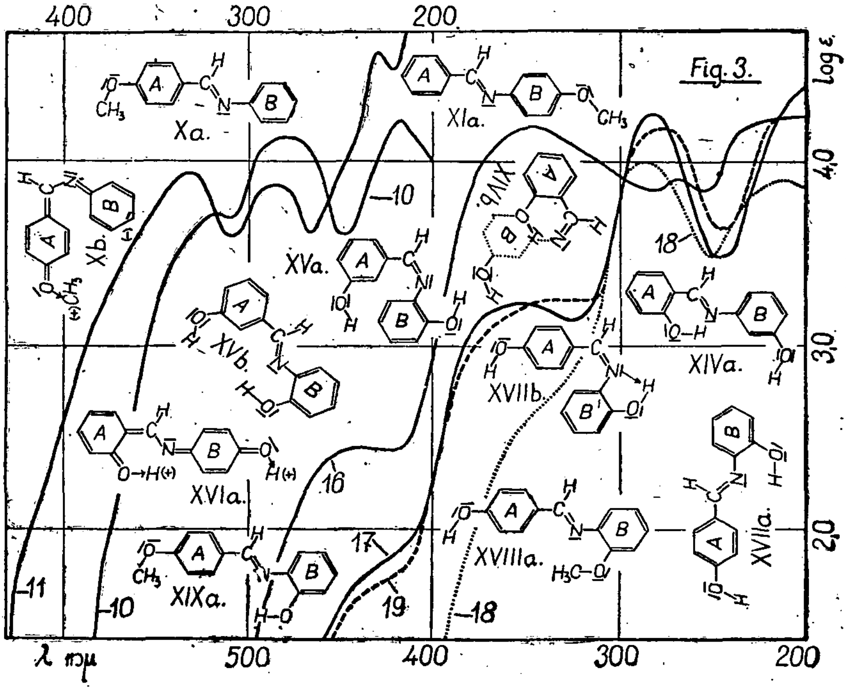

Fig. 3. Curves: 10: 4-methoxybenzalaniline. 11: benzal-4-methoxyaniline. 16: 2-hydroxybenzal-4-methoxyaniline. 17: 4-methoxybenzal-2-hydroxyaniline. 18: 4-hydroxybenzal-2-methoxyaniline. 19: 2-methoxybenzal-4-hydroxyaniline.

By 4-methoxybenzalaniline (X) the methoxy group neither by the cis (3/Xb), nor by the trans (3/Xa) form hinders the mesomerism (cf. 2/VIIIa-c). The absence of the first band (3/10) and the similar shape of the extinction curve to that of I (1/1) shows that the etherification causes much greater obstacle to the mesomerism by the derivatives of benzalaniline than by the phenols (12). The structure differences between the extinction curves of X (3/10) and I (1/1) are due to the inductive effect of the methoxy group.

By benzal-4-methoxyaniline (XI) the mesomerism is the same as by X (cf. 3/Xa-b) with the difference that here the B-ring is in the mesomerism (3/XIa). So we cannot satisfactorily explain the shifting of the extinction curve (3/11) toward the longer wave lenghts.

By 2-hydroxybenzal-2-methoxyaniline (XII) the mesomerism is similar to that of 2-hydroxybenzal-2-hydoxyaniline (1) and of II (cf. 1/IIa-d) apart from the steric hindrance of the methoxy group (2/XIIa). In the case of trans form, it is diminished cf. XIIb. In the case of cis form cf. 1/IIb. So we could expect an extinction curve (2/12) of a similar structure to that of II (1/2), what the shape of the two curves proves. The structure differences are due to the fact that the quinoidal structure XIIb is in some way more advantageous.

By 2-methoxybenzal-2-hydroxyaniline (XIII) the mesomerism is similar to that of 2-hydroxybenzal-2-hydroxyaniline (1) and of III (cf. 1/IIIa-c) apart from the steric hindrance of the methoxy group both in the case of cis and of trans (2/XIIIa-b) form. So we should expect to obtain by XIII (2/13) and by III (1/3) curves of a similar shape. The appearance of the first band by XIII (2/13) shows that the quinoidal structure is in some way more advantageous (2/XIIIb). The extinction curves of both compounds are very similar to that of 2-hydroxybenzal-2-hydroxyaniline (1). The difference is due to the etherification of the one hydroxy group.

By the 2-hydroxybenzal-3-hydroxyaniline (XIV) the mesomerism of the HO-group in 2-position dominates the mesomerism of the ground state (cf. 1/IIa-e), to what refers the similarity of its curve (1/14) to that of II (1/2). The HO-group in the meta position has inductive effect and hinders the development of the quinoidal structures, what is to prove by drawing diagramms. In the case of cis (3/XIVb) the steric hindrance of the mesomerism is similar as by II (cf. 1/IIb and 3/XIVb). By the trans form (3/XIVa) it is not hindering.

By 3-hydroxybenzal-2-hydroxyanilin (XV) the steric hindrance falls out both in the cis (3/XVa) as in the trans (3/XVb)form. The mesomerism is a counterpart of XIV. The increase of the number of the bands (1/15) refers to the similar mesomerism of the HO-groups in the 2' and in 3 position, respectively, and to that, that the structures of different energy have separate excitation.

By 2-hydroxybenzal-4-hydroxyaniline (XV) the mesomerism is hindered in the case of cis form just as by II (cf. 1/IIb). By the trans form this hindrance falls out (3/XVIa). The mesomerism is more complicated than by the former compounds (1). In the ground state the structures (cf. 1/IIa-d and 2/IXa beginning from the ring A and B, respectively and moreover 3/XVIa) are possible. So we should expect an extinction curve of a similar shape to II (1/2) and really we obtain such one (3/16).

By the 4-hydroxybenzal-2-hydroxyaniline (XVII) the steric hindrance of the HO-group falls out both by the cis (3/XVIIb) and by the trans (3/XVIIa) form. The mesomerism is a counterpart of XVI. The different form of the extinction curve (3/17) compared with that of VIII (2/8) shows that the two HO-groups participate in the mesomerism approximately in the same manner. Comparing the extinction curves of XVI (3/16) and XVII (3/17) we see that the intensity of the first two bands is strongly different.

By the 4-hydroxybenzal-2-methoxyaniline (XVIII) the methoxy group in the 2-position shows the same steric hindrance (3/XVIIIa) as by v (cf. 1/va-b). Apart from this the mesomerism is similar to that of VIII (cf. 2/VIIa-c). So we expect a similar curve. The great structure differences (2/8 and 3/19, resp.) among them the missing of the first band is due perhaps to the short closing of mesomerism due to the H-bond. (cf. 1/Va-b) or the steric hindrance of the mesomerism.

By the 4-methoxybenzal-2-hydroxyaniline (XIX) 3/XIXa)the steric hindrance falls out both in the cis (cf. 1/IIIa) and in the trans (cf. 1/IIIb) form. The mesomerism is similar to that of III (cf. 1/IIIa-c) or of XVII (cf. 3/XVIIa-c). The great structure differences (1/3) are due to that, that by XIX (3/19) both group participate in the mesomerism as by XVII (3/17).

Summary.

The appreciation of the possible structures of the ground and of the excited state allows generally the explaining of the structure differences by the extinction curves of the derivatives of benzalaniline.

The phenyl nucleus bound to the C and to the N atom of the azomethine group respectively behaves differently with regard to its mesomerism.

By the 2 and 4 hydroxy derivatives appears a first band on the limit of the visible. Since this band is missing by the 2' and 4' derivatives, the quinone-imine structure is much less representated in the ground state than the quinone-methine structure.

According to the extinction curves, the investigated benzalaniline derivatives are present in the trans form.

The free rotation of the radicals is generally restricted, their probable situation is given in the figures.

Szeged, (Hungary) January 1948.

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On the Light Absorption of Polychromates

By Á. KISS and K. BIRÓ.

(Received January 1948.)

Introduction.

The composition of chromate solutions was established by Jander and his coworkers (1). They have shown that the condensation reactions leading to the formation of oxygen bridges lead to characteristic changes in the absorption spectra. The greater the molecular weight of the resulting aggregates the flatter and smoother are the absorption curves and the beginning of the light absorption is shifted the more towards longer wave lengths. Characteristic extinction curves could be correlated with all different states of aggregation indicated by diffusion (1b). Biró (2) has measured the light absorption of polychromate solutions to elucidate the mechanism of light absorption.

The experimental methods and apparatus were earlier described (3). All the preparations used of analytical purity, and if necessary purified by further recrystallisation. The solutions were carefully filtered through Jena glass filters and their concentrations analytically controlled. All solutions were prepared with spectroscopically pure water distilled from Jena glass apparatus.

The extinction curves.

In order to obtain comparable data, we have evaluated all the extinction curves with the same precision. The extinction curve of a 0,001 m K_2CrO_4 solution in 0,01 m KOH (Fig. 1, Curv. 1 = 1/1) was used as reference (4). This curve is reproduced in all figures with dotted line.

0,001 m K_2CrO_4 in 0,01 m KOH has two bands at 370 and 270 mμ, a rising absorption at 210 mμ and another maximum at 420 mμ (1/1). The band at the longer wave length shows a variation with the concentration (5). In 2,52 m solution the steeply descending absorption is shifted towards longer wave length 1/1a).

0,001 m $K_2Cr_2O_7$ in water has one sharp and one less sharp band at 350 and 260 mμ respectively, a faint band at 440 mμ, furthermore a rising absorption at 210 mμ (2). This curve is changed with changing concentration (1/2a).

0,001 m CrO_3 in water has an extintion curve (1/3) structure similar to that of a $K_2Cr_2O_7$ solution, though it is lower (6a). The extinction curves of CrO_3 solutions are strongly influenced by the concentration (1/3a-3d). With increasing concentration the extinction rises in the region of the first and second bands (1/3a-3b) of the reference curve (1/1). In concentrated (8, 72 m) solutions a flat minimum is observed at 700 mμ (1/3d).

The maxima and minima of the reference curve (2/1) are smoothed in the presence of increasing $HClO_4$ concentration (2/2-9). The second band disappears nearly completely already in presence of 0,01 m $HClO_4$ and the first is shifted toward shorter wave lengths (2/4). The descending limb of the first band reaches into longer wave lengths and a new flat band appears around 430 mμ (2/4). In 0,1, 1,0, 3,0 and 5,0 m $HClO_4$ the two bands of the reference curve (2/1) is shifted toward longer wave lengths (2/5-8). In 7,0 m $HClO_4$ we obtain an almost structureless curve (2/9) with little intensity. The curves measured in different concentrated $HClO_4$ have only in smaller concentration regions constant section points.

The changes produced by HCl in the reference curve 3/1) are similar 3/2-7). The reference curve (3/1) and the curves measured in different concentrated HCl (3/2-7) have only in smaller concentration regions constant section points. In concentrated HCl solutions the Cl_2 formation troubles the extinction measurements.

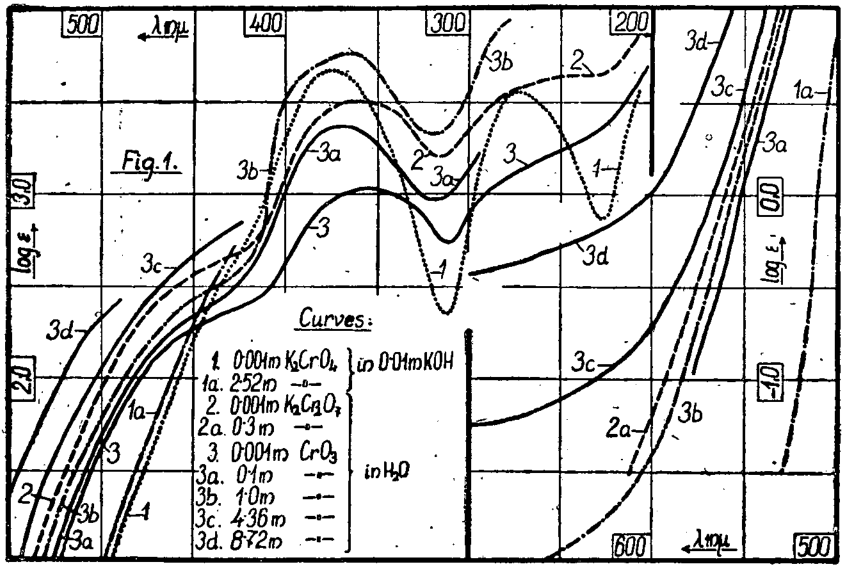
Fig. 1.

Increasing concentration of H_2SO_4 has a similar effect (4/2-6). Beginning from 12 m H_2SO_4 the extinction increases slowly and the curves are almost structureless (5/4-7). The curves at corresponding $HClO_4$, HCl and H_2SO_4 concentrations are not identical. The common points of the curves at different H_2SO_4 concentrations are not so constant as those at the presence of the other acids. The curve obtained in presence of concentrated H_2SO_4 (5/7) shows a general rise towards the longer wave lengths and has flat bands at 440, 390, 320 and 280 mμ. K_2CrO_4, $K_2Cr_2O_7$ and CrO_4 have similar curves in concentrated H_2SO_4.

Due to the strong absorption of the nitrate ion it was not possible to evaluate the effect of nitric acid below 350 mμ (6/2-7). The remaining less characteristic part of the curve shows the changes on the concentration of HNO_3 as in the cases formerly discussed. This is the reason why the data of Jander and Spandau (1b) had to be complemented.

In the case of K_2CrO_7, and CrO_3 we obtained similar effects as in the case of K_2CrO_4.

The constitution of chromate solutions.

Alkaline chromate solutions contain mostly the CrO_4^{2-} ion. This is supported by the weak effect of concentration on the extinction curves

(1/1 and 1a). It is not possible to explain the failure of complying with Beer's law with the assumption of the formation of higher complexes (5).

Neutral chromate solutions contain, depending on the concentration, furthermore the ions: $HCrO_4^-$, $Cr_2O_7^{2-}$ and $HCr_2O_7^-$ (6), and this is supported by the concentration dependence of the extinction curves.

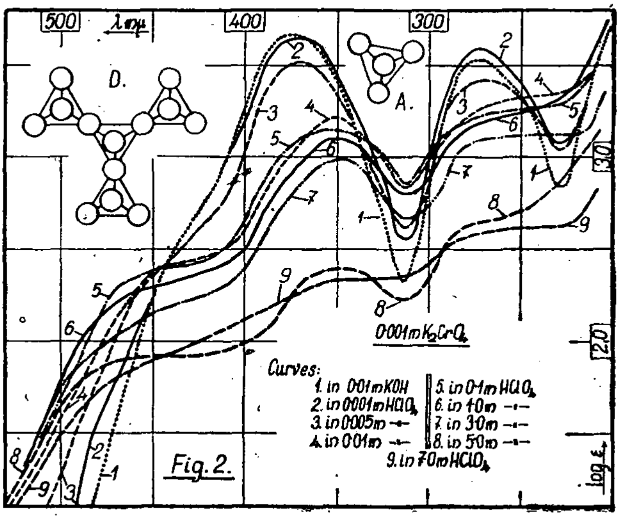

Fig. 2.

$K_2Cr_2O_7$ solutions have mostly the ion: $Cr_2O_7^{2-}$. At lower concentration the ions $HCr_2O_7^-$, CrO_4^{2-} and $HCrO_4^-$ are also present (7). Bichromate solutions show strong deviations from Beer's law (6), as the ions higher complexes. The distribution of charge and thus the extinction are thereby vastly influenced.

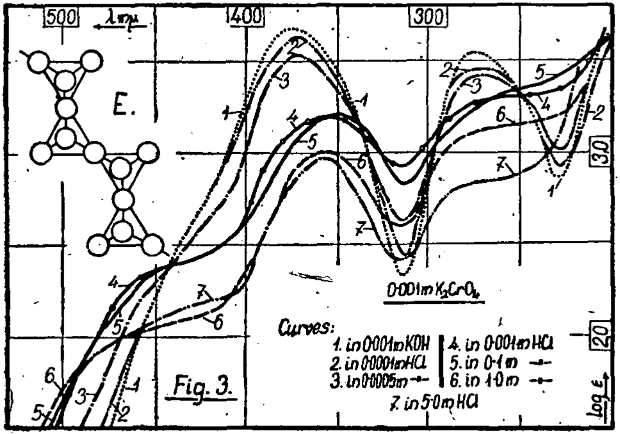

Fig. 3.

In the solution of CrO_3 in water, the ion CrO_7^{2-} is dominating (8). However, other ions, like $HCr_2O_7^-$, CrO_4^{2-} and $HCrO_4^-$ have to be taken account. In more concentrated solutions of CrO_3 higher polimers are formed.

Normal chromates crystallise from alkaline and neutral solutions, bichromates from acetic acid solutions and tri-and tetrachromates from more acid solutions (a).

According to the results of diffusion experiments (1) the CrO_4^{2-} ion (diffusions coefficient $D_{10}=0\ 57$) is present in alkaline solutions. In the solutions containing 0,01—4,0 m HNO_3 the $Cr_2O_7^{2-}$ ion exists, it has a diff. coeff. of $D^{10}=0{,}635$. The $Cr_3O_{10}^{2-}$ ion is observed in 5,0—10,0 m HNO_3 solutions, it has a diff. coeff $D_{10}=0{,}58\ 0{,}59$. The chromate ion being much smaller than the $Cr_2O_7^{2-}$ and $Cr_3O_{10}^{2-}$ ions, it is supposed, that it has to be hydrated with 12 molecules of water, and for similar reason the molecule of $Cr_2O_7^{2-}$ should contain 3 molecules of water. Thus, the degree of hydratation is diminishing with increasing aggregation.

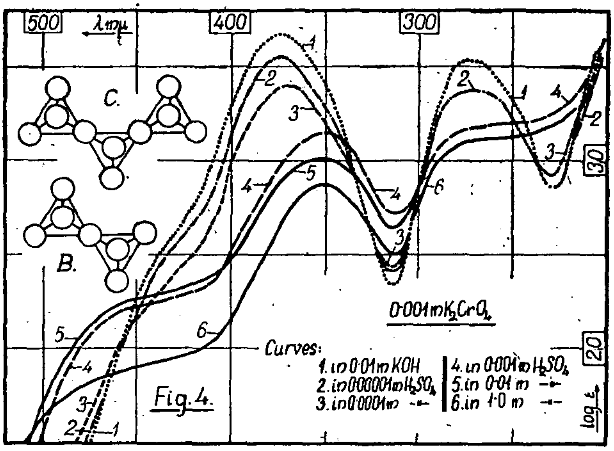

Fig. 4.

As the diff. coeff. is rather constant in the above mentioned intervals of hydrogen ion concentration, either one of the ions is always preponderantly present at the corresponding hydrogen ion concentration. The change from one type of ion to the other occurs in a sharp interval.

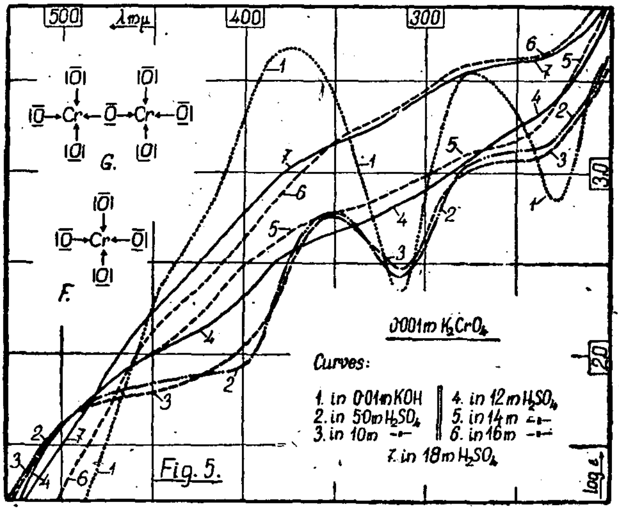

Fig. 5.

According to its Raman spectrum, the CrO_4^{2-} ion has a tetrahedral configuration Polychromates form chains similar to the aliphatic hydrocarbons. It follows from the condensations reactions with elimination of water:

$$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O$$
$$Cr_2O_7^{2-} + CrO_4^{2-} + 2H^+ = Cr_3O_{10}^{2-} + H_2O$$
$$Cr_3O_{10}^{2-} + CrO_4^{2-} + 2H^+ = Cr_4O_{13}^{2-} + H_2O$$

that the neighbouring tetrahedra joined through their corners (2/D, 3/E, 4/B and C). Condensation and chemical hydration are facilitated by the lone electron pairs of the oxygen atoms (5/F and G, 6/H). If they are all utilized the chromate ion is able to bind 12 molecules of water, which agrees with the results of the diffusion experiments (1b). The sharp decline in hydration is the result of the strong dehydrating effect of the acids.

In concentrated CrO_3 solutions a quasi crystalline structure is obtained due to very strong aggregation, this is inferred from the dark red colour of CrO_3 (10). In concentrated sulfuric acid the complex $HO{\cdot}SO_2OCrO_2OH$ is formed (6a), this is shown by the atypical structure of the extinction curve. The formation of chromylsulfate $CrO_2{\cdot}SO_4$ is also possible (6a).

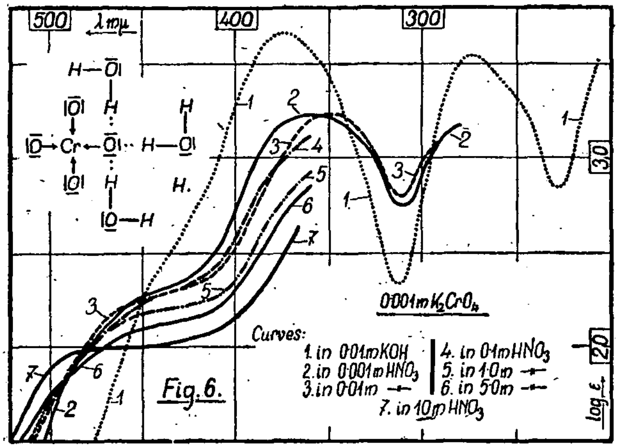

Fig. 6.

On the mechanism of the light absorption.

The electron configuration according to Smith-Stoner in case of chromate ion is the following:

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s$$

In the case of tetrahedrical configuration the coordinative valence electrons would be $3d^6\,4s^2$. As the aggregation through oxygen bridges admits lone electrone pairs (5/g), there will be the same electron configuration around the chromic ion as around the chromate ion.

The light absorption results in the extinction of the electrons of the chromic ion and those of the coordinative valence electrons. The first band must be ascribed to the coordinative valence electrons as it reacts stronger to the state of aggregation (5). The second band corresponds to the excitation of the electrons of the chromic ions proper. The shift observed in the longer wave length portion of the first band and the appearance of a new band in the case of the polychromates must be attributed to the extension of the system of coordinative valence electrons due to aggregation. It is remarkable that the aggregation of chromic ions through oxygen bridges and complex formation have a similar effect (i. e, a sharp rise in extinction in the visible part of the spectrum and in the near ultraviolet) (11). In the hope of obtaining better information about the mechanism involved, we have applied the method previously described (12) but we met no succes.

From the constancy of the diffusion coefficients (1a) and the nearly constant crossing of the extinction curves it appears likely that an equilibrium exists between two successive states of aggregation of the chromate ion. Thus the extinction curve in dilute acids could be calculated from the extinction of the CrO_4^{2-} and $Cr_2O_7^{2-}$ ions. However, the calculated curve does not fit the experimental data. We have to suppose that apart from the equilibrium between the two above mentioned ions equilibria between other ions must exist, i. e. the extinction curve reacts a more sensitive way than the diffusion coefficient. It is for this reason that the absorption studies of Jander and Spandau (16) had to be extended through the present studies.

Summary.

The extinction curves of K_2CrO_4, $K_2Cr_2O_7$ and CrO_3 in water and in different concentrations of $HClO_4$, HCl, HNO_3 and H_2SO_4 have been studied.

The formation of polychromates has a complicated and specific influence in the case of these acids. The extinction curves in dilute acid solution cannot be calculated from the other data by assuming that there is an equilibrium between to states of aggregation. In concentrated sulfuric acid solutions the formation of heteropoly acids has to be taken into account. Further investigations are in progress on these lines.

Szeged, (Hungary) August 1947.

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Dirctor: Prof. Paul Fröhlich

The Behaviour of Gelatineous Dyestuffs in Rotating Magnetic Field

by P. Fröhlich, L. Szalay and P. Szőr (Szeged, Hungary).

Introduc ion.

The behaviour of dyestuffs in magnetic field has not been extensively investigated till now. Most of the results chiefly refer to crystalphosphors. A de Hemptinne (1) expected the magnetic field to have an influence on extinction, but he could not point out any change. Later C. Gutton (2) found that the magnetic field — if it is not constant — increases the intensity of fluorescence emission. Gudden and Pohl (3) ascertained a quenching when excited dyestuffs were put into an electric field of very great intensity. This phenomenon was detailed and quantitatively investigated by F. Schmidt (4). Schmidt's results suggested to E. Rupp (5) to investigate the dyestuffs in a magnetic field of great field strength. E. Rupp found that the behaviour of dyestuff in magnetic field is similar to that in electric field.

Later Hinderer (6) investigated the effect of alternating electric field on fluorescence emission and recently similar investigations were carried out by G. Destriau (7). Destriau's researches showed that the originally unexcited dyestuff has an emission without an excitation in a very intensive alternating electric field.

All the researches up till now show that neither constant magnetic field nor constant electric field cause an influence on physical properties of dyestuffs. A Stark effect was not observed at all. A Zeeman effect was to be found on dyes which have a spectrum similar to line spectrum (8). I. Weiss could not observe a magnetic quenching of fluorescence emission even at field strength of about 60.000 gauss/cm. (9).

Fröhlich and Gombay (10) pointed out that a constant electric field of middling field strength does not influence the percentage of partially polarized phosphorescence emission. An effect of magnetic field on physical properties of gelatineous dyestuffs was not investigated at all.

From the researches up till now we can suppose that a constant magnetic field causes no changes in physical properties of dyestuffs, but a change in the state of magnetic field, effects a change in the structure of dyes.

In this paper we investigated the effect of rotating magnetic field on gelatineous dyestuffs.

Experimental Technique.

From a painted gelatine-plate of 0,1 mm thickness we made a circle-shaped disk having a diameter of 3,5 cm (11). The centre of the the disk was fitted to a fine Wollaston-wire. The circle shaped plate hung in a rotating magnetic field so that its plane was horizontal and it could be rotated round a vertical axis. The first experiments showed that the currents of air caused by the warming of measuring space when the magnetic field was switched on had so great an influence on the swinging system that the measurements were not reproductive at all. Therefore we had to put the whole system into vacuum.

The arrangement of the apparatus is shown in Fig. 1. We removed the air from a glass vessel by means of a vacuum pump. The upper and the lower end of the vessel was closed with two glass plates. The vessel had an opening closed by stop-cock (B) to the pump. The air pressure was 2—3 Hgmm during the measurements measured by mercury manometer. The measurements were carried out by means of a mirror (T). Therefore the glass cylinder had a circle-shaped opening closed by a flat glass plate before the mirror, and we set a mm-scale in 1 m distance from the mirror in the usual manner.

The lower part of the vessel with the gelatine plate (A) was put into the rotating magnetic field. As after switching the current the temperature of the measuring space slowly rose we used an air cooling,

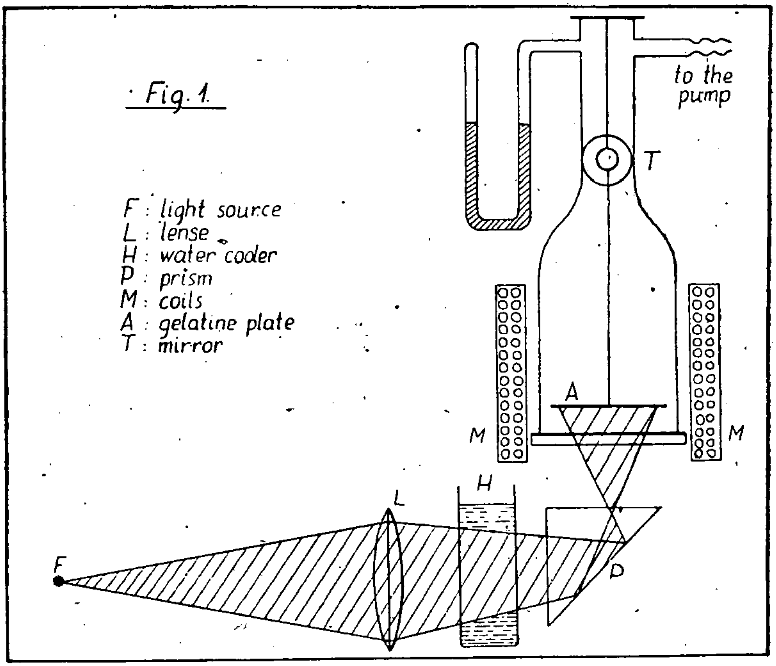
Fig. 1.

To know the influence of excitation we excited the plate (A) with an electric lamp of 1000 W (F). Light from F passes through a lense (L), and a prism (P), and a water cooler (H) to absorb the heat-rays.

On switching the magnetic field, the gelatine plate began to rotate. The turning away was about 15—20 mm on the scale. So the readings happened very easily. Immediately after switching the plate began to move very rapidly and the mirror was swinging. The amplitude of the swinging was 2—3 mm on the scale. While the mirror was swinging we took a mean value of the scale divisions. After 1—2 min when the swinging had ceased a direct reading was possible.

We investigated gelatine plates without any dye and also painted gelatine plates having different concentrations. The measurements refer to Rhodulin Orange N. To give the concentration we used a logarithmic one. —c concentration means 10^{-c} gr dye/cm^3 dry gelatine. All the measurements were taken at room temperature.

Results.

If we put the gelatine plate into a rotating magnetic field in the described manner it began to rotate. After some time the rotation ceased and the plate had a new resting point measured on the scale.

a) *The direction of the rotation of magnetic field.*

First of all we investigated the influence of direction of magnetic field rotation. The direction of rotating agrees with that of the hand of clock. The results referring to the different concentrations are shown in Table I. The time is given in minutes and the turning of the plate from its resting point is measured in scale divisions. The turning of the gelatine plate depends on the time which passes after the switching on of magnetic field, This dependence is shown in Fig. 2. where the time was measured on the horizontal axis in minutes and the turning of the plate on the vertical axis in scale divisions. As is to be seen, the unpainted gelatine plate had the

Table I.

gelatine without any dye		c = — 1,00		c = — 1,75		c = — 2,25		c = — 3,00		c = — 3,50	
min.	scale div.	min.	scale div.	min.	scale div.	min.	scale div.	min.	scale div.	min.	scale div.
1	0,8	1	0,7	1	0,4	1	0,3	1	0,6	1	1,1
3	1,3	2	0,8	3	1,4	6	1,4	2	0,7	2	1,4
7	1,8	3	1,0	5	2,0	9	2,1	3	0,8	3	1,6
10	2,1	4	1,1	7	2,3	14	3,0	9	1,8	10	2,8
13	2,2	5	1,2	14	2,5	17	3,5	15	2,6	28	4,1
25	2,2	10	1,5	25	2,7	21	4,3	25	3,1	49	4,6
switching of the magnetic field		15	1,9	45	3,3	27	5,3	34	3,9	switching of the magnetic field	
		20	2,1	55	3,2	34	6,4	64	4,6		
1	1,9	25	2,3	switching of the field		49	8,6	70	4,7	1	4,1
4	1,3	30	2,5			66	10,4	switching of the field		7	3,4
7	1,0	48	2,6	2	2,8	79	12,4			14	2,9
12	0,8	switching of the magnetic field		5	2,0	85	13,3	6	4,3	32	1,4
				15	1,1	110	13,5	12	3,2	60	0,0
		1	2,2	30	0,2	switching of the field		18	2,0		
		4	1,9					25	1,6		
		8	1,3			1	10,5				
		19	0,2			9	8,0				
						15	5,4				
						40	0,3				

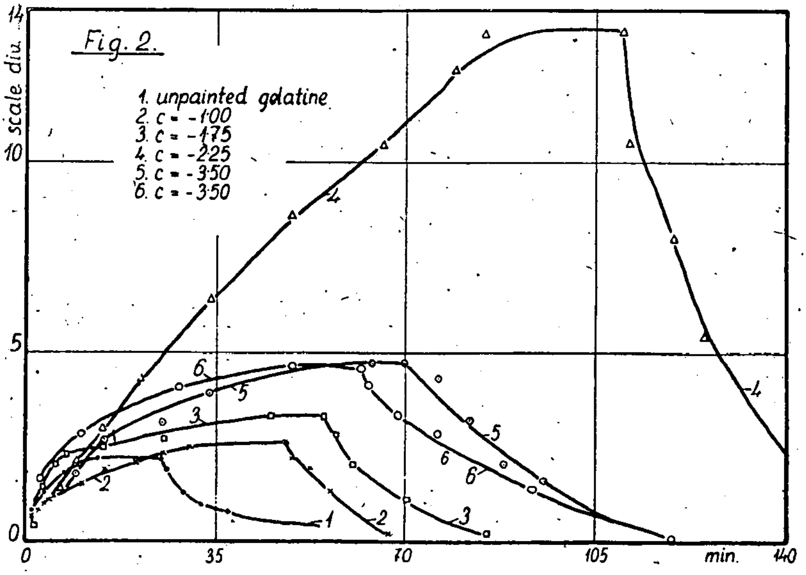
Fig. 2.

smallest turning in magnetic field. The rate of turning of painted plates was much greater. Fig. 2. shows that there is an optimal concentration from the point of view of maximal turning. This can be seen from the fact that, the curve belonging to concentration of —2,25 everywhere goes above the curves belonging to other concentrations. The time of reaching the maximum at plates of different concentrations depends also on concentration. If the maximum is greater then its reaching required more time.

Unpainted gelatine plate required 20 minutes and the painted one having a concentration of —2,25 required 100 minutes for reaching the maximum. Taking into account the fact that the swinging of the system ceased after 5 minutes when the swinging was caused by the turning of the torsion head, we have to suppose that the long duration of turning caused by magnetic field was effected by a change in the structure of the gelatine plate. This is a very important result because this peculiar behaviour of dyestuffs shows the existence of an interesting new magnetic effect which has never been observed before. Since the long duration of turning is in connection with the change of structure, the time of reaching maximum is evidently the duration of change of structure. As is to be seen the plates do not take their original resting point after the ceasing of magnetic field in 5 minutes as we could expect. There are concentration at which the reaching of the original resting point requires 40 minutes. This also supports the supposition of a change in structure of gelatine plate.

When the magnetic field rotates in the oposite direction (namely its rotation does not agree with that of the hand of a clock) then the behaviour of gelatine plates essentially alters compared to the former case. This is clearly shown in Fig. 3.

Above all we can see that, in the moment of switching on of the magnetic field, the direction of the rotation of field and that of the plate are the same, but after one minute the latter begins to rotate in the opposite direction. Consequently in this case the plates rotate only for a very short time in the same direction as the magnetic field, after this short time they rotate in the opposite direction and at last when the maximum is reached they take a new resting point.

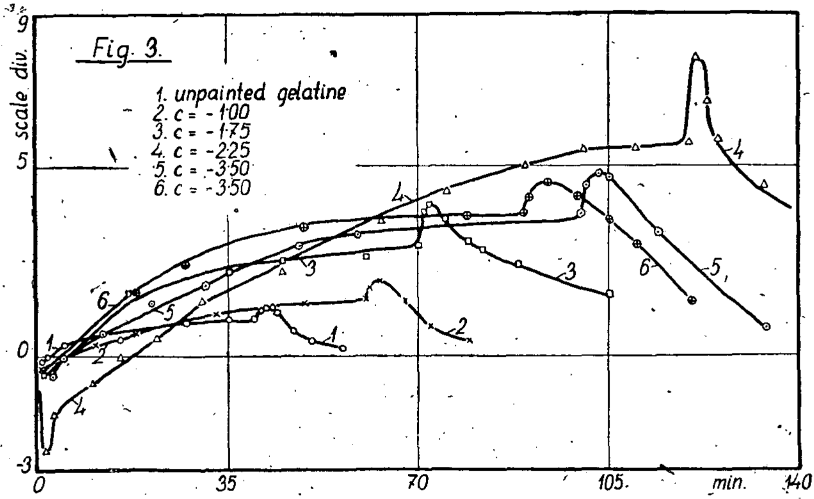
Fig. 3.

Comparing the rate of maximum in the two cases we see that it is higher at every concentration if the plates rotate in the same direction as the magnetic field. If we stop the magnetic field the plates do not turn back to their original resting point but are rotating for 5—6 minutes as if the magnetic field were still present. After 5—6 minutes the plates turn back and they tend to take their original resting point. The optimal concentration from the point of view of maximal turning is the same as it was in the former case. Fig. 3. was drawn from Table II.

Table II.

unpainted gelatine		c = — 1,00.		c = — 1,75		c = — 2,25		c = — 3,00		c = — 3,50	
min.	scale div.	min.	scale div.	min.	scale div.	min.	scale div.	min.	scale div.	min.	scale div.
1	— 0,1	1	— 0,3	1	— 0,3	1	— 2,5	1	— 0,4	1	— 0,2
2	0,0	2	0,0	2	0,0	3	— 1,5	2	— 0,3	2	0,3
5	0,3	3	0.1	17	1,7	10	— 0,7	4	— 0,2	18	1,7
15	0.4	11	0,3	20	1,8	15	0,0	5	0,0	27	2,4
27	0,9	18	0,6	35	2,2	22	0,5	8	0,2	49	3,4
35	1,0	33	1,1	45	2,4	30	1,5	12	0,6	79	3,7
40	1,0	49	1,4	60	2,6	45	2,2	21	1,4	90	3,8
switching of the field		60	1,5	70	2,9	63	3,6	31	1,9	switching of field	
						75	4,3	42	2,5		
1	1,2	switching of field				90	5,0	48	2,9	1	4,2
2	1,3	1	1,8	1	3,8	100	5,4	59	3,2	2	4,4
3	1,3	2	1,9	2	4,0	110	5,5	100	3,8	3	4,5
4	1,2	3	2,0	5	3,6	120	5,6	switching of field		4	4.6
7	0,7	4	1,9	9	3,3	switching of field				5	4,5
10	0,4	7	1,5	10	3,0			1	4,5	8	4,3
16	0,2	12	0,8	11	3,0	1	7,9	2	4,6	10	4,2
		20	0,4	12	2,8	3′	6,7	3	4,8	15	3,5
				18	2,4	5	5,7	4	4,8	20	2,9
				35	1,6	14	4,5	5	4,7	30	1,4
						30	2,4	14	3,2		
						55	1,3	34	0,7		

Consequently we found on plates, investigated in rotating magnetic fiel having different direction of rotation, a very interesting phenomenon, namely that the direction of rotating of gelatine plates does not depend on the direction of rotating of magnetic field one minute after the switching on of magnetic field. The measurement happened in the following order: first we put the plate into the magnetic field in which its rotation agreed with that of the field and then we put it into the magnetic field rotation of which was opposite.

b) *The behaviour of excited plates.*

As we have described before we investigated the behaviour of excited gelatine plates in rotating magnetic field. The excitation was begun when the magnetic field was switched on. The behaviour of excited plates in rotating magnetic field is quite similar to that of the unexcited ones, the only difference between the two cases is that excited plates turn away in the magnetic field at a higher rate. As the phenomenon is just the same in the two cases we do not give detailed results. We give only the results which are necessary for comparing the behaviour of excited gelatine plates with that of the unecited ones. This is to be seen in Fig. 4. The concentrations were

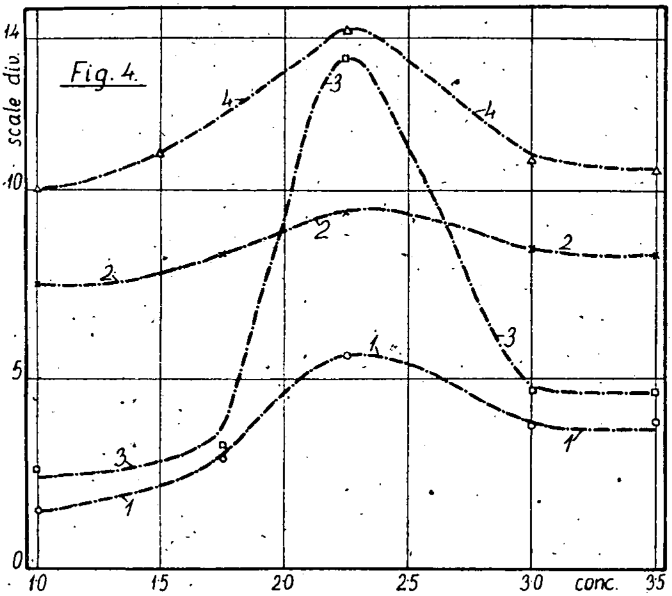

Fig. 4.

measured on the horizontal axis in logarithmic ones. The maximal turning from the ground resting point was measured on the vertical axis in scale divisions. The results are found in Table III.

Table III.

concentration	turning in unexcited	opposite direction excited	turning in unexcited	the same direction excited
—1,00	1,5	7,5	2,6	10,1
—1,75	2,9	8,3	3,2	11,0
—2,25	5,6	9,5	13,5	14,2
- 3,00	3,8	8,4	4,7	10,8
—3,50	3,8	8,2	4,6	10,5

The 1. curve in Fig. 3. represents the concentration dependence of maximal turning of the unexcited gelatine plate rotating in the same direction as the magnetic field. The 3. curve shows the same dependence but on excited plates. The 2. curve represents the concentration dependence of maximal turning of the unexcited gelatine plate rotating in the opposite direction as the magnetic field, and the 4. curve shows that of the excited plate.

The excited plates do not turn back to their original resting point after ceasing of magnetic field only when the excitation ceases too. Therefore we had to take into account this circumstance so that we corrigated the corresponding columns of Table III. substracting the turning caused by the excitation without magnetic field from that caused by magnetic effect during excitation.

These results showed that the effect of magnetic field is greater during excitation than in unexcited state. The optimal concentration is the same in an excited and unexcited state.

Conclusions.

As the gelatine plate turning in rotating magnetic field reaches its new resting point much later than if the same turning were caused by means of the torsion head, it is quite sure that the magnetic field causes a change in the structure of gelatineous dyestuff. The peculiar behaviour which manifests itself in turning of the plate opposite the magnetic field is not to be explained from these investigations in an acceptable manner. Gombay (12) found a similar phenomenon in connection with his investigations referring to the electrical conductivity of gelatineous dyestuffs. Namely he detected that during an uniform raising of temperature a new electromotive force rises which causes a current flowing in a direction independent from the outer electromotive force. The analogy between Gombay's results and our investigations is not complete, but even so far is very surprising.

Undoubtedly the molecules ot dyestuff play an important part in the existence of turning of plates which is to be seen from the concentration dependence of the turning.

The turning of the gelatine plate in rotating magnetic field can be explained in the following way. The molecules of dye are disordered without magnetic field. At the switching on ot the magnetic field an electron shift is formed in a very short time and the molecules of dyestuff become polary. The magnetic field has an influence on the polary molecules, they come to an ordered state. This molecular arrangement causes the turning of the plate.

To give an exact and detailed explanation of change of structure caused by rotating magnetic field we have to stretch out the investigations.

Summary.

We investigated the behaviour of gelatineous dyestuffs (Rhodulin Orange N) in rotating magnetic field.

1. A painted gelatine plate hung in rotating magnetic field rotates, and takes a new resting point. At the moment of switching on of magnetic field the direction of rotation of plate and that of the magnetic field are the same. Later the direction of rotation of plate does not depend on the direction of rotation of magnetic field.

2. The rate of turning of plate depends on concentration of dyestuff. There is an optimal concentration of — 2,25.

3. The behaviour of excited and unexcited plates in rotating magnetic field is the same, but the rate of turning of excited plates is greater than that of the unexcited ones.

Szeged, Hungary August, 1948.

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Les Actions a Distance de R. d'Aubry de Puymorin.

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Le sujet de ce travail est un sommaire des actions à distance au point de vue de la physique atomique moderne.

Le chapitre premier précise les ideés attachées à l'électron. L'auteur définit le but de l'ouvrage en deux directions: *a)* Remplacer l'idée vectorielle du champ de force par celle du densité d'énergie pour tenir compte du fait que l'électron n'est pas une point charge, mais a un volume fini . *b)* Élaborer une énergétique laquelle est apte à traiter les phenomènes en connexion avec l'électron. Le sujet des deux chapitres suivants est cette énergétique generale. L'auteur suppose que toute énergie est énergie cinétique des atomes ou des particules élementaires. Il définit les systemes idéaux de tel façon que la definition renferme l'idée des champs.

Comme consequence il obtient la loi du changement de la force avec la vitesse que la Rélativité explique d'une autre point de vue: par l'augmentation de la masse avec la vitesse. L'autre consequence est la relation connue $\varepsilon = m^2$ mais par une expliquation cinétique et une relation entre la vitesse de propagation d'onde et celle des particules du milieu, vérifiée dans le cas des gaz monoatomiques.

Les deux derniers chapitres traitent les conséquences de cette énergétique en connexion avec les actions à distance. L'auter obtient deux actions entre les électrons: *a)* la répulsion Coulombienne, au coefficient 2/3 et *b)* l'attraction Newtonienne mais sans le coefficient gravitant G. En supposant que la masse des électrons étant seule douée de propriété gravifique, il déduit une relation trés remarquable $G = {}^2/_9\,(Nm)^2$ et donne au nobre Avogadro un sens profondi. Pour ce but il introduit une nouveaux systeme d'unités de mesures: systemes a 2 grandeurs fondamentales dans laquelle toute masse agissante (gravifique, électrique on magnéfique) a la dimension L^3T^{-2} et le G est un nombre pure, sans dimension.

La classification des forces termine cet ouvrage lequel est digne d'attention par ses hypotheses audacieuses et ses résultat remarquables.

R. Pauncz