(8 mm.) and then redistilled, b.p. 79.7° (8 mm.), m.p. 5.75°. *m*-Chloromercurianisole,[21] prepared in 58% yield, m.p. 157–160°, was crystallized from carbon tetrachloride (6 ml./g.) and dioxane (2 ml./g.), m.p. 163.9–164.4°.[22] Crystallization of *o*-bromomercurianisole[23] from dioxane (2 ml./g.) gave a melting point of 188.6–189.5°. Interaction of silver acetate and *o*-chloromercurianisole followed by potassium iodide gave *o*-iodomercurianisole,[24] m.p. 171.3 and 171.7° after crystallization from benzene (6.5 ml./g.) and dioxane (7 ml./g.). Methyl *p*-chloromercuribenzoate, prepared according to Nesmeyanov[21] in 17% yield, m.p. 248–254°, was crystallized from ethanol (10 ml./g.) and ethyl acetate (50 ml./g.), m.p. 253.4–255.0° as contrasted to Nesmeyanov's 259°.

_o_-Chloromercurianisole.—Mercuric acetate (318 g., 1 mole) was heated with 864 g. (8 moles) of anisole for 48 hr. The hot mixture was filtered and cooled to precipitate 55 g. (15%) of *p*-acetoxymercurianisole, m.p. 171–175°, which was crystallized from ethanol (17 ml./g.), m.p. 176–177°.[25] The reaction and crystallization liquors were treated with an excess of aqueous sodium chloride and the mixture was steam distilled. From the distillate 2.5 g. (0.7%) of *o*-chloromercurianisole, m.p. 175–177°, was collected. It was crystallized from chloroform (17 ml./g.) and ethanol (30 ml./g), m.p. 179–179.4°.

_p_-Chloromercurianisole.—The residue from the steam distillate yielding the *ortho* isomer was filtered, washed with water and dried. This mixture of mono- and dichloromercurials, m.p. 218–236°, was continuously extracted with dioxane leaving 75 g. of insoluble infusible dichloromercurianisole. The extract, evaporated, left 175 g. (51%) of *p*-chloromercurianisole, m.p. 240–246°. This crude product was crystallized from ethyl acetate (70 ml./g.), m.p. 252.5–252.7°.

_m_-Bromomercurianisole.—According to the method of Nesmeyanov[21] a solution of 3.69 g. (0.03 mole) of *m*-anisidine in 11 ml. of 40% hydrobromic acid plus 6 ml. of water (0.075 mole) was diazotized with 2.4 g. (0.03 mole) of sodium nitrite. The cold solution was quickly added to 10.8 g. (0.03 mole) of mercuric bromide in 11 ml. of 40% hydrobromic acid plus 6 g. of ice and shaken. The double salt (13.3 g., 78%, m.p. 72–73°) was filtered and washed with cold water and ether, then added portionwise with stirring to a cooled suspension of 4.4 g. (0.69 atom) of copper powder in 200 ml. of acetone. After 12 hr. the precipitate was filtered and the residue was extracted with acetone. The extract was evaporated until crystals separated which were washed with ether, 3.5 g. (40%), m.p. 137–139.2°, crystallized from carbon tetrachloride (10 ml./g.), m.p. 152.3–152.3°.

Anal. Calcd. for C_7H_7BrHgO: C, 21.7; H, 1.82. Found: C, 21.7; H, 1.92.

_m_-Chlorophenylmercuric Chloride.—Nesmeyanov's method, as outlined above, was employed with *m*-chloroaniline to yield the double salt (88%, m.p. 128.4–128.7°, dec.) which was converted in 57% yield to *m*-chlorophenylmercuric chloride, m.p. 210–212°. When crystallized from ethanol (25 ml./g.) this melted at 212.0–212.4°.

Anal. Calcd. for $C_6H_4Cl_2Hg$: C, 20.7; H, 1.11. Found: C, 20.6; H, 1.37.

_p_-Bromomercurianisole.—A mixture of 10 g. (0.027 mole) of *p*-acetoxymercurianisole and 8.5 g. (0.07 mole) of potassium bromide in 250 ml. of ethanol was refluxed for 15 min. It was then cooled and the crystals filtered, ethanol washed and dried, 10 g. (96%), m.p. 232–237°. Repeated crystallization from dioxane (9 ml./g.) and ethyl acetate (50 ml./g.) gave a m.p. of 258.5–259.5° as contrasted to 187° previously reported.[23]

_p_-Iodomercurianisole.—Use of potassium iodide in the previous procedure gave an 82% yield, m.p. 226–229°. This was crystallized from ethyl acetate (55 ml./g.) and dioxane (8 ml./g.), m.p. 237.8–238.1°, contrasted to 227° previously reported.[23]

Dielectric Constant of Diphenylmercury.—A series of pellets varying in thickness as shown in Fig. 1 was prepared in a cylindrical die[12] having a 0.25 inch bore. The compound was finely ground and was pressed at 8000 lb. dead load under a vacuum of about 20 mm. The pellets, which were not transparent, were weighed and measured. Densities calculated from these measurements were low (av. 2.31) indicating slight pellet distortion. Densities by flotation averaged 2.37 as compared with the reported value of 2.318.[26] In order to ensure absence of air space between the pellets and the plates of the modified micrometer caliper which served as a measuring device, the end surfaces were coated completely with a pasty zinc amalgam. From the extrapolated value of dielectric constant at minimal pellet thickness (2.87) the distortion polarization was calculated $P_{E+A} = (\epsilon - 1)M/(\epsilon + 2)d = 59.2$.

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[21] A. N. Nesmeyanov, *Ber.*, **62**, 1010 (1929).

[22] W. Konig and W. Schnarmbeck, *J. prakt. Chem.*, [2] **128**, 153 (1930).

[23] A. Michaelis and J. Rabinerson, *Ber.*, **23**, 2342 (1890).

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[25] O. Dimroth, *ibid.*, **35**, 2853 (1902).

[26] "International Critical Tables," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1926, p. 121.

TORONTO, CANADA

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN AND THE NATIONAL BUREAU OF STANDARDS]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XXVIII. The Hydration of Azo Dyes in Organic Solvents

BY WALLACE R. BRODE, IRA L. SELDIN, PAUL E. SPOERRI AND GEORGE M. WYMAN

RECEIVED OCTOBER 15, 1954

The addition of water to alcoholic solutions of 4-amino, 4-dimethylamino, 4-hydroxy and 4-methoxy substituted azobenzenes gives rise to a new absorption band at a somewhat longer wave length than that of the main absorption band in the visible region, indicating the formation of some new species. This new band is attributed to the formation of a hydrogen bond between the azo group and water.

Introduction

In connection with some work on conjugated polyazo benzenes, a sample of 4,4'-diaminoazobenzene was prepared and carefully purified. In contrast with the spectra of other aminoazo compounds reported earlier,[1] the spectrum of this compound in 95% ethanol solution showed a strong shoulder on the long wave length side of the principal absorption band in the visible region, strongly suggestive of the presence of another species, perhaps some impurity. However, although the shoulder was not altered in intensity by repeated purification, it was enhanced by dilution of the solvent with increasing amounts of water until it appeared in 10% ethanol solution as a separate band of equal intensity, as shown in Fig. 1. As a result of this observation, it was decided to study the influence of water on the spectra of a large number of similar azo dyes, in the hope of arriving at a better understanding of this unusual solvent effect.

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[1] W. R. Brode, J. H. Gould and G. M. Wyman, THIS JOURNAL, **75**, 1856 (1953).

TABLE I

METHODS OF PREPARATION AND MELTING POINTS OF SUBSTITUTED AZOBENZENES

No.	Substituents	Method	Melting point, °C. Obsd.	Lit.	Ref.
I	4,4′-Diamino-	Redn.	250	250–251	[a]
II	4-Amino-	Coupling	124–125	126	[b]
III	4-Dimethylamino-	Coupling	116–117	116–117	[b]
IV	4,4′-Tetramethyldiamino-	[c]	261–262	265	[n]
V	4-Dimethylamino-4′-hydroxy-	Coupling	203–204	203–204	[b]
VI	4-Hydroxy-	Coupling	154.0–154.5	154–155	[d]
VII	4-Methoxy-	[e]	54.5–55.5	56	[n]
VIII	4-Hydroxy-4′-methyl-	Coupling	152.5–153.0	151	[b]
IX	3-Chloro-4-hydroxy-	Coupling	87.5	88	[f]
X	4-Chloro-4′-hydroxy-	Coupling	157.5–158.0	157	[b]
XI	4,4′-Dihydroxy-	Redn.	217–218	216–218	[g]
XII	4,4′-Dimethoxy-	Redn.[h]	158–159	160	[n]
XIII	4-Hydroxy-2,2′,4′,6-tetramethyl-	Coupling	133.5–134.0	.....	...
XIV	4-Hydroxy-2,2′,4′,6,6′-pentamethyl-	Coupling	136.0–136.5	.....	[b]
XV	4-Amino-4′-nitro-	Coupling	210–211	210–212	[j]
XVI	4-Hydroxy-4′-nitro-	Coupling	213	212–213	[k]
XVII	4-Dimethylamino-4′-nitro-	Coupling	229–233	225–230	[l]
XVIII	4,4′-Dimethyl-	Oxidn.	143.0–143.5	144	[m]
XIX	4,4′-Dinitro-	Oxidn.	216	216	[m]

[a] O. N. Witt and E. Kopetschni, *Ber.*, **45**, 1136 (1912). [b] These compounds were described in reference 4. [c] Provided through the courtesy of Dr. Max T. Rogers. [d] G. Oddu and E. Puxeddu, *Ber.*, **38**, 2755 (1905). [e] Provided through the courtesy of Dr. Marion M. Davis. [f] W. R. Brode and L. E. Cheyney, *J. Org. Chem.*, **6**, 341 (1941). [g] R. Willstaetter and M. Benz, *Ber.*, **39**, 3495 (1906). [h] R. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3738 (1948). [i] E. Noelting and F. Binder, *Ber.*, **20**, 3015 (1887). [k] W. R. Brode, *ibid.*, **61**, 1722 (1928). [l] R. Meldola, *J. Chem. Soc.*, **45**, 107 (1884). [m] S. Mehta and M. Vakilwala, THIS JOURNAL, **74**, 563 (1952). [n] "Beilstein," Vol. XVI.

This change in relative intensity of the separate parts of a multiple component absorption band has been noted previously in an earlier paper in this series,[2] in the influence of change from alcoholic to aqueous solutions on the alkaline spectra of phenylazophenol.

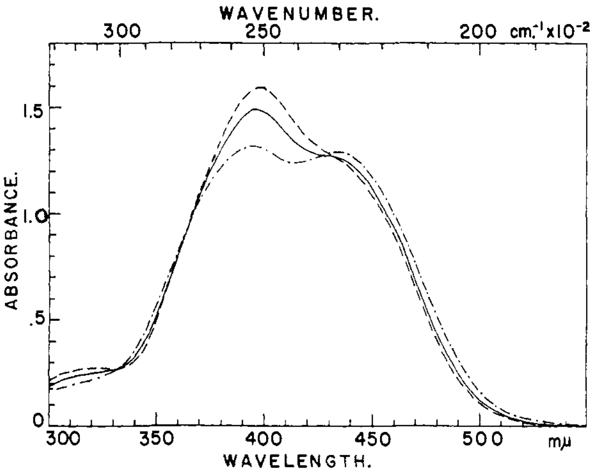

Fig. 1.—Absorption spectra of 4,4′-diaminoazobenzene (dye I) in: 95% ethanol (----); 50% ethanol (——); 10% ethanol (-·-·-·); *c* 0.0060 g./l., *l* 2.00 cm.

Experimental

A. **Preparation of Dyes.**—The dyes were prepared according to standard methods and purified by recrystallization. The methods of preparation and the melting points of the dyes are shown in Table I.

B. **Preparation of Solutions.**—Approximately 6 mg. of each dye was weighed and dissolved in 100 ml. of 95% ethanol. Ten-ml. portions of this stock solution then were diluted to 100 ml. with 95% ethanol, with water or with mixtures of the two. A similar technique was used for the preparation of solutions in other solvents.

C. **Measurement of the Absorption Spectra.**—The absorption spectra were determined by means of a Cary recording quartz spectrophotometer (model 12), using matched fused quartz absorption cells with 95% ethanol in the reference cell.

Results

(a) **Aminoazo Compounds.**—The spectra of dyes II and III in 95% and 10% ethanol solutions are shown in Fig. 2. The shape of the spectral absorption curves of these dyes changes considerably as a result of the addition of water. This change which is similar to that of dye I in-

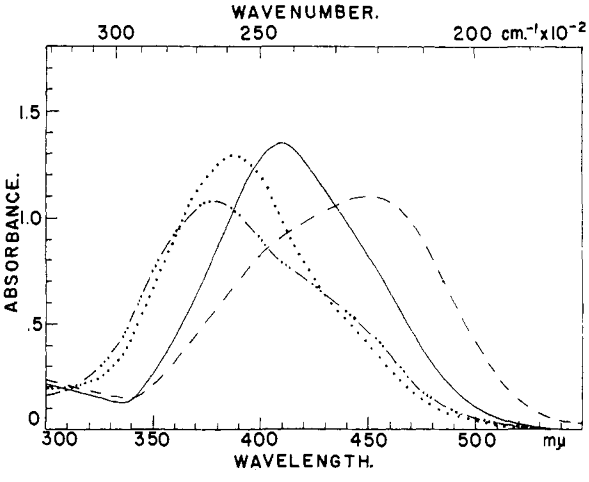

Fig. 2.—Absorption spectra of 4-aminoazobenzene (dye II) in: 95% ethanol (.....); 10% ethanol (-·-·-·-·); *c* 0.0053 g./l., *l* 2.00 cm.; and 4-dimethylaminoazobenzene (dye III) in: 95% ethanol (——); 10% ethanol (----); *c* 0.0051 g./l., *l* 2.00 cm.

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(2) W. R. Brode, *J. Research Natl. Bur. Standards*, **2**, 501 (1929).

volves a decrease of absorption in the region of the main absorption band and increase of absorption at somewhat longer wave lengths. Dyes IV and V also were found to behave in a similar manner.

(b) **Hydroxy and Methoxyazo Compounds.**—The spectra of the typical compounds VI and VII in 95% and 10% ethanol solutions are shown in Fig. 3. The principal change in the spectra of these compounds involves a decrease in the intensity of the principal band, accompanied by the appearance of increased absorption between the principal (350 mμ) and the secondary (430 mμ) absorption bands. This same behavior also was observed for the substituted 4-hydroxyazobenzenes VIII, IX, X and XI, and for 4,4'-dimethoxyazobenzene (XII). 4-Hydroxyazobenzenes containing methyl groups in the 2- and 6-positions exhibited a similar change in spectra on the addition of water to the solvent.

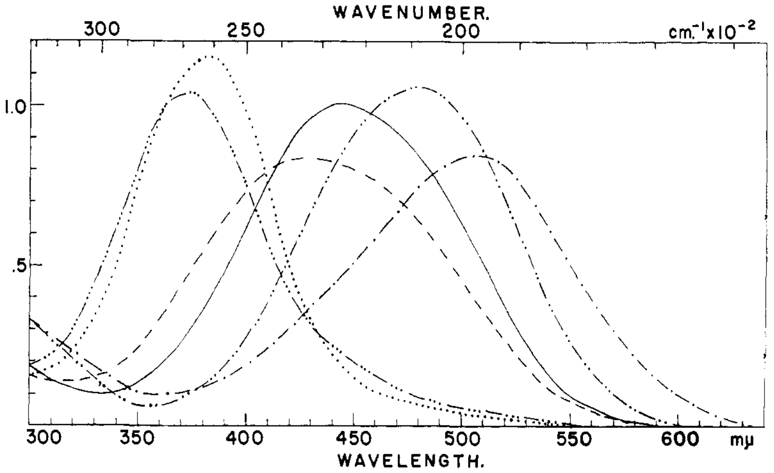

Fig. 4.—Absorption spectra of 4-amino-4'-nitroazobenzene (dye XV) in: 95% ethanol (——); in 10% ethanol (----); *c* 0.0021 g./l., *l* 5.00 cm.; and 4-hydroxy-4'-nitroazobenzene (dye XVI) in: 95% ethanol (.....); 10% ethanol (-·-·-·-·); *c* 0.0053 g./l., *l* 2.00 cm.; and 4-dimethylamino-4'-nitroazobenzene (dye XVII) in: 95% ethanol (—··—··); 25% ethanol (—·—·); *c* 0.0020 g./l., *l* 5.00 cm.

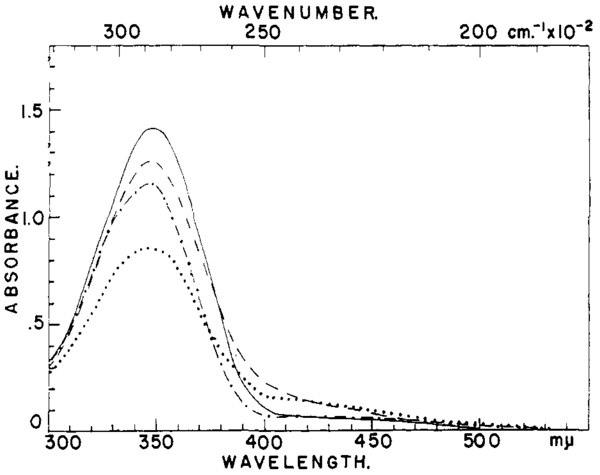

Fig. 3.—Absorption spectra of 4-hydroxyazobenzene (dye VI) in: 95% ethanol (——); 10% ethanol (----); *c* 0.0058 g./l., *l* 2.00 cm.; and 4-methoxyazobenzene (dye VII) in: 95% ethanol (-·-·-·); 10% ethanol (.....); *c* 0.0051 g./l., *l* 2.00 cm.

(c) **Nitroamino- and Nitrohydroxy- Compounds.**—The effects of water on the spectra of the nitroazobenzenes XV, XVI and XVII in ethanol solution are shown in Fig. 4. Although the addition of water causes some shifts in the wave length and the intensity of the main absorption bands, for only one of them (XVI) is there a sign of the appearance of a new band (460 mμ). This band, however, is of considerably weaker intensity than the bands observed for the other *para*-substituted 4-hydroxyazobenzenes (*cf.* Fig. 3).

Discussion of Results

The appearance of a new absorption band, accompanied by a decrease in the intensity of an existing one (which occurs upon dilution with water, with the great majority of the compounds studied), suggests the formation of some new species in solution. Since this effect was first observed with compounds containing free amino and hydroxy groups (I and V), it first was thought to be attributable to azo-quinoid tautomerism, similar to that reported for hydroxy derivatives of benzeneazonaphthalene.[3,4] However, when it was found that compounds that do not contain $-NH_2$ or $-OH$ groups conjugated to the azo linkage (*e.g.*, III, VII and XII) also exhibited this effect, it was clear that this explanation could not be valid for all of these compounds. The possibility of *trans* → *cis* isomerization as the cause of the appearance of the new absorption band also was eliminated by comparing these absorption curves with those reported in two earlier papers[1,5] on the geometrical isomerism of dyes of this type.

The structural feature that dyes I–XII have in common consists of the presence of at least one *para*-substituent possessing an unshared electron-pair ($^{+}$M group) and thus capable of entering into resonance with the azo-group.[6]

In contrast with the spectra in Figs. 1–4, the spectra of 4,4'-dimethyl- and 4,4'-dinitroazobenzene show no new region of absorption upon the addition of water. Thus it is apparent that the presence of such a $^{+}$M substituent is essential for the appearance of the new band and hence for the formation of the new species in solution. One consequence of the presence of such a substituent in the *para* position would be an enhancement in the basicity of the nitrogen atom of the azo group which is farthest from the substituted benzene ring, by contribution from the resonance structure A.

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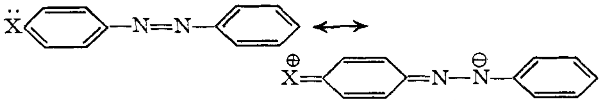
[4] A. Burawoy, A. G. Salem and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952).

[5] W. R. Brode, J. H. Gould and G. M. Wyman, This Journal, **74**, 4641 (1952).

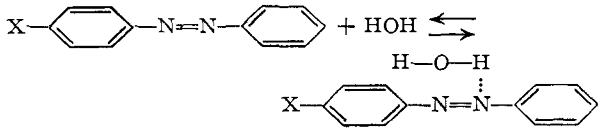
[6] H. B. Watson, "Modern Theories of Organic Chemistry," Oxford University Press, New York, N. Y., 1943, p. 88.



A

In the case of the *p*-disubstituted compounds there would be an increase in the basicity of both nitrogen atoms as a result of contributions from two structures of this type. (This effect of $^+$M groups in *para* positions in aromatic azo compounds was recognized years ago, when Hantzsch suggested that salt formation of *p*-aminoazobenzenes with strong acids occurred through the azo groups.[7])

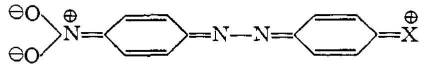
This concept readily suggests that under the conditions of this study the new species is formed by the addition of water to the azo group, by means of hydrogen bonding, according to the equation



The reaction is not unlike the hydration of ammonia or aliphatic amines, except that a large excess of water is needed in order to obtain appreciable amounts of the solvated dye. Since even in 10% ethanol a dye such as dye I seems to be converted only partially (10–50%) to the hydrate, the equilibrium constant for the above reaction must be of the order of 10^{-2}. The hydrated azo dyes appear to be exceedingly weak bases, inasmuch as the new absorption bands do not correspond to those obtained on the addition of acids to these dyes.[8]

Indirect evidence in support of the hydration hypothesis is available from many sources. The existence of intramolecular hydrogen bonds between azo and *o*-hydroxy groups was established first by infrared measurements.[9] Recently the formation of intermolecular hydrogen bonds between azobenzene and benzyl alcohol also has been observed, utilizing the same technique.[10] The observed inhibition of the *trans* → *cis* isomerization of azo dyes in hydroxylic solvents also suggests solvation.[1]

Since the proposed mechanism of hydrate formation involves reaction at the azo group, it may be expected that the introduction of bulky substituents *ortho* to the azo groups would hinder the reaction. In accordance with this expectation, it was found that for dyes XIII and XIV, containing 3 or 4 methyl groups in *ortho* positions to the azo group, respectively, the diffuse absorption at 405 mμ was not enhanced as strongly as that of the sterically unhindered hydroxyazo dyes VI–XII on the addition of water. The behavior of *p*-nitro-substituted dyes also is consistent with this picture. The $^-$M nitro group, conjugated with the $^+$M amino or hydroxy group will minimize the basicity of the azo group due to the large contribution from the important resonance structure B,[11] and thus inhibit the formation of the hydrated species.

B 

The formation of a hydrate possessing a new absorption band, also was observed when water was added to solutions of these dyes in other organic solvents that are miscible with water, *e.g.*, acetone or dioxane. Furthermore, the addition of absolute ethanol to benzene or acetone solutions of some of the aminoazo dyes also was found to give a similar but weaker effect. Consequently, it seems that solvate formation of azo dyes with hydroxylic solvents is a general phenomenon and that azo dyes containing strong $^+$M groups in the *para* position are capable of forming solvates even with alcohols.

Unfortunately, it is not possible to calculate the spectral absorption curves for the new species for two reasons: (1) Solvents of different dipole moments cause displacements in the wave lengths of absorption bands[11,12,13] thus making the analysis of absorption curves of mixtures by subtraction difficult, and (2) the possibility of solvation in 95% ethanol makes the reference curve for such subtractions uncertain. However, the approximate wave lengths of the new absorption maxima may be determined readily by inspection.

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[8] *Cf.* W. R. Brode, *J. Research Natl. Bur. Standards*, **2**, 52 (1929); also, unpublished data of the authors.

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[10] M. St. C. Flett, *J. Soc. Dyers Colourists*, **68**, 59 (1952).

[11] *Cf.* S. E. Sheppard and P. T. Newsome, THIS JOURNAL, **64**, 2937 (1942).

[12] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[13] W. R. Brode, *J. Phys. Chem.*, **30**, 56 (1926).