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ULTRAVIOLET ABSORPTION SPECTRA OF AROMATIC AMINES IN ISOOCTANE AND IN WATER

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ADVANCE RESTRICTED REPORT

ULTRAVIOLET ABSORPTION SPECTRA OF AROMATIC AMINES IN ISOOCTANE AND IN WATER

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SUMMARY

A study of the ultraviolet absorption spectra in the 3200 A to 2500 A region of 27 aromatic amines in isooctane and in water solutions is presented. A brief discussion of the relation between the molecular structure of the amines and their absorption spectra is included.

Certain factors that affect the absorption spectra of aromatic amines were experimentally investigated. The spectra were found to be different for the two different solvents. In aqueous aromatic amine solutions the pH was found to be an important factor; the addition of acid to a neutral water solution shifted the absorption spectrum of the amine toward the spectrum of the basic aromatic structure of the amine. Irradiation of aromatic amine solutions with ultraviolet light caused changes in the absorption spectra; water solutions of the amines were more rapidly affected than isooctane solutions.

INTRODUCTION

Ultraviolet absorption spectrometry provides a sensitive tool that can be applied to the analysis for aromatic amines in solution (reference 1). For a particular amine, a plot of intensity of light absorption against wavelength gives a curve, or spectrum, characteristic of the amine in the solvent used. Because such plots can aid in the identification of an unknown material and are used in quantitative spectrophotometric analysis, it is desirable to have available a catalog of carefully determined absorption spectra of pure aromatic amines in appropriate solvents. Absorption spectra for some simple aromatic amines have been published in references 2 to 5 but these data were obtained with various types of equipment and often with different solvents; as a result a comparison of absorption spectra of different aromatic amines in the same solvent is difficult to make.

In connection with the development of fuel additives for the Army Air Forces, the Cleveland laboratory of the NACA determined absorption spectra from 3200 A to 2500 A wavelengths for 27 monoaryl amines both in isooctane and water. The data were obtained with a photoelectric spectrophotometer. A study was made of some factors that might affect the spectra and a correlation was attempted between spectra and molecular structure.

INSTRUMENTS AND MATERIALS

Instruments

The absorption data were obtained with a photoelectric spectrophotometer having quartz-prism optics and 1-centimeter matched quartz absorption cells. The design features and the performance characteristics of the spectrophotometer are described in reference 6. Ultraviolet light was supplied by a hydrogen discharge lamp. The extinctions of the solutions measured at each selected wavelength were read directly from a calibrated dial on the instrument. The extinction is defined as the negative logarithm of the ratio of light transmitted through a cell that contains the absorbing solution to the light transmitted through a matched cell that contains only the solvent.

With this instrument, the measured extinctions for an aromatic amine in hydrocarbon solutions were found to be proportional to the concentrations of the amine for extinction values up to 1.0. Validity of the Beer-Lambert relation for extinction values less than 1.0 was assumed for water solutions of aromatic amines. The precision of the spectrophotometer as evaluated in reference 1 showed that the absorption spectra of the aromatic amines could be reproduced within 1/2 percent.

Aromatic Amines and Solutions

The 27 aromatic amines were prepared by the Organic Synthesis Laboratory of the Fuels and Lubricants Division and are believed to be better than 95 percent pure. They are as follows:

Aniline
N-Methylaniline
N-Ethylaniline
N-Propylaniline
N-Isopropylaniline
N-Butylaniline
N-*tert*-Butylaniline
N,N-Dimethylaniline
N,N-Diethylaniline
o-Toluidine
m-Toluidine
p-Toluidine
o-Ethylaniline
p-Ethylaniline
o-Isopropylaniline
p-Isopropylaniline
p-*tert*-Butylaniline
N-Methyl-*p*-toluidine
N-Ethyl-*p*-toluidine
N-Isopropyl-*p*-toluidine
2,4-Xylidine
2,5-Xylidine
2,6-Xylidine
Xylidines (technical)
N-Methyl-2,4-xylidine
2,4-Diethylaniline
Mesidine

The physical properties are listed in table 1.

The isooctane used as a solvent was Rohm and Haas pure isooctane (2,2,4-trimethylpentane). The measured isooctane solutions were prepared by a double-dilution procedure in order to conserve the solvent. About 0.3 gram of the aromatic amine was dissolved in about 35 grams of isooctane, both quantities being accurately weighed. About 0.25 gram of this solution was weighed and then diluted to 50 milliliters with isooctane.

The distilled water had a pH between 5.6 and 5.9, as measured with a commercial pH meter. For the water solutions, about 0.1 gram of the aromatic amine was weighed and diluted to 2 liters with distilled water. When the surface tension of the amine made direct solution in water difficult, as was the case for several of the more complex amines, the amine was dissolved with a measured quantity of hydrochloric acid, neutralized with a predetermined titer of sodium hydroxide, and finally diluted to the desired concentration with water.

The final concentrations of aromatic amine in the solutions were approximately 0.05 gram per liter for both solvents. The solutions were prepared in subdued light and, when necessary, stored temporarily in a dark room. The temperature of the solutions was approximately 25° C. The effect of variable temperature on the extinctions of the amine solution was not investigated.

PROCEDURE FOR OBTAINING ABSORPTION SPECTRA

The extinctions of known concentrations of aromatic amines in isooctane and in water were measured spectrophotometrically at about 16 wavelengths λ between 3200 A and 2500 A. For the measurements of the isooctane solutions, spectrophotometer slit widths of 0.5 millimeter were used for wavelengths less than 2700 A and 0.3 millimeter for longer wavelengths. The narrower slit widths were used in order to resolve better any band structure in the absorption pattern. Except for the patterns that show resolved fine structure, the width of the slits was found to have little effect on the extinctions measured.

From the measured extinctions, corrected for unequal light transmission of the windows of the cells, the specific extinctions were calculated by the equation

$$k = \frac{E}{cl}$$

where

k specific extinction, liters per gram-centimeter

E measured extinction

c concentration of solute, grams per liter of solvent

l length of cells, centimeters

The averages of the two specific extinctions obtained with two independently prepared solutions were plotted against wavelength to obtain the absorption spectrum for the amine. The data for an amine were redetermined when values of these specific extinctions failed to agree within 2 percent at wavelengths near the absorption maximum. In order to illustrate the method, the experimental data for o-ethylaniline in isooctane and in water are given in table 2.

FACTORS THAT AFFECT ABSORPTION SPECTRA

Some of the factors that may affect the absorption spectra of aromatic amines are: (1) nature of the solvent, (2) purity of the aromatic amines, and (3) photochemical decomposition of the aromatic amines. Each of these factors and its possible effect on the validity of the absorption data will be discussed in the following sections.

Nature of the Solvent

Nonpolar and polar solvents. - The absorption spectrum of a substance in solution depends in part on the dipole moments of the solvent and the solute (reference 7). The absorption spectra of aromatic amines are different in the nonpolar solvent, isooctane and in the polar solvent, water. Because of the nonpolar character of hydrocarbons, particularly paraffins and naphthenes, which are suitable as solvents, the absorption spectra of an aromatic amine in different hydrocarbons are probably very similar.

pH of water solutions. - The influence of the acidity of water solutions on the absorption spectra of seven aromatic amines was studied. The results for aniline, which are typical, are shown in figures 1 and 2. The absorption spectra of the eight aniline solutions of various pH value shown in figure 1 demonstrate that the addition of hydrochloric acid to a 0.005 percent aniline solution radically changes the absorption spectrum. At pH 3.3, the specific extinction of aniline at 2850 A is only about 7 percent of that at pH 5.8. In 5 percent hydrochloric acid (curve not shown) absorption peaks appear in the 2700 A to 2300 A region that correspond to the absorption maxima of the basic aromatic structure of the amine. For example, the peaks of aniline and N-alkylanilines in aqueous hydrochloric acid correspond to the peaks of benzene and those for acidified toluidines correspond to toluene (see references 8 and 9).

Figure 2 shows that increasing the pH from 5.8 to 10.7 by the addition of sodium hydroxide resulted in an increase in the specific extinction of aniline of about 4 percent. The equilibrium between aniline and water in acid and basic aqueous solutions has been investigated spectrometrically (reference 8); the addition of salt (NaCl) to the solution had no effect except when sufficient salt was added to alter the pH of the solutions. This result is in agreement with the findings of reference 9.

Purity of Aromatic Amines

The purity of each aromatic amine prepared at the Cleveland laboratory and used in these tests was dependent upon the purity of the base materials, the method required for synthesis, and the difficulty of isolating the pure amine from byproducts produced during its synthesis. The simple amines, such as aniline and N-methylaniline, which were purified commercial products, were probably better than 99 percent pure, whereas the purity of aromatic amines having isomers difficult to synthesize separately and with similar physical and chemical properties, such as the xylidines, was less. All 27 aromatic amines were estimated to be better than 95 percent pure.

The impurities of any particular amine were primarily structurally related isomers; inasmuch as the absorption spectra of most structurally related aromatic amine isomers are similar in many respects, however, the absorption data for the amines are probably not greatly in error because of these impurities. The absorption curves for isomeric aromatic amines reveal that, in many cases, the presence of as much as 5 percent of an isomeric impurity in an aromatic amine does not change the magnitude of the specific extinction of the pure amine by as much as 1 percent. The presence of 5 percent of _o_-toluidine in _p_-toluidine, however, would increase the specific extinction of _p_-toluidine at 2800 A about 3.6 percent.

Photochemical Decomposition of Amines

The effect of irradiation with light of isooctane and water solutions of aromatic amines was investigated and qualitative results of some of the studies are presented in the two following sections.

Isooctane solutions. - Successive extinction measurements of 0.005 percent isooctane solutions of three aromatic amines that were continuously exposed to ultraviolet light in the spectrophotometer showed no serious changes in the extinctions between 2900 A and 2700 A during exposures up to 1 hour.

In order to determine the effect of strong ultraviolet light on the extinction measurements, 1 percent solutions of 5 aromatic amines in isooctane were exposed to radiation from a quartz mercury-arc lamp. The amines tested were N-methylaniline, N-ethylaniline, N,N-diethylaniline, N-tert-butylaniline, and o-toluidine. The solutions were contained in stoppered quartz cells placed 2 inches from the lamp. Samples of these solutions withdrawn at intervals up to 5 hours exposure showed significant changes in the absorption spectra. The spectra for two of these amines at various intervals of exposure are shown in figure 3.

Similar exposures to light from an ordinary 100-watt incandescent lamp, from which the radiation is primarily in the short infrared and visible regions of the spectrum, showed no significant effect after 75 hours. In this case the solutions were contained in stoppered test tubes placed about 6 inches from the lamp.

Water solutions. - The effects of ultraviolet light in the spectrophotometer on the extinctions of water solutions of 5 aromatic amines (aniline, N-ethylaniline, N-isopropylaniline, N,N-dimethylaniline, and N,N-diethylaniline) varied; the amount and type of variation seemed to depend on the structure of the amine. In general, the extinctions of the aromatic amine solutions tended to decrease rapidly after about 10 minutes exposure to ultraviolet light of 2850 A wavelength. Illustrative data for N-isopropylaniline in water are given in figure 4. These results indicate that measurements of the extinctions of aromatic amines in water should be completed rapidly and systematically, preferably within 5 minutes.

The extinctions of water solutions of 5 aromatic amines (aniline, N-isopropylaniline, N,N-diethylaniline, technical xylidines, and N-methyl-xylidines) kept in glass bottles in a well-lighted room increased as much as 2 percent a day. Samples of the same solutions kept in a dark room showed no significant changes in extinction for periods up to 2 months.

DISCUSSION OF ABSORPTION SPECTRA

The absorption spectra for the 27 aromatic amines are shown in figures 5 to 19. Two sets of curves are plotted for each figure; for one set isooctane was the solvent and for the other distilled water was the solvent. The absorption curves are arranged with structurally related compounds plotted on a single graph in order to facilitate comparison.

The effect of the solvent in modifying the ultraviolet-light absorption is illustrated by a comparison of the absorption curves of an aromatic amine in isooctane and in water. For each of the amines the maximum specific extinction of the aromatic amine is less in water than in isooctane and the position of the absorption maximum shifted roughly 70 A toward shorter wavelengths. (See fig. 5.) For the more complex aromatic-amine molecules, N,N-diethylaniline and N-*tert*-butylaniline, the characteristic absorption band at about 2900 A is suppressed in water (figs. 7 and 13).

Correlation of Molecular Structure and Absorption Spectra

Theoretical considerations of the correlation between absorption spectra and molecular structure are given in references 10, 11, and 12. Only qualitative aspects observed in these tests will be discussed.

Most of the absorption plots are smooth curves that have absorption maxima near 2900 A wavelength and absorption minima at about 2700 A. Aniline and some of the *p*-substituted aromatic amines in isooctane, however, show some resolved fine structure in the absorption band in the 2900 A region, as shown in figures 6(a) and 15(a).

The effect of successively replacing the two amino hydrogen atoms of aniline with alkyl groups is shown in figures 6 and 7. Figures 8 and 9 show the effects of methylating the nitrogen for *p*-toluidine and 2,4-xylidine.

Absorption spectra for the three toluidines and for three of the six xylidines are given in figures 10 and 11. When the positions of alkyl substitutions are involved, the absorption spectra of isomers differ. The absorption maximum for *o*-toluidine occurs at a shorter wavelength than for *m*- or *p*-toluidine and is about 20 percent greater in magnitude than either of the other two isomers in both solvents. The curves for the xylidines differ less markedly.

The absorption spectra of N-propylaniline and N-isopropylaniline and of N-butylaniline and N-*tert*-butylaniline in isooctane, shown in figures 12(a) and 13(a), are similar except for the magnitudes of the absorption peaks. The curve for N-*tert*-butylaniline in water (fig. 13(b)) shows suppression of the absorption band at 2900 A.

Aromatic amines that can be classified as members of a homologous series, such as the N-alkylanilines series or the N-alkyl-*p*-toluidines series, appear to have similar absorption spectra with maxima and minima at corresponding wavelengths. The approximate wavelengths of the absorption maxima and minima for six families studied are given in table 3. The curves for these aromatic amine families are given in figures 14 to 18.

The effect of methylating the aromatic ring of aniline is shown in figure 19.

Comparison of Absorption Data with Results of Other Investigations

Absorption data obtained with other spectrophotometers of similar design should be similar, though not necessarily identical, to the data for individual aromatic amines given in this report. Aside from other factors that affect the absorption spectra, some of which have been discussed in previous sections of this report, differences in the spectra obtained with other instruments may be due to differences in the resolution of the instruments or differences in the amount of stray light (reference 15). Data for some of the amines obtained at this laboratory with a 1.5 meter grating spectrograph gave values about 8 percent higher for the calculated specific extinctions of the amines.

The absorption data given in this report are compared in table 4 with some of the results reported in reference 5 for individual aromatic amines. The wavelengths λ of the absorption maxima and the corresponding specific molecular extinctions ε are listed.

The data of Klingstedt (references 2 and 3) show nine resolved bands for aniline at about 2900 A and seven for p-toluidine in hexane, more than were obtained with the spectrophotometer at this laboratory with isooctane as the solvent, but show only single broad bands for o- and m-toluidine, which agrees with this investigation. It was found in reference 2 that solutions of aniline and p-toluidine in water, alcohol, and carbon tetrachloride had only a single broad absorption band near 2900 A.

The wavelengths of the absorption maxima reported by Klingstedt are in excellent agreement with the data obtained at this laboratory. The results listed in references 4 and 5 show several discrepancies with the present data and no resolution of fine structure was evident even for aniline in hexane.

CONCLUDING REMARKS

The absorption spectra of the 27 monoaryl amines studied were different for the two solvents used, isooctane and water. The maximum specific extinction for an aromatic amine is less in water than in isooctane and the absorption maximum occurs at shorter wavelengths in water solutions.

The pH of water solutions was found to have a pronounced effect on the absorption spectra of aromatic amines. The addition of acid to a neutral water solution shifted the absorption spectrum of the amine toward the spectrum of the basic aromatic structure of the amine. The addition of base increased the absorption up to a solution pH of about 9.0, beyond which little further effect was noted.

Ultraviolet light produced photochemical effects on aromatic amines in isooctane and in water solutions, as evidenced by changes in the absorption spectra. Water solutions of aromatic amines were more rapidly affected by light irradiation than isooctane solutions.

The absorption spectra of structurally similar aromatic amine compounds are similar; for any one family, such as the N-alkylanilines family, the p-alkylanilines family, or the N-alkyl-p-toluidine family, the absorption maxima and minima occur at corresponding wavelengths. Isomers that result from different positions of alkyl substitutions have absorption spectra that differ in wavelength pattern.

Absorption data obtained with other spectrophotometers of similar design should be similar, though not necessarily identical, to the data for individual aromatic amines given in this report.

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REFERENCES

1. Tischler, Adelbert O.: Quantitative Analysis for Aromatic Amines in Aviation Fuels by Ultraviolet Spectrophotometry. NACA ARR No. E5H27, 1945.

2. Klingstedt, F. W.: Spectroscopie. - Spectres d'Absorption Ultraviolets de l'Aniline et des Toluidines. Comptes Rendus, t. 176, Jan. 22, 1923, pp. 248-250.

3. Klingstedt, F. W.: Über die Ultravioletton Absorptionsspektren Einiger Mono- und Biderivate des Benzols. Acta Acad. Aboensis Math. et Phys. (Åbo, Finland), III.5, 1924, pp. 1-82.

4. Ramart-Lucas, Pauline, and Wohl, Anna: Chimie Organique. - Stabilité Comparée des Isomères Suivant Leurs Spectres d'Absorption des Arylamines. Comptes Rendus, t. 196, June 12, 1933, pp. 1804-1806.

5. Wohl, Anna: Etude Spectrale sur les Arylamines et Leurs Chlorhydrates. Bull. Soc. Chim. de France (Memoires), vol. VI, ser. 5, 1939, pp. 1312-1319.

6. Carey, H. H., and Beckman, Arnold O.: A Quartz Photoelectric Spectrophotometer. Jour. Optical Soc. Am., vol. 31, no. 11, Nov. 1941, pp. 682-689.

7. Scheibe, G.: Die Veränderlichkeit der Absorptionsspektren in Lösungen in Beziehung zur Ladungsverteilung der Moleküle und Zusammenhänge zwischen Absorption und Refraktion. (III.) No. 212, Berichte d. D. Chem. Gesellschaft, Abteilung B (Abh.), Jahrg. 59, Nr. 6, June 9, 1926, pp. 1321-1334.

8. Flexser, Leo A., Hammett, Louis P., and Dingwall, Andrew: The Determination of Ionization by Ultraviolet Spectrophotometry: Its Validity and Its Application to the Measurement of the Strength of Very Weak Bases. Jour. Am. Chem. Soc., vol. 57, no. 11, Nov. 1935, pp. 2103-2115.

9. Kumler, W. D., and Strait, L. A.: The Ultraviolet Absorption Spectra and Resonance in Benzene Derivatives—Sulfanilamide, Metanilamide, p-Aminobenzoic Acid, Benzenesulfonamide, Benzoic Acid and Aniline. Jour. Am. Chem. Soc., vol. 65, no. 12, Dec. 1943, pp. 2349-2354.

10. Sklar, Alfred L.: Theory of Color of Organic Compounds. Jour. Chem. Phys., vol. 5, no. 9, Sept. 1937, pp. 669-681.

11. Mulliken, Robert S.: Intensities of Electronic Transitions in Molecular Spectra. I. Introduction. Jour. Chem. Phys.: vol. 7, no. 1, Jan. 1939, pp. 14-20; II. Charge-Transfer Spectra: vol. 7, no. 1, Jan. 1939, pp. 20-34; III. Organic Molecules with Double Bonds. Conjugated Dienes: vol. 7, no. 2, Feb. 1939, pp. 121-135; IV. Cyclic Dienes and Hyperconjugation: vol. 7, no. 5, May 1939, pp. 339-352; V. Benzene: vol. 7, no. 5, May 1939, pp. 353-356; VI. Molecular Refractivities of Organic Compounds: vol. 7, no. 5, May 1939, pp. 356-363; VII. Conjugated Polyenes and Carotenoids: vol. 7, no. 5, May 1939, pp. 364-373; VIIIa. Odd-Numbered Conjugated Polyene Chain Molecules and Organic Dyes (with notes on optical anistropy and Raman intensities): vol. 7, no. 8, Aug. 1939, pp. 570-572.

12. Sponer, H., Nordheim, G., Sklar, A. L., and Teller, E.: Analysis of the Near Ultraviolet Electronic Transition of Benzene. Jour. Chem. Phys., vol. 7, no. 4, April 1939, pp. 207-220.

13. Hogness, T. R., Zscheile, F. P., Jr., and Sidwell, A. E., Jr.: Photoelectric Spectrophotometry. An Apparatus for the Ultra-Violet and Visible Spectral Regions: Its Construction, Calibration, and Application to Chemical Problems. Jour. Phys. Chem., vol. 41, no. 3, March 1937, pp. 379-415.

TABLE 1. - PHYSICAL PROPERTIES OF AROMATIC AMINES

Amine	Boiling range at 760 mm (°C)	Refractive index n_D^{20}	Density at 20° C (grams/ml)
Aniline	184.0-184.5	1.5853	1.0220
N-Methylaniline	195.0-196.0	1.5704	.9860
N-Ethylaniline	203.0-204.0	1.5538	.9607
N-Propylaniline	220.5-223.5	1.5425	.9448
N-Isopropylaniline	206.5-209.0	1.5404	.9374
N-Butylaniline	240.0-240.5	1.5339	.9323
N-*tert*-Butylaniline	[a]95.0 (16 mm)	1.5270	.9244
N,N-Dimethylaniline	192.5-193.5	1.5580	.9564
N,N-Diethylaniline	215.0-217.0	1.5418	.9347
o-Toluidine	198.5-201.5	1.5718	.9989
m-Toluidine	202.5-203.5	1.5674	.9893
p-Toluidine	[b]44.0- 44.4	-------	--------
o-Ethylaniline	211.0	1.5602	.9810
p-Ethylaniline	216.0	1.5547	.9672
o-Isopropylaniline	219.0-220.0	1.5464	.9643
p-Isopropylaniline	225.5-226.5	1.5432	.9514
p-*tert*-Butylaniline	[a]96.5- 98.0 (5-6 mm)	1.5388	.9446
N-Methyl-*p*-toluidine	209.0-211.0	1.5570	.9610
N-Ethyl-*p*-toluidine	217.0-220.0	1.5439	.9441
N-Isopropyl-*p*-toluidine	222.0-223.0	1.5319	.9238
2,4-Xylidine	215.0-215.5	1.5601	.9751
2,5-Xylidine	216.0	1.5596	.9755
2,6-Xylidine	216.0-217.0	1.5616	.9768
Xylidines (technical)	216.0-219.5	1.5601	.9771
N-Methyl-2,4-xylidine	221.0-222.0	1.5542	.9582
2,4-Diethylaniline	241.0-242.0	1.5433	.9511
Mesidine	[a]110.0 (15 mm)	1.5502	.9615

[a]Distilled under reduced pressure.
[b]Melting range of solid.

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TABLE 2. - SPECTROPHOTOMETRIC DATA ON o-ETHYLANILINE IN ISOOCTANE AND IN WATER

Wave-length λ (A)	Isooctane				Water			
	o-Ethylaniline concentration (grams/liter)				o-Ethylaniline concentration (grams/liter)			
	0.0639		0.0498		0.0505		0.0514	
	Extinctions				Extinctions			
	E	k	E	k	E	k	E	k
2500	0.840	13.15	0.666	13.37	0.505	10.00	0.508	9.88
2550	.475	7.44	.374	7.51	.290	5.74	.289	5.62
2600	.364	5.70	.288	5.78	.259	5.13	.262	5.10
2650	.400	6.26	.315	6.32	.334	6.61	.340	6.62
2675	.464	7.26	.364	7.31	.397	7.86	.403	7.84
2700	.559	8.75	.437	8.78	.468	9.26	.475	9.24
2750	.792	12.41	.622	12.48	.617	12.21	.629	12.24
2800	1.040	16.27	.812	16.30	.701	13.88	.713	13.87
2825	1.126	17.62	.882	17.70	.702	13.90	.713	13.87
2850	1.180	18.46	.926	18.59	.669	13.24	.679	13.20
2875	1.170	18.31	.919	18.45	.597	11.82	.610	11.87
2900	1.095	17.14	.859	17.25	.494	9.78	.502	9.76
2950	.805	12.60	.632	12.68	.289	5.72	.293	5.70
3000	.333	5.21	.263	5.28	.145	2.87	.146	2.84
3050	.075	1.17	.060	1.20	-----	------	-----	------
3100	.014	.22	.013	.26	.029	.57	.028	.55
3150	.004	.06	.006	.12	-----	------	-----	------
3200	.003	.05	.004	.10	.008	.16	.007	.14

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TABLE 3. - WAVELENGTHS OF ABSORPTION MAXIMA AND MINIMA FOR SIX STRUCTURALLY RELATED FAMILIES OF AROMATIC AMINES

Aromatic amine family	Solvent			
	Isooctane		Water	
	Wavelength λ (A)		Wavelength λ (A)	
	Maximum	Minimum	Maximum	Minimum
o-Alkylanilines	2860	2605	2815	2585
m-Alkylanilines[a]	2880	2640	2830	2615
p-Alkylanilines	2920	2670	2855	2635
N-Alkylanilines	2950	2700	2850	2700
N-Alkyl-*p*-toluidines	3025	2745	2905	2720
2,4-Dialkylanilines	2925	2650	2865	2620

[a] Data presented are for *m*-toluidine, only representative amine of this group tested.

TABLE 4. - COMPARISON OF ABSORPTION MAXIMA WITH RESULTS OF OTHER INVESTIGATIONS

Aromatic amine	Source			
	Reference 3		NACA	
	Solvent			
	Hexane		Isooctane	
	Wavelength λ (A)	Specific molecular extinction ε (liters/mole-cm)	Wavelength λ (A)	Specific molecular extinction ε (liters/mole-cm)
Aniline	2918	1470	2920	1555
	2877	1470	2880	1770
	2840	1470	2840	1720
	2808	1470	2810	1590
p-Toluidine	2968	1750	2960	1820
	2933	1750	2930	1840
	2897	1750	2900	1770
o-Toluidine	2850	1750	2850	2220

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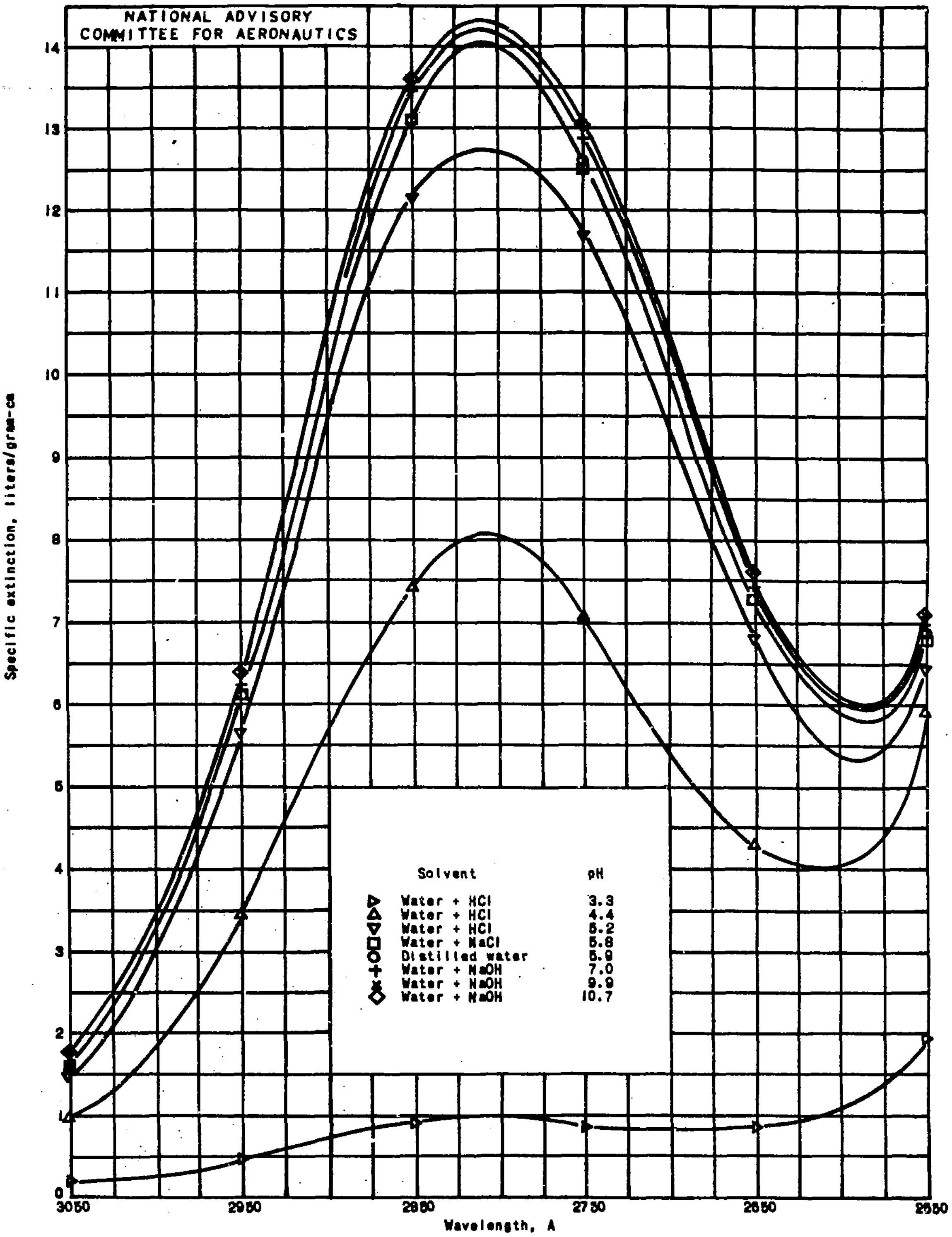


Figure 1. - Effect of acidity on absorption spectrum of aniline in water. Concentration of aniline, 0.005 percent.

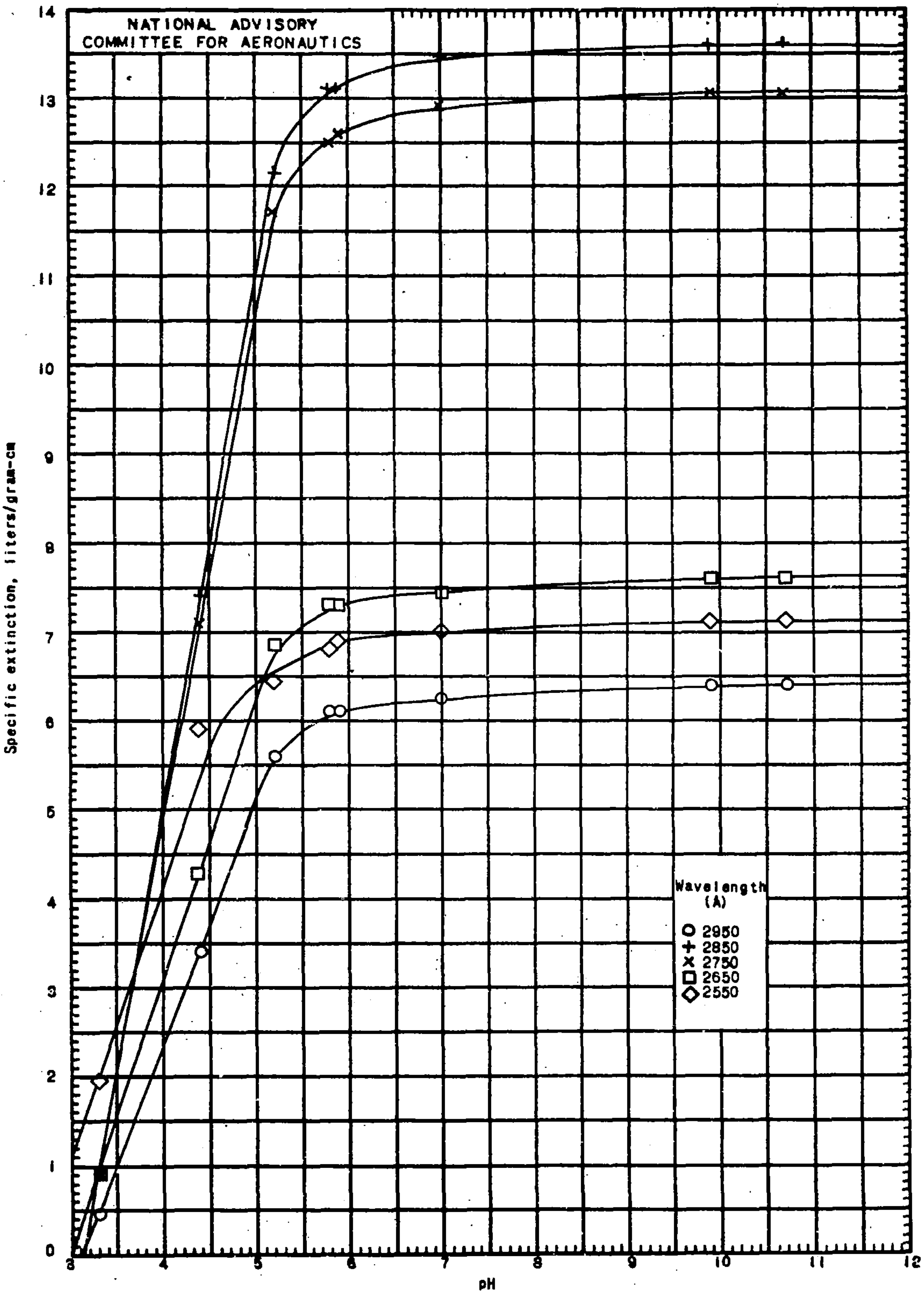
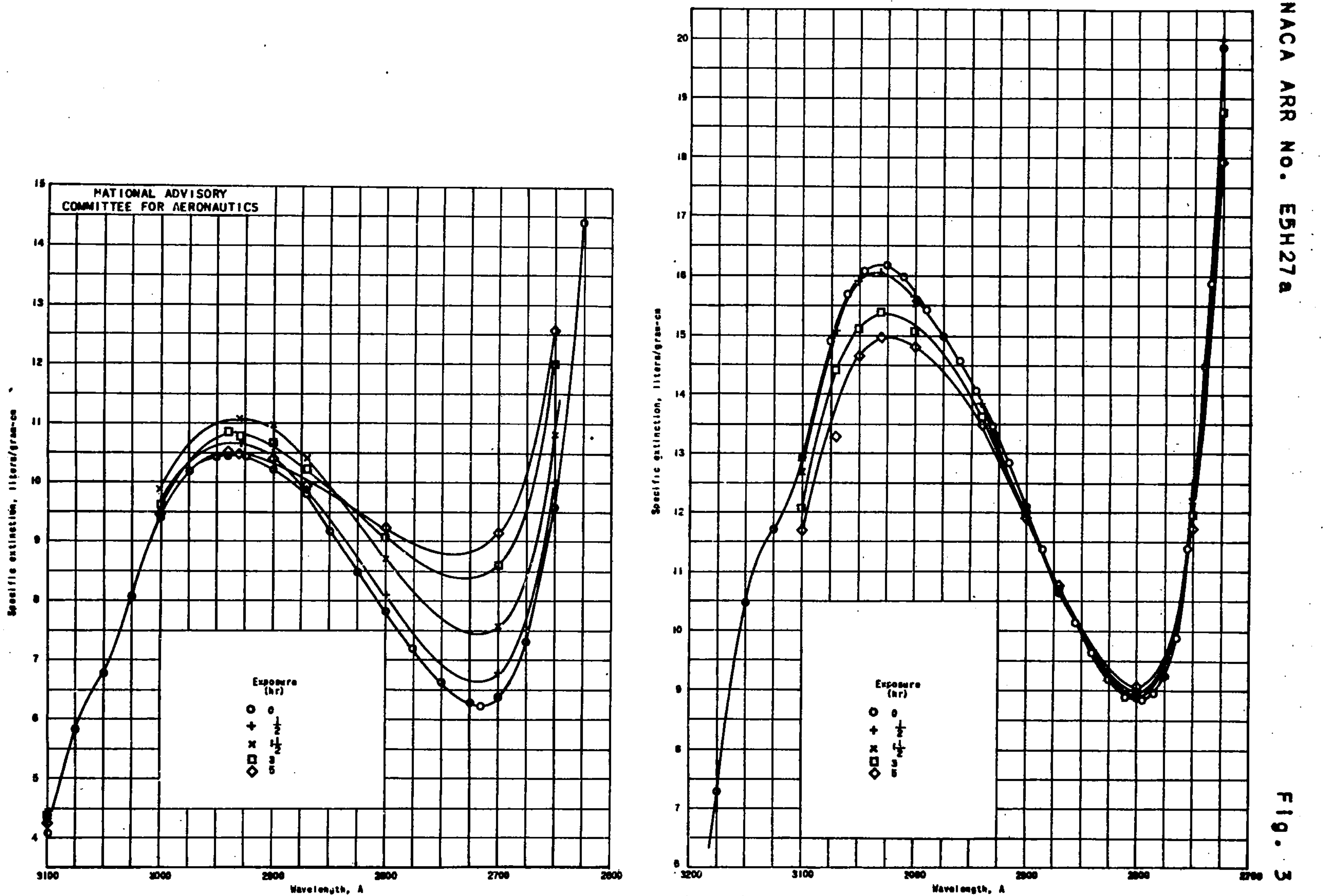


Figure 2. - Effect of pH of aqueous solutions of aniline on specific extinction at various wavelengths.



(a) N-*tert*-butylaniline.

(b) N,N-diethylaniline.

Figure 3. - Effect of ultraviolet light on absorption spectra of 1 percent solutions of N-*tert*-butylaniline and N,N-diethylaniline in isooctane.

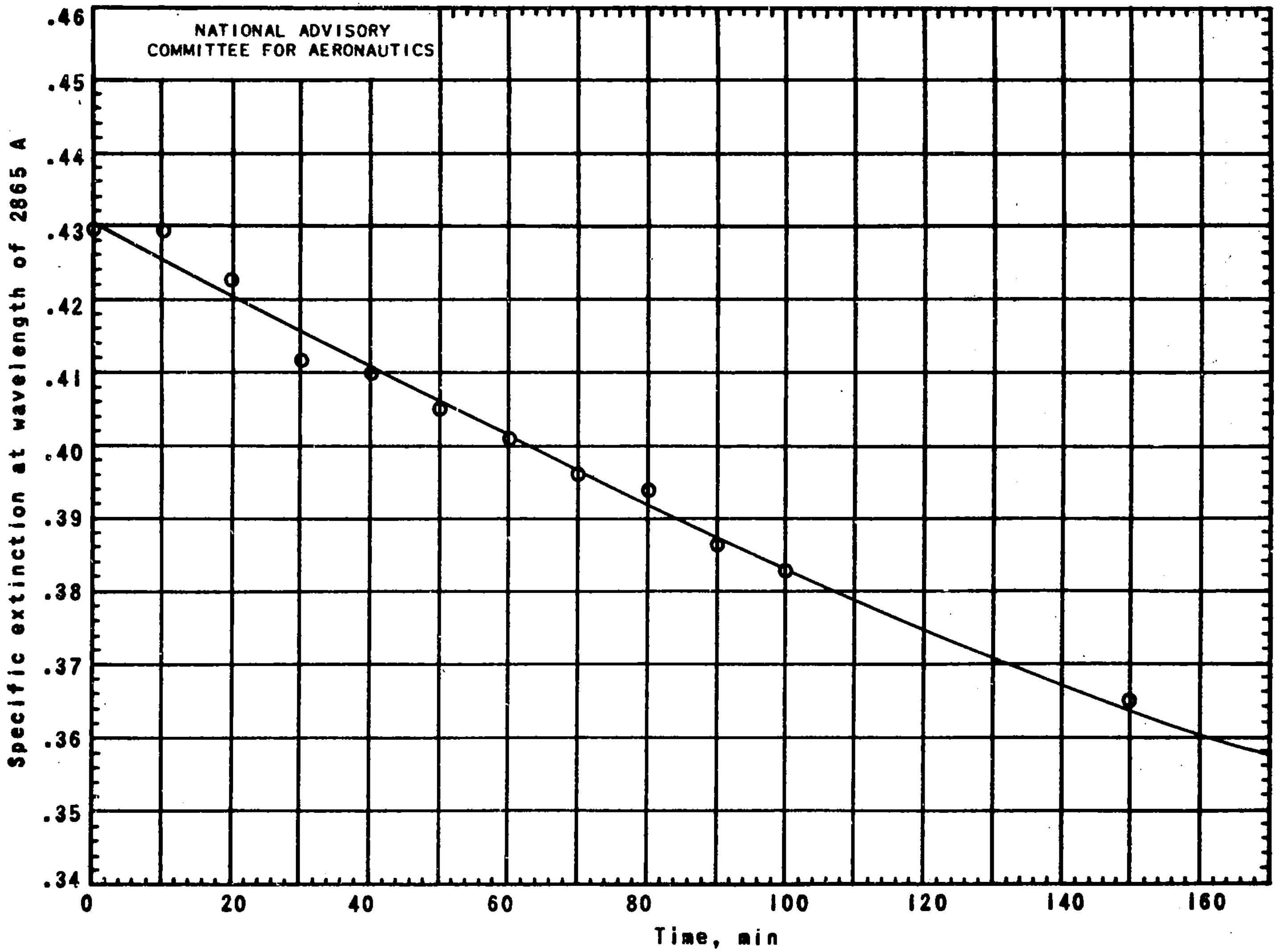


Figure 4. - Effect of exposure of N-isopropylaniline in water solution to ultraviolet light in spectrophotometer. Amine concentration, approximately 0.045 gram per liter. Slit widths, 0.5 millimeter.

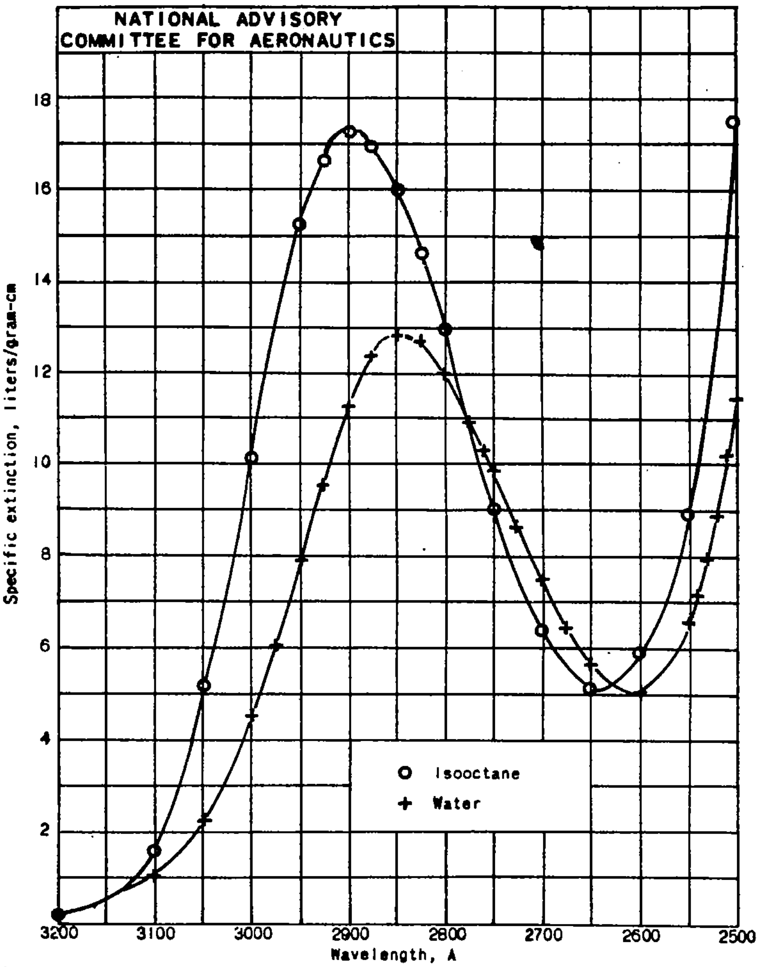
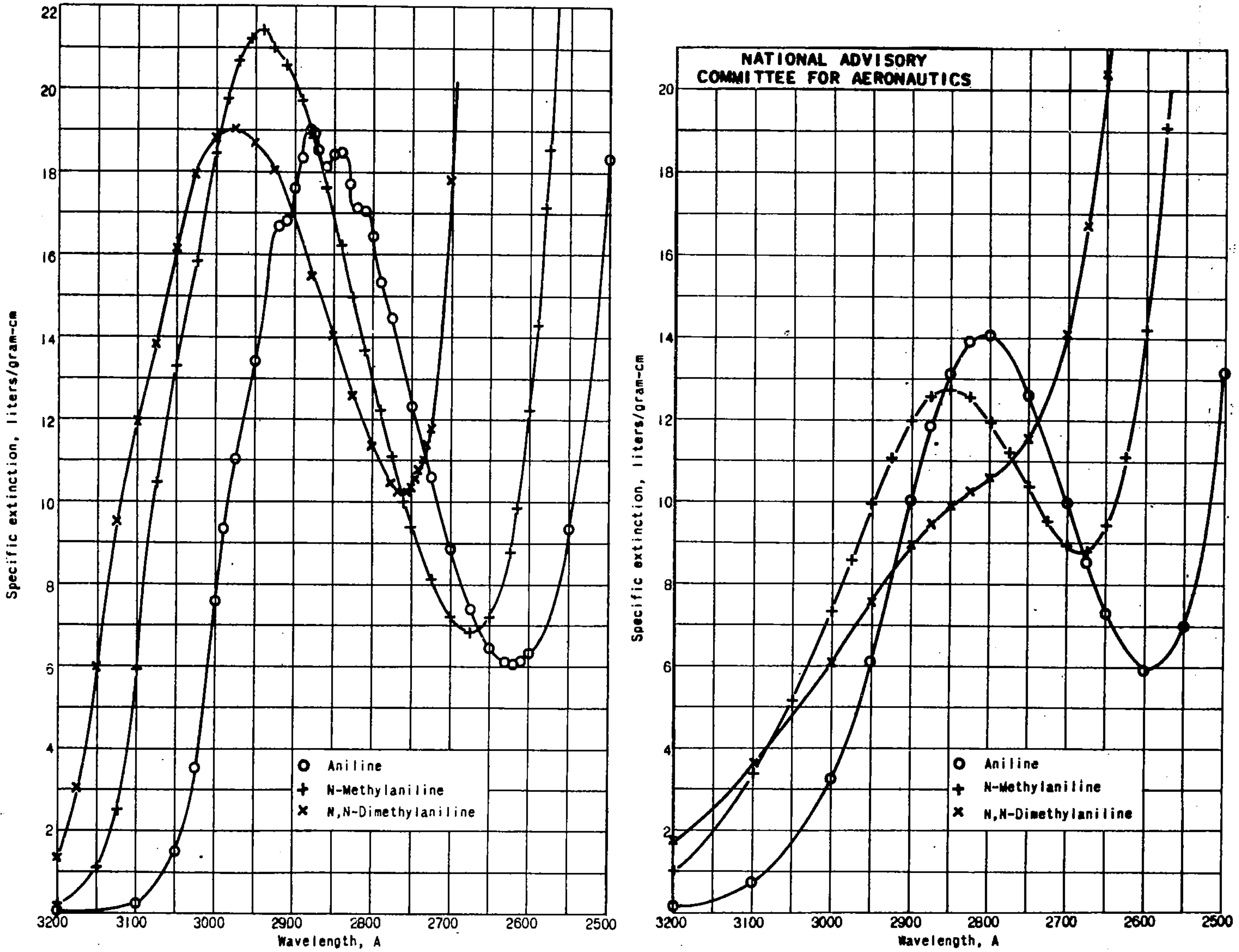


Figure 5. - Absorption spectrum of technical xylidines in isooctane and in water.

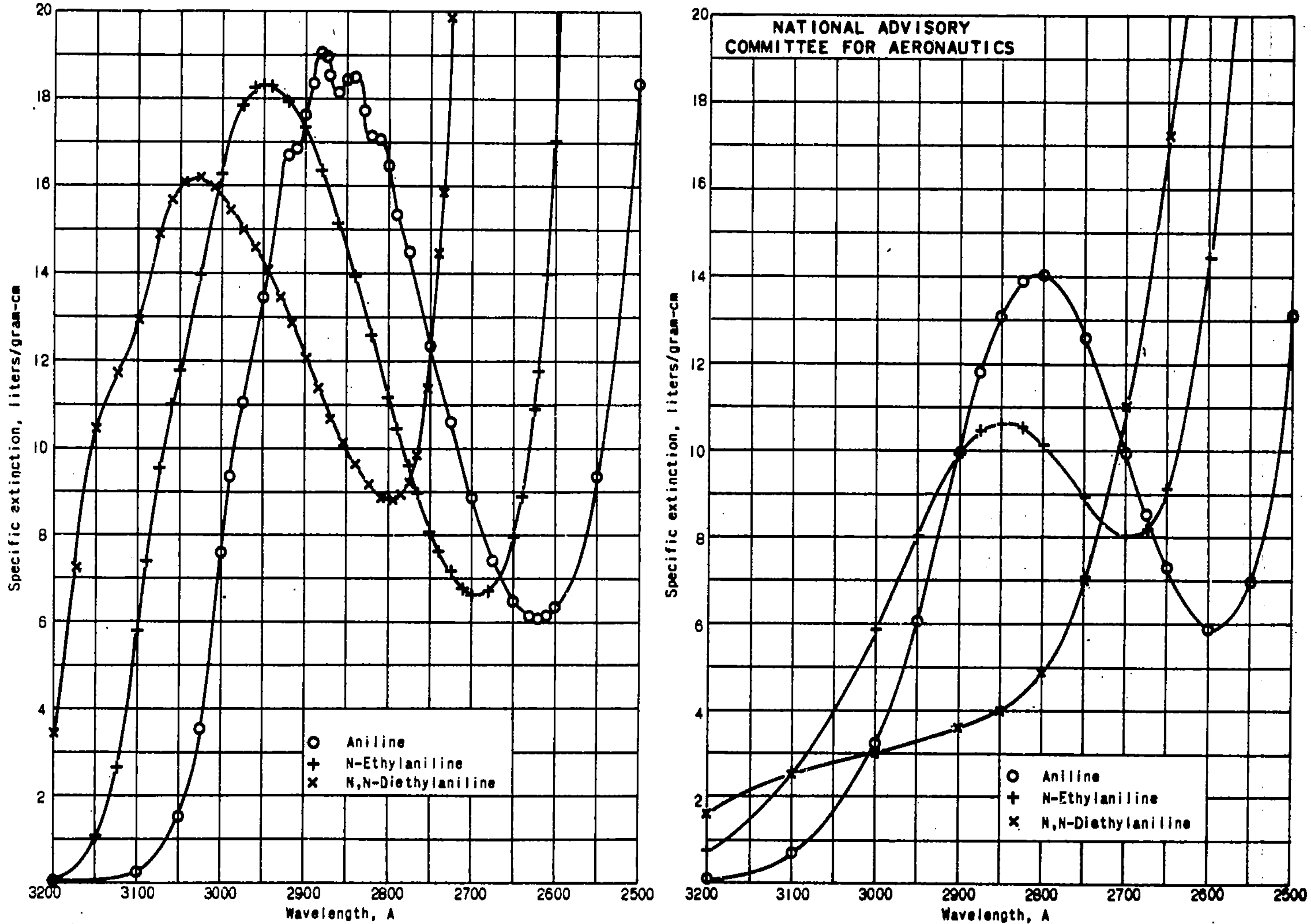


(a) Isooctane.

(b) Water.

Figure 6. - Absorption spectra of aniline, N-methylaniline, and N,N-dimethylaniline in isooctane and in water.

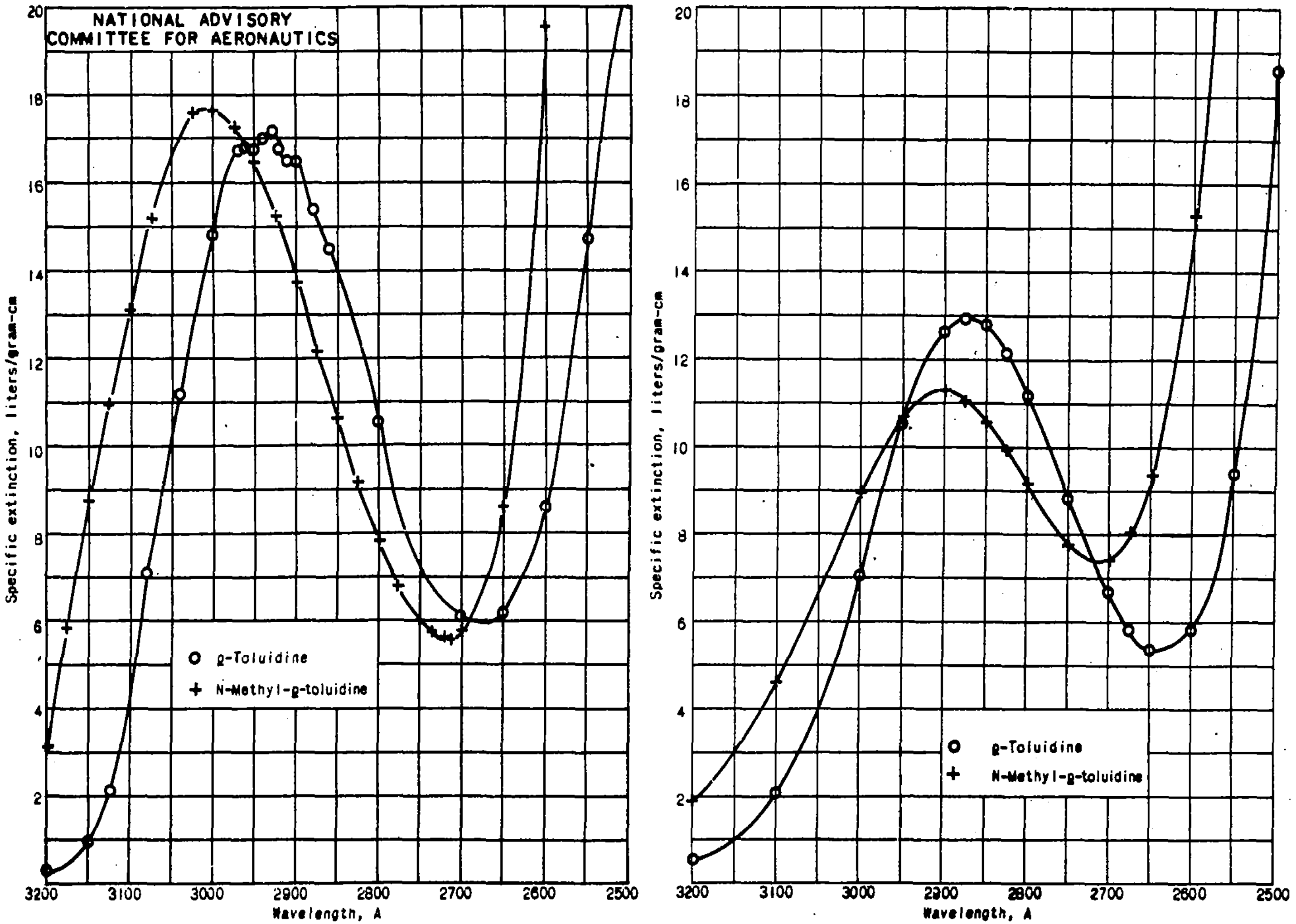
Fig. 6



(a) Isooctane.

(b) Water.

Figure 7. - Absorption spectra of aniline, N-ethylaniline, and N,N-diethylaniline in isooctane and in water.

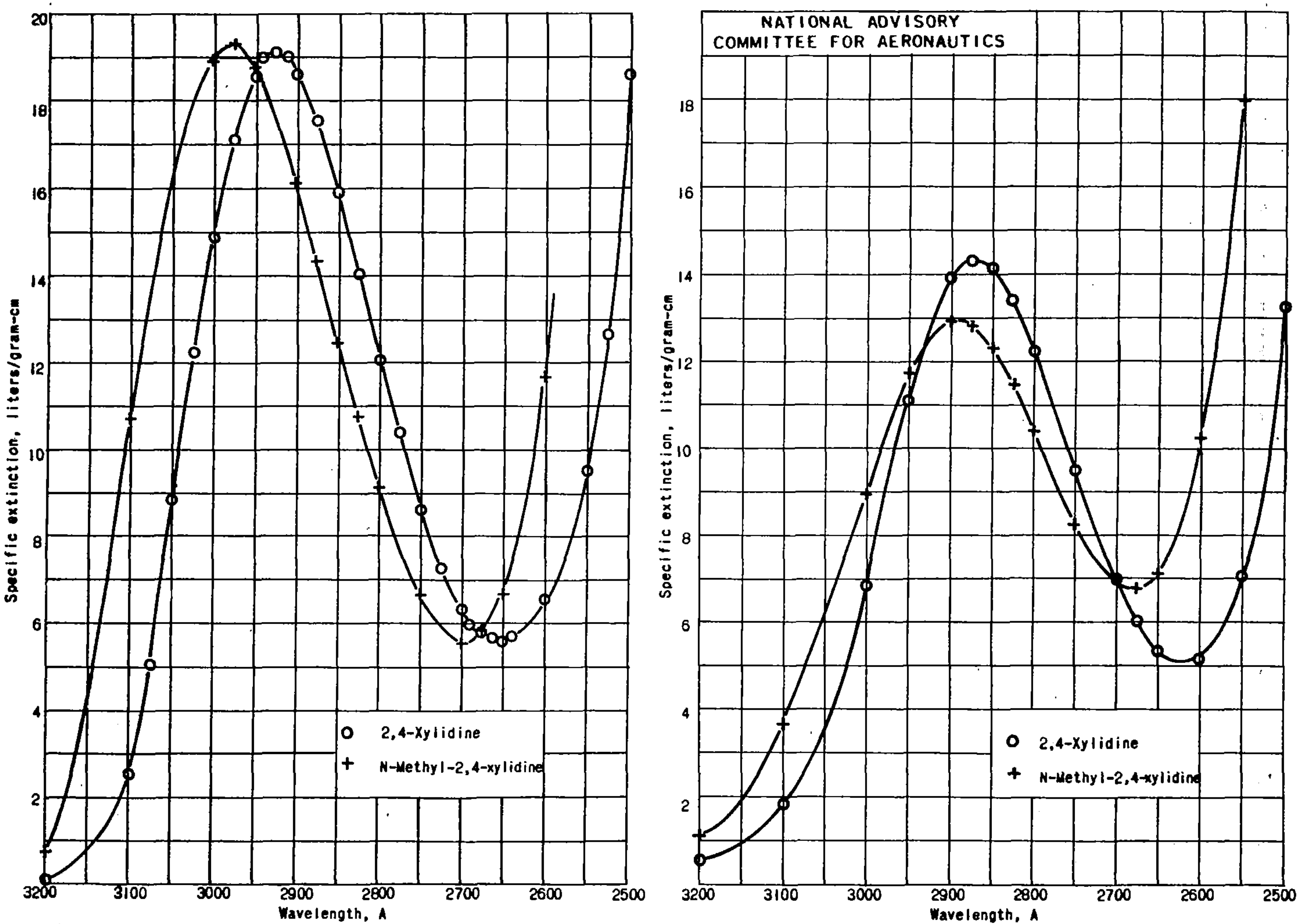


(a) Isooctane.

(b) Water.

Figure 8. - Absorption spectra of p-toluidine and N-methyl-p-toluidine in isooctane and in water.

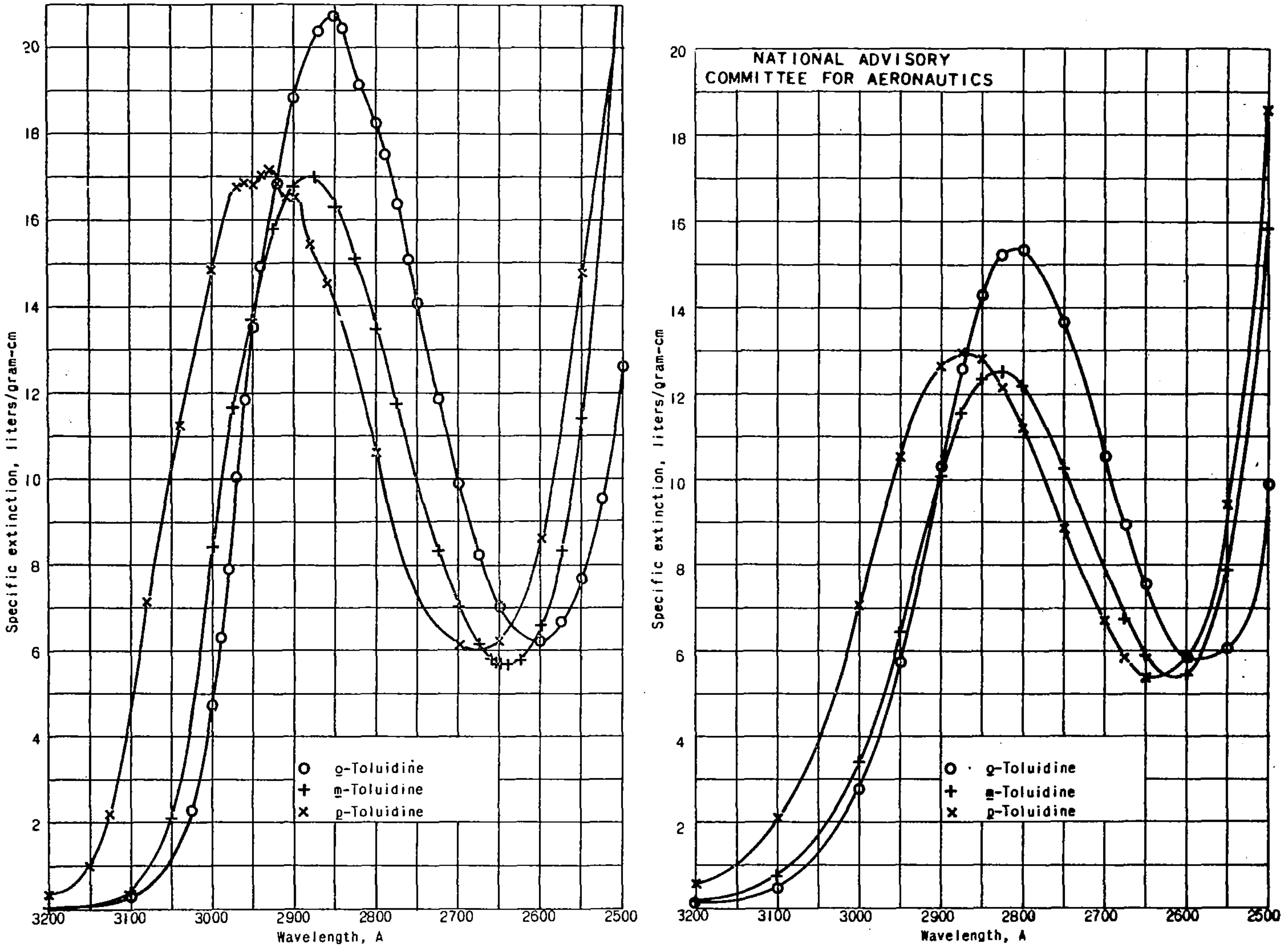
Fig. 9



(a) Isooctane.

(b) Water.

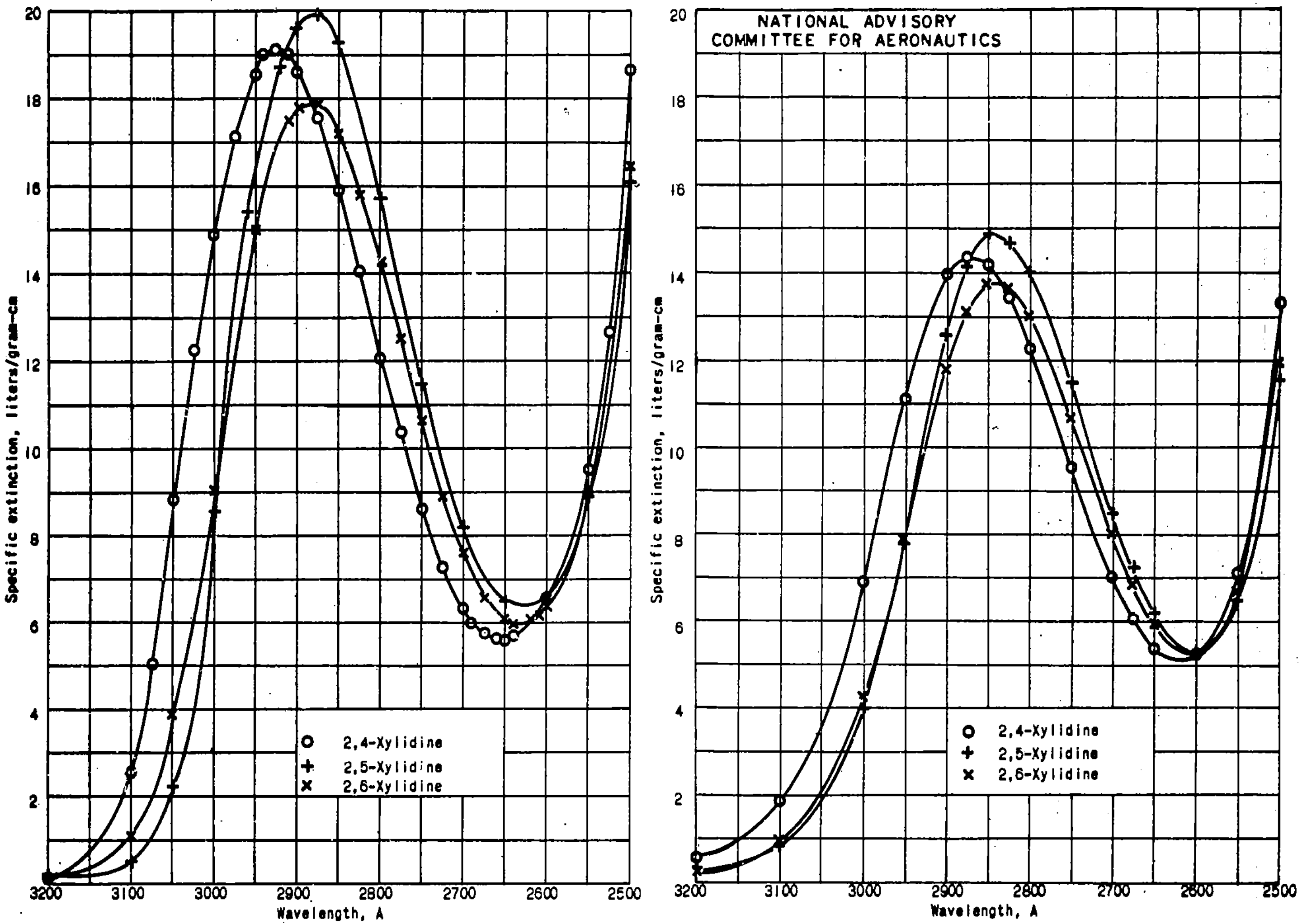
Figure 9. - Absorption spectra of 2-4-xylidine and N-methyl-2,4-xylidine in isooctane and in water.



(a) Isooctane.

(b) Water.

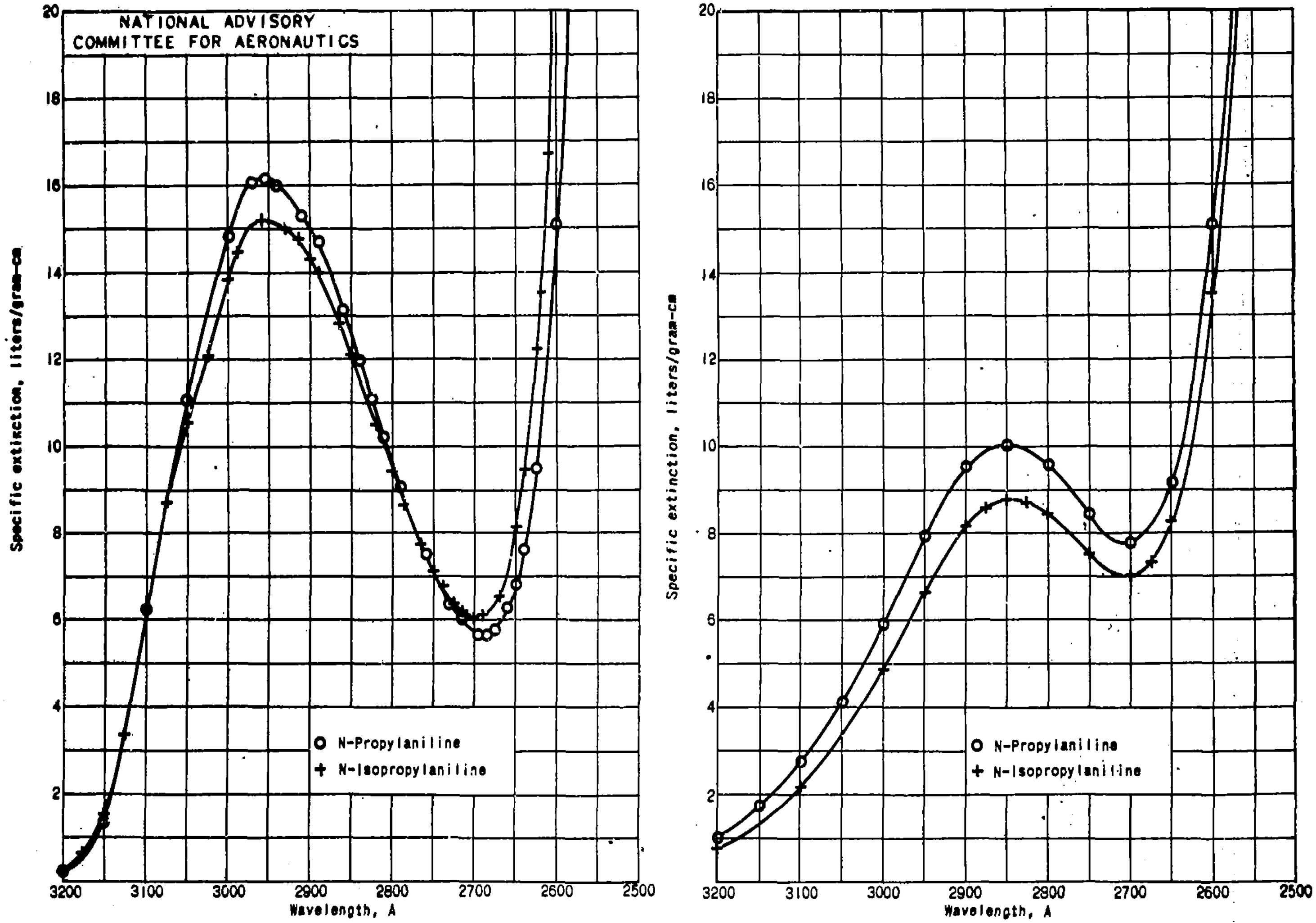
Figure 10. - Absorption spectra of toluidines in isooctane and in water.



(a) Isooctane.

(b) Water.

Figure 11. - Absorption spectra of three xylidines in isooctane and in water.

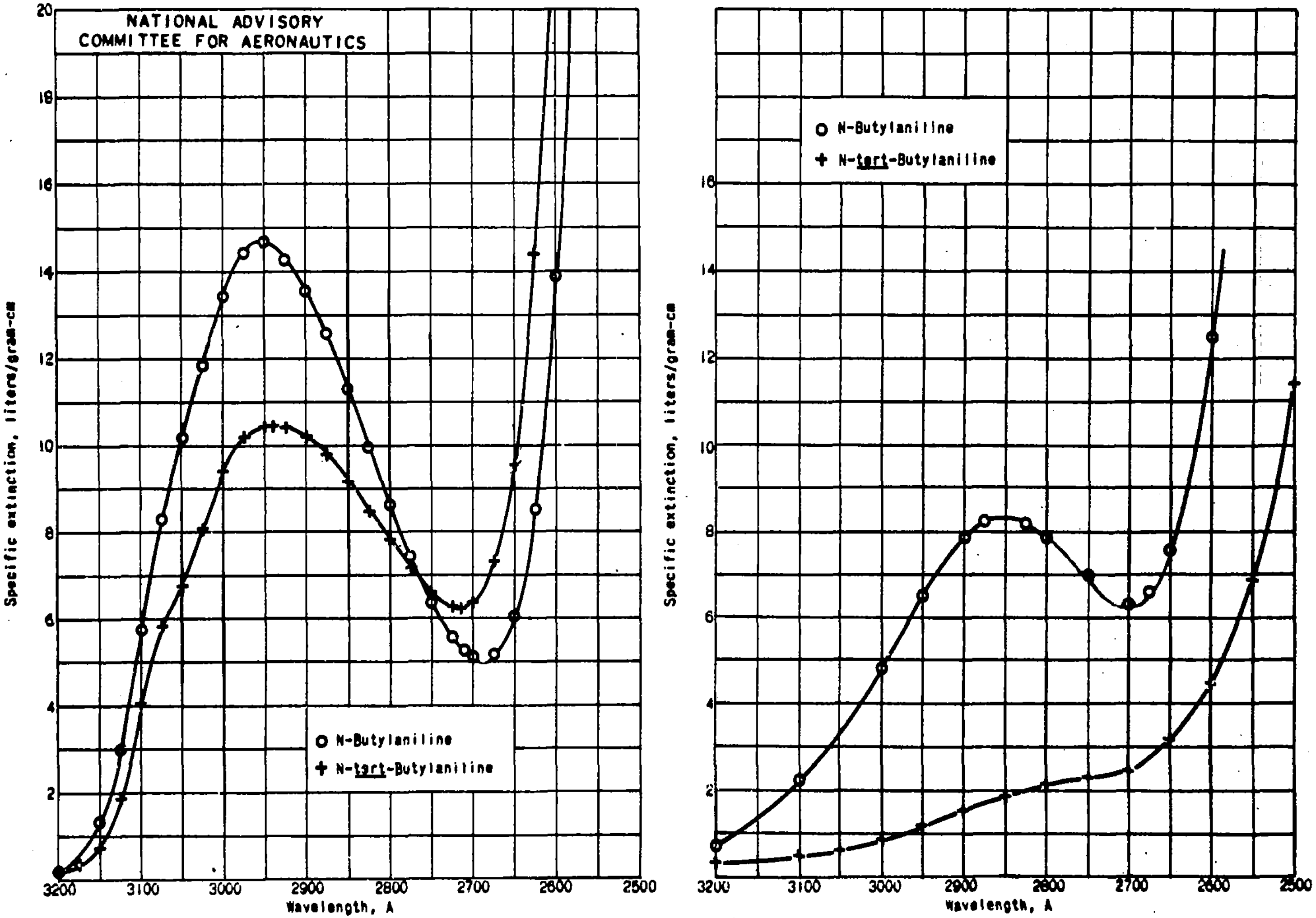


(a) Isooctane.

(b) Water.

Figure 12. - Absorption spectra of N-propylaniline and N-isopropylaniline in isooctane and in water.

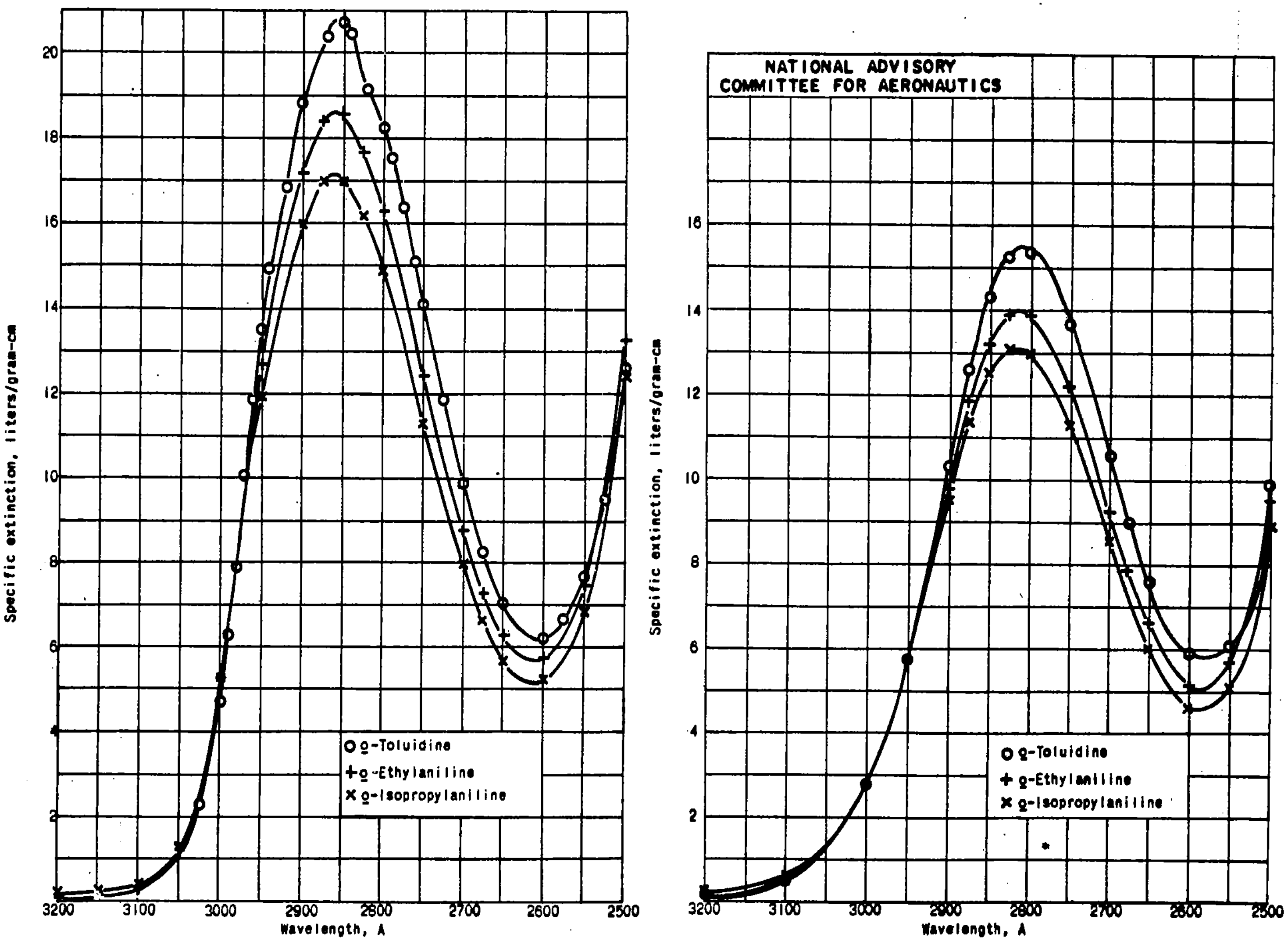
Fig. 12



(a) Isooctane.

(b) Water.

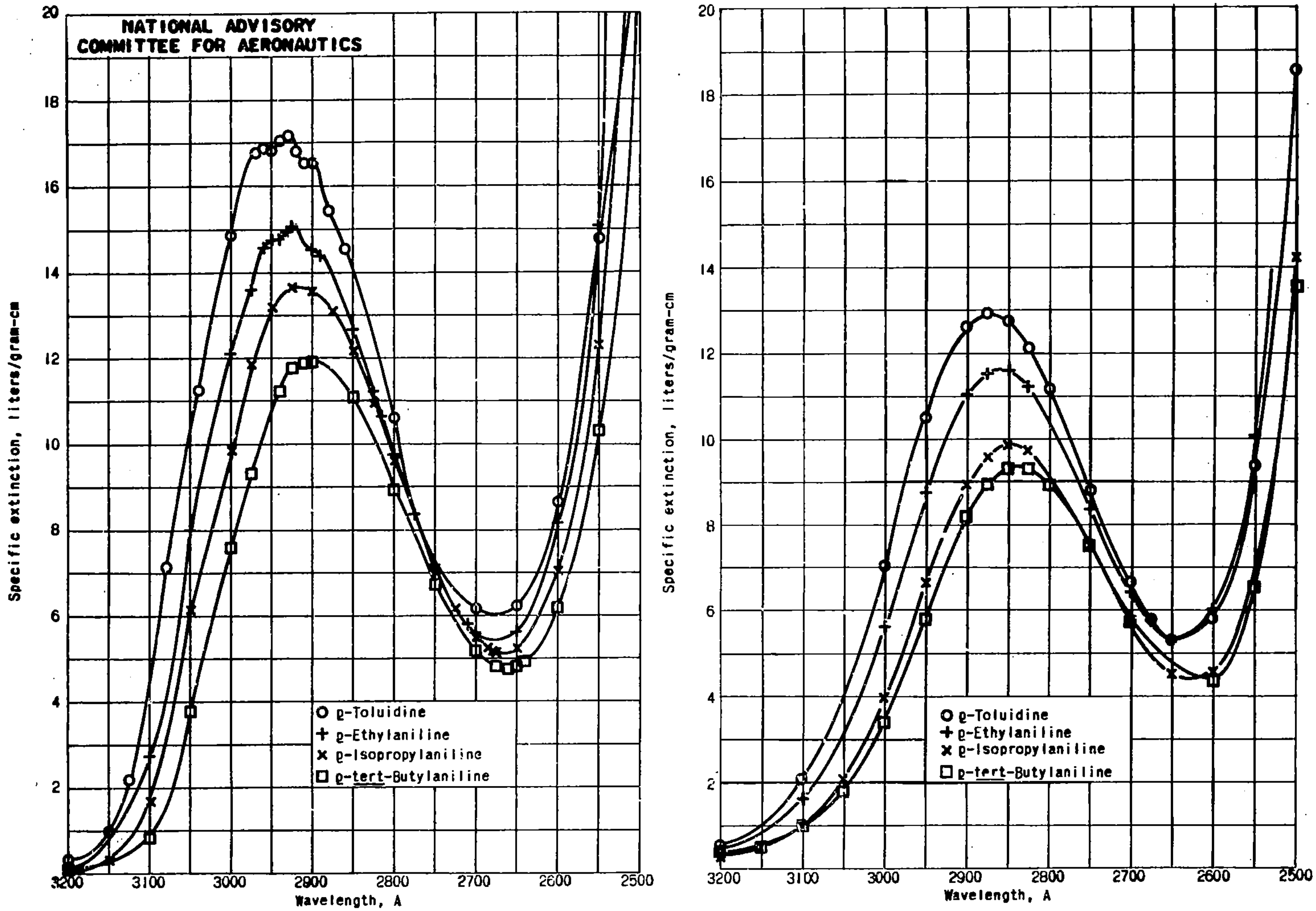
Figure 13. - Absorption spectra of N-butylanilines and N-*tert*-butylaniline in isooctane and in water.



(a) Isooctane.

(b) Water.

Figure 14. - Absorption spectra of three o-alkylanilines in isooctane and in water.

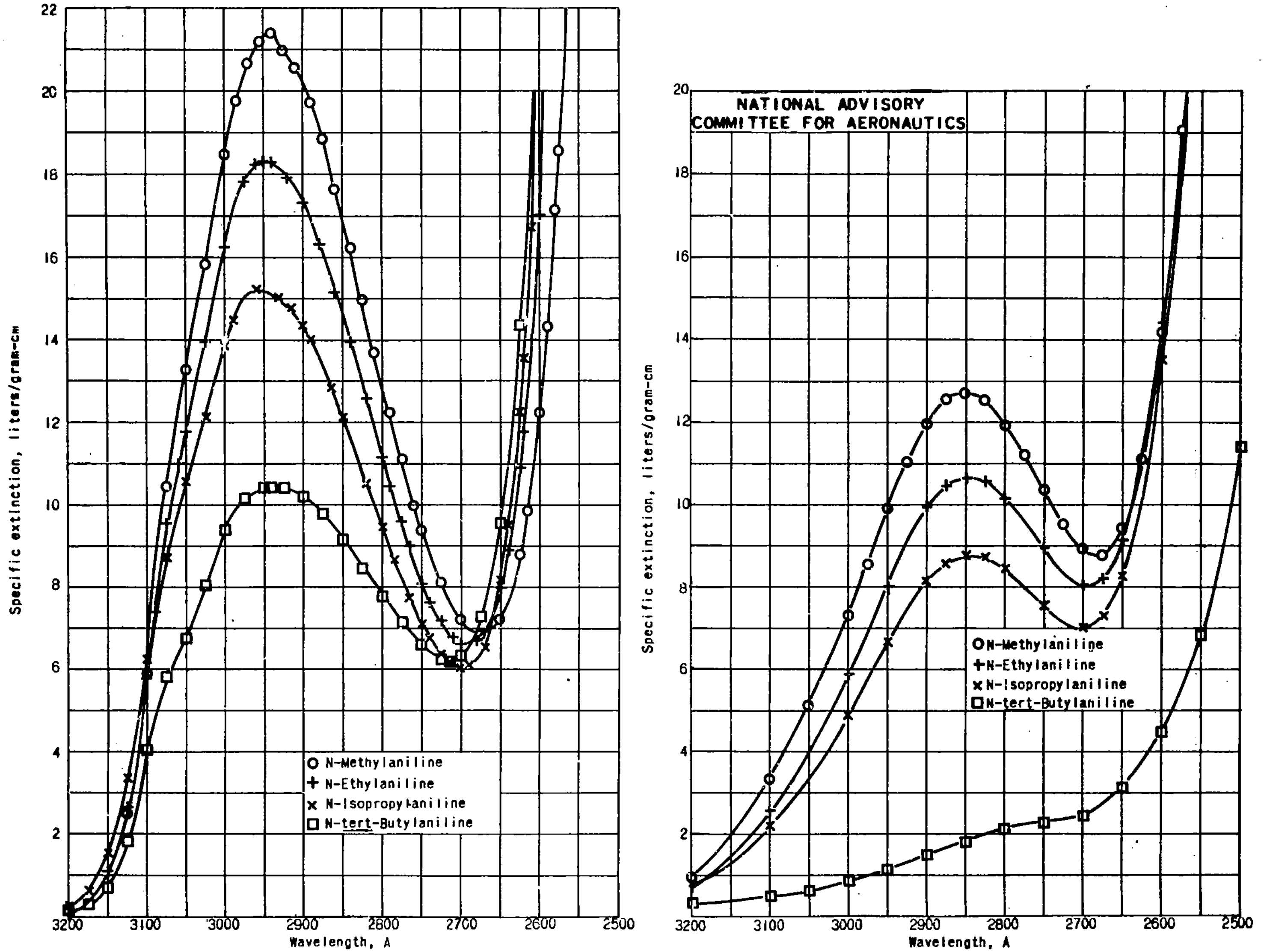


(a) Isooctane.

(b) Water:

Figure 15. - Absorption spectra of four p-alkylanilines in isooctane and in water.

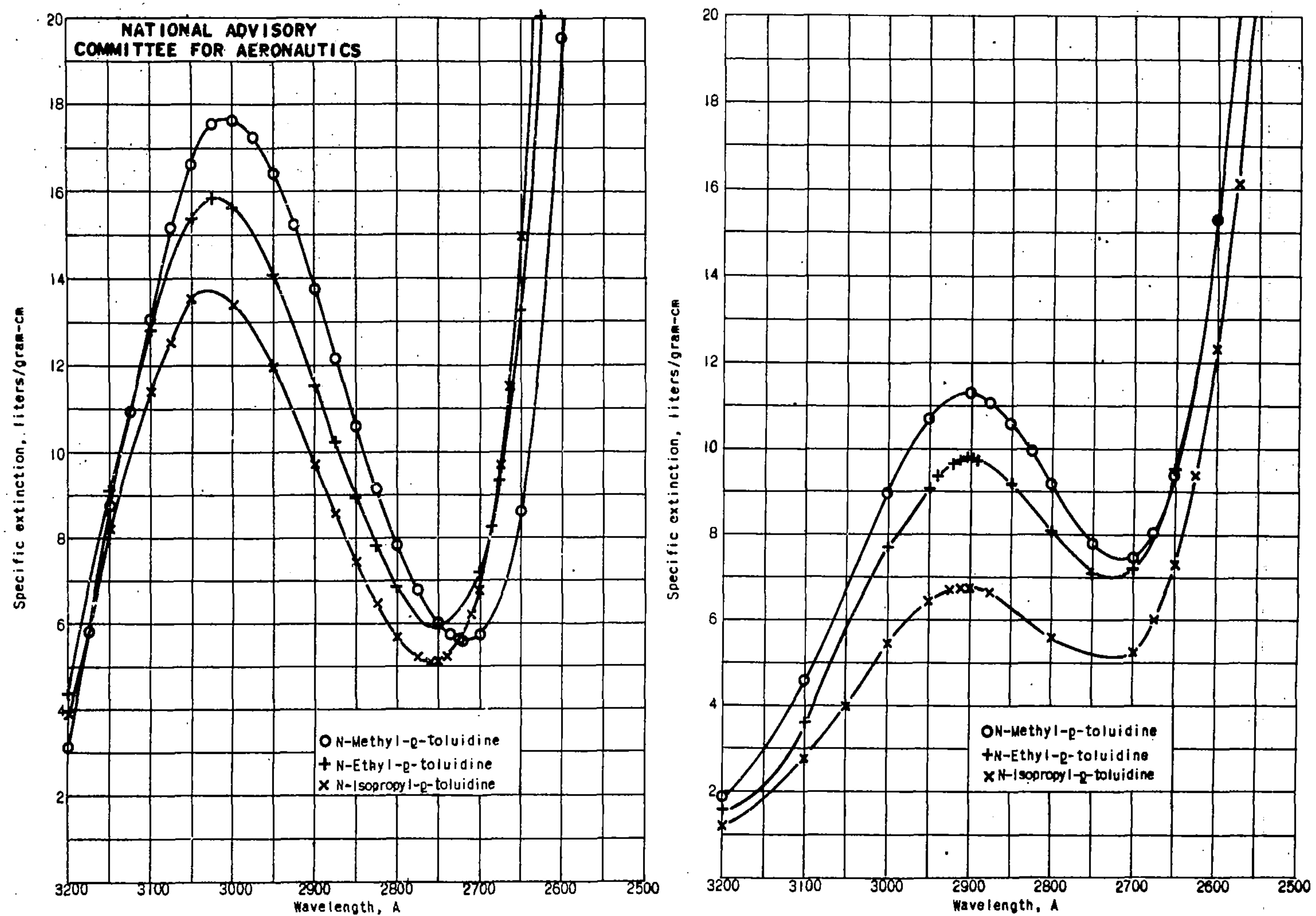
Fig. 16



(a) Isooctane.

(b) Water.

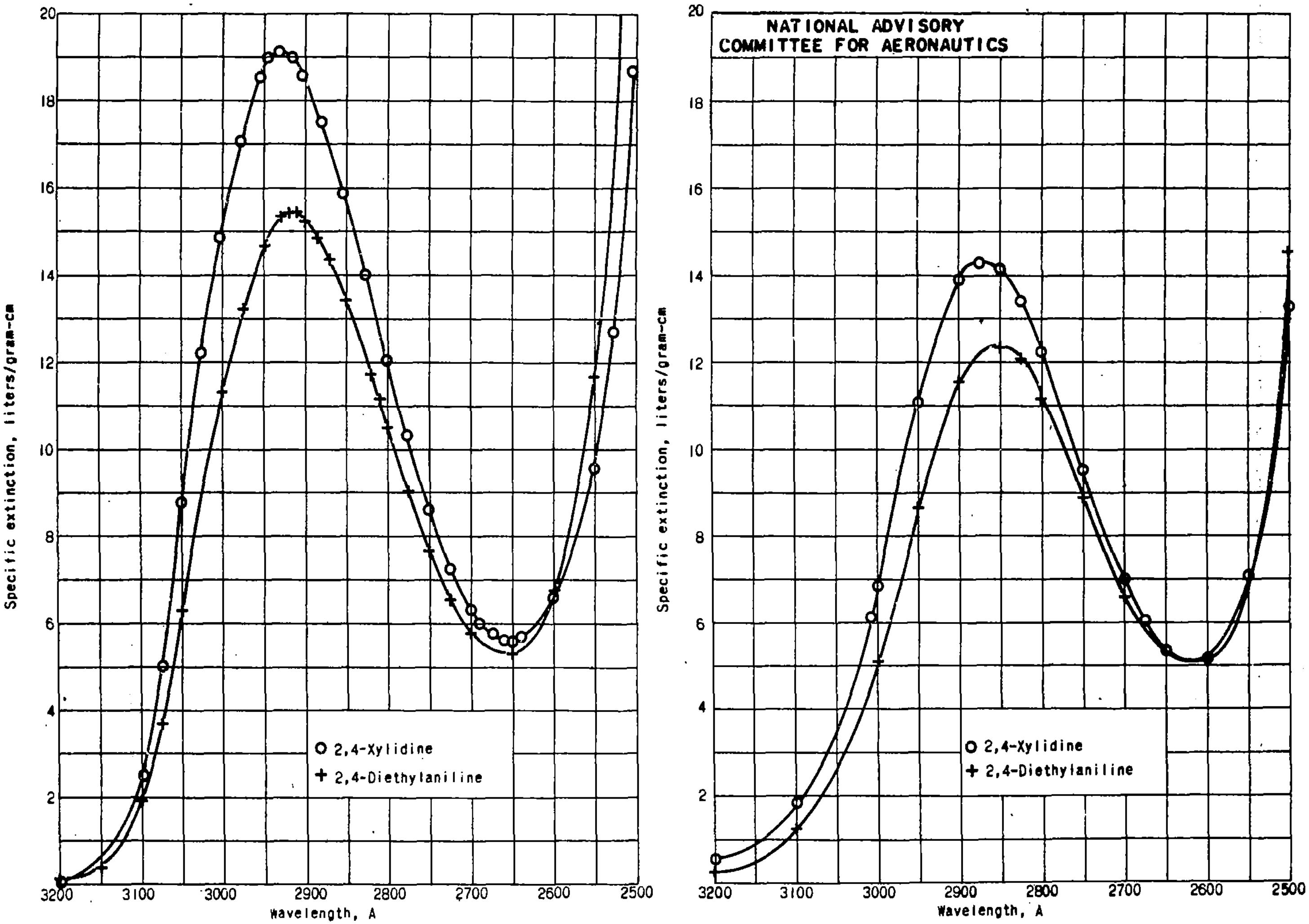
Figure 16. - Absorption spectra of four N-alkylanilines in isooctane and in water.



(a) Isooctane.

(b) Water.

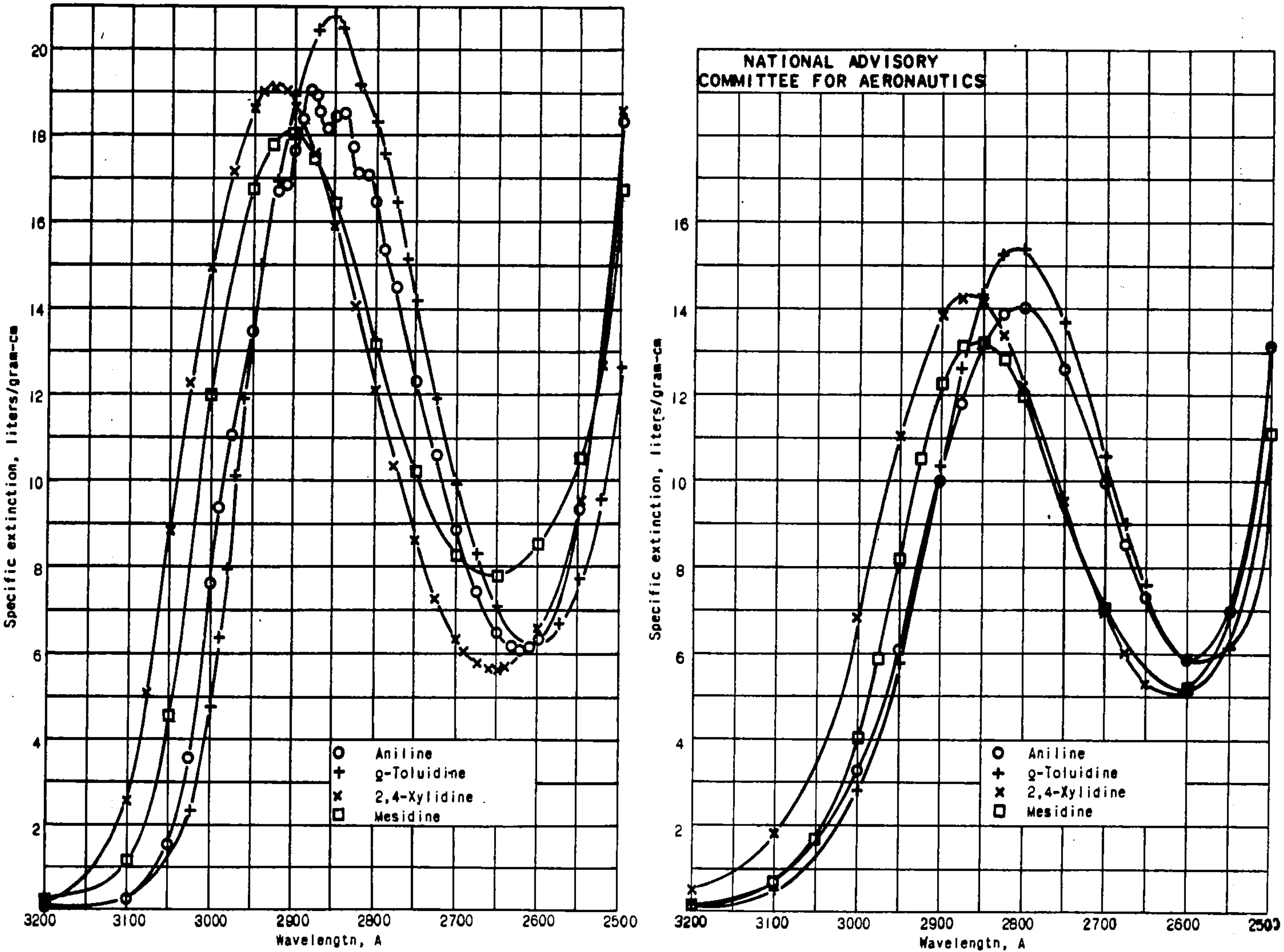
Figure 17. - Absorption spectra of three N-alkyl-p-toluidines in isooctane and in water.



(a) Isooctane.

(b) Water.

Figure 18. - Absorption spectra of 2,4-xylidine and 2,4-diethylaniline in isooctane and in water.



(a) Isooctane.

(b) Water.

Figure 19. - Absorption spectra of aniline, o-toluidine, 2,4-xylidine, and mesidine in isooctane and in water.