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THE LOW-TEMPERATURE SOLUBILITY OF ANILINE, THE TOLUIDINES, AND SOME OF THEIR N-ALKYL DERIVATIVES IN AVIATION GASOLINE

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

MEMORANDUM REPORT

for the

Army Air Forces, Materiel Command

THE LOW-TEMPERATURE SOLUBILITY OF ANILINE, THE TOLUIDINES, AND SOME OF THEIR N-ALKYL DERIVATIVES IN AVIATION GASOLINE

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SUMMARY

Tests were made to determine the solubilities in gasoline at low temperatures of 15 of the aromatic amines from the NACA exploratory program on aromatic amines as antiknock additives. Solubilities of aniline, the toluidines, and several of their respective N-alkyl derivatives were measured in three different gasolines at temperatures as low as -65° C and at concentrations as high as 16 percent by weight. Solubility at -60° C was a particular objective of the test work.

The solubility data for the amines are summarized in the following table by interpolating or extrapolating the experimental results to obtain the solubility at -60° C. The data for the xylidines are included for comparison.

SOLUBILITY OF AROMATIC AMINES IN THREE AVIATION FUELS AT -60° C

[Percentages by weight]

Amine	Grade 65, aromatics extracted	Extracted grade 65 plus 15 percent (by volume) aromatics[a]	Grade 130[b]
Aniline	< 0.5	0.5	----------
N-Methylaniline	3.6	12.0(-62° C)	14.3
N-Ethylaniline	>10	>10	>10
N-Propylaniline	>10	>10	>10
N-Isopropylaniline	>10	>10	>10
N-Butylaniline	2.0	5.6	3.8
N-tert-Butylaniline	>10	>10	>10
N,N-Dimethylaniline	4.7	9.7	8.3
N,N-Diethylaniline	>10	>10	>10
o-Toluidine	1.3	4.2	4.4
m-Toluidine	<0.5	2.6	3.6
p-Toluidine	<0.5	<0.5	<0.5
N-Methyl-p-toluidine	>10	>10	>10
N-Ethyl-p-toluidine	>10	>10	>10
N-Isopropyl-p-toluidine	>10	>10	>10
Xylidines (commercial)[c]	3.7	>10	>10

[a]Mixed aromatics consisted of five parts xylene, two parts cumene, and one part toluene.

[b]Specification AN-F-28, Amendment-2.

[c]Previously reported.

INTRODUCTION

At the request of the Army Air Forces, Materiel Command, the NACA is conducting at its aircraft engine research laboratory a general investigation on the suitability of aromatic amines as antiknock components for aviation gasoline. The initial program comprises, as exploratory tests, the determination of antiknock effectiveness, solubility in gasoline at low temperatures, and suitability for overwater storage of 30 or 40 structurally related aromatic amines. Data on knock-limited power for 12 of these amines have been presented in reference 1.

The purpose of this report is to present the solubilities in gasoline at low temperatures of 15 of the aromatic amines from this program; namely, aniline, the toluidines, and several of their respective N-alkyl derivatives. Solubilities were measured at temperatures as low as -65° C, 5° below the usual Army-Navy solubility specification of -60° C, and at concentrations as high as 16 percent by weight, well above the 1- to 3-percent range in which the amines would normally be used in gasoline. Solubility at -60° C was a particular objective in obtaining the data.

In 1943 R. F. Marschner of the Standard Oil Company prepared a memorandum of some of the scattered data on the separation temperatures of amines in aviation gasolines; this memorandum indicates the marked effect of gasoline composition upon the separation temperature. In order to permit observation of the effect of fuel composition on solubility, the fuels chosen for the solubility measurements herein reported were an aromatic-free gasoline, a gasoline of known aromatic composition, and a typical current grade 130 aviation fuel.

Acknowledgement is made to Dr. A. R. Jensen of the Fuels and Lubricants Division at Cleveland for his contributions to the analytical techniques used.

The tests reported herein were conducted during April 1943 to March 1944.

APPARATUS AND PROCEDURE

Cloud-point method. - The general method for determining low-temperature solubility was to cool a solution of known concentration to the temperature at which incipient separation of the sample was observed, the cloud point. The apparatus used, which provides stirring and convenient temperature control of the sample, is shown in figure 1 and has been previously described in reference 2. For some of the amines this method was not used because supercooling of the test sample failed to give reproducible values for the incipient-separation temperatures.

Saturation method. - For the cases where supercooling of the amine solution made the direct measurement of the cloud point unreliable, excess amine was added to the gasoline and a sample of the resulting saturated gasoline solution was withdrawn at a constant temperature for analysis.

The apparatus used to obtain the samples is shown in figure 2. About 150 milliliters of an amine solution is put into the test tube. The filter tube is emptied of solution by blowing air through this tube until bubbles appear at the chamois filter; the pinch clamp is thon closed. The solution is cooled and stirred until amine separates from the gasoline. At constant temperature, a sample of the saturated gasoline solution is drawn through the filter tube into the receiving vessel by slightly reducing the pressure in this vessel. The receiving vessel is maintained at a low temperature to minimize vaporization losses from the samples.

For analysis, a portion of the cold sample was transferred to a tared, tightly stoppered bottle and weighed. This sample was then extracted in a separatory funnel with three successive 5-milliliter portions of 1:1 hydrochloric acid (HCl). The acid extract was transferred quantitatively to a 50-milliliter bottle with a narrow calibrated neck. (Babcock milk test bottles were found to be satisfactory.) In order to liberate the amine, 20 to 25 milliliters of 45-percent potassium hydroxide (KOH) was added, together with sufficient water to raise the liquid level within the range of the graduated neck. The bottle was centrifuged in an 11-inch radius centrifuge at 1700 rpm for about 5 mintues. The graduated bottle was cooled at 20° C in a constant-temperature bath and the volume of amine read directly to within ±0.03 milliliter. This volume and the amine density were used to calculate weight percentage. Data obtained by this method for methylaniline were found to be in agreement with cloud-point data in the region of -60° C.

An alternate method of analysis (reference 3) involving the use of phthalic anhydride was used for the amines that were solid or too soluble in water at 20° C to permit use of the centrifugal analysis. The gasoline sample was mixed with a dry benzene solution containing a weighed amount of phthalic anhydride. The mixture was periodically shaken for 45 mintues. Standard aqueous 0.1 normal KOH was then added in an amount equivalent to the phthalic anhydride. The excess KOH was titrated with standard 0.05 normal HCl to a phenolphthalein end point. The weight percentage of amine was calculated as follows:

$$\text{Weight percentage amine} = \frac{100\ (\text{mol. wt. amine})(\text{ml of acid})\ (\text{normality of acid})}{(\text{wt. of amine-gasoline sample})\ (1000)}$$

GASOLINE AND AROMATIC-AMINE SPECIMENS

The following three fuels were used for all the solubility determinations:

1. Grade 65 base stock from which the aromatic hydrocarbons were successively extracted with 10 percent fuming sulfuric acid and silica gel

2. The extracted grade 65 gasoline to which was added 15 percent by volume of an aromatic-amine mixture consisting of five parts xylene, two parts cumene, and one part toluene

3. Grade 130, specification AN-F-28, Amendment-2. (Different batches of this fuel were used during the course of the tests.)

The aromatic amines tested (see table I) either were purchased as the best grade obtainable and subsequently purified or were synthesized and purified at this laboratory. All are believed to be at least 95 percent pure.

RESULTS AND DISCUSSION

Figures 3, 4, and 5 present the solubilities of the amines in the aromatic-free gasoline, in the gasoline of 15 percent aromatic content, and in the grade 130 fuel, respectively. The amines not appearing on the curves were soluble to at least 10 percent by weight at -60° C in each of the gasolines. They were:

N-Ethylaniline
N-Propylaniline
N-Isopropylaniline
N-tert-Butylaniline
N,N-Diethylaniline
N-Methyl-p-toluidine
N-Ethyl-p-toluidine
N-Isopropyl-p-toluidine

The greater solubilizing effect of the methyl radical when attached to the nitrogen of aniline than when attached to the aromatic ring is noted. Lengthening the carbon chain attached to the nitrogen of aniline resulted in greater gasoline solubility for only a limited chain length, as evidenced by the relatively low solubility of N-butylaniline compared with N-propylaniline.

The composition of the gasoline influenced the amine solubilities to a large extent; 15 percent aromatics added to the fuel approximately doubled or trebled the amine solubility. Solubility of the amines in the grade 130 gasoline was similar to that in the gasoline containing 15 percent added aromatics. Representative samples of the various batches of grade 130 fuel generally contain 12 to 20 percent aromatics.

The solubility of an aromatic amine in the aromatic-free aviation gasoline at -60° C may be taken as an indication of the maximum concentration to which the amine may be used in current aviation gasolines on the basis of solubility alone. The aromatic hydrocarbons present in most of the current gasolines would provide a margin of safety in preventing separation of the amine at -60° C.

SUMMARY OF RESULTS

The solubilities of aromatic amines at -60° C as determined by interpolating or extrapolating the experimental data are presented in table II. The data for xylidines are included for comparison.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, June 5, 1944.

REFERENCES

1. Branstetter, J. Robert: Knock-Limited Performance of Blends of AN-F-28 Fuel Containing 2 Percent Aromatic Amines - I. NACA Memo. rep., April 17, 1944.

2. Olson, Walter T.: The Low-Temperature Solubility of Technical Xylidines in Aviation Gasoline. NACA Memo. rep., June 4, 1943.

3. Kamm, Oliver: Qualitative Organic Analysis. John Wiley & Sons, Inc., 2d ed., 1932, p. 208.

TABLE I

PHYSICAL PROPERTIES OF AROMATIC AMINES TESTED

Amine	Boiling range at 760 mm (°C)	Index of refraction, $n_{D\,20^\circ C}$	Density, $d_{20^\circ C}$ (grams/ml)
Aniline	184.0 - 184.5	1.5853	1.0220
N-Methylaniline	195.0 - 196.0	1.5704	.9860
N-Ethylaniline	204.0 - 205.0	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	----------	----------
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

[a]Distilled under reduced pressure.

[b]Melting point was measured instead of boiling range for this solid.

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TABLE II

SOLUBILITY OF AROMATIC AMINES IN THREE AVIATION FUELS AT -60° C

[Percentages by weight]

Amine	Grade 65, aromatics extracted	Extracted grade 65 plus 15 percent (by volume) aromatics[a]	Grade 130[b]
Aniline	<0.5	0.5	-----------
N-Methylaniline	3.6	12.0 (-62° C)	14.3
N-Ethylaniline	>10	>10	>10
N-Propylaniline	>10	>10	>10
N-Isopropylaniline	>10	>10	>10
N-Butylaniline	[c]2.0	[c]5.6	[c]3.8
N-tert-Butylaniline	>10	>10	>10
N,N-Dimethylaniline	4.7	9.7	8.3
N,N-Diethylaniline	>10	>10	>10
o-Toluidine	1.3	4.2	4.4
m-Toluidine	< 0.5	2.6	3.6
p-Toluidine	[d]<0.5	[d]< 0.5	[d]< 0.5
N-Methyl-p-toluidine	>10	>10	>10
N-Ethyl-p-toluidine	>10	>10	>10
N-Isopropyl-p-toluidine	>10	>10	>10
Xylidines (commercial)[e]	3.7	>10	>10

[a]Mixed aromatics consisted of five parts xylene, two parts cumene, and one part toluene.

[b]Specification AN-F-28, Amendment-2 (different batches used).

[c]Saturation method, centrifugal analysis.

[d]Saturation method, phthalic-anhydride analysis.

[e]Data from reference 2.

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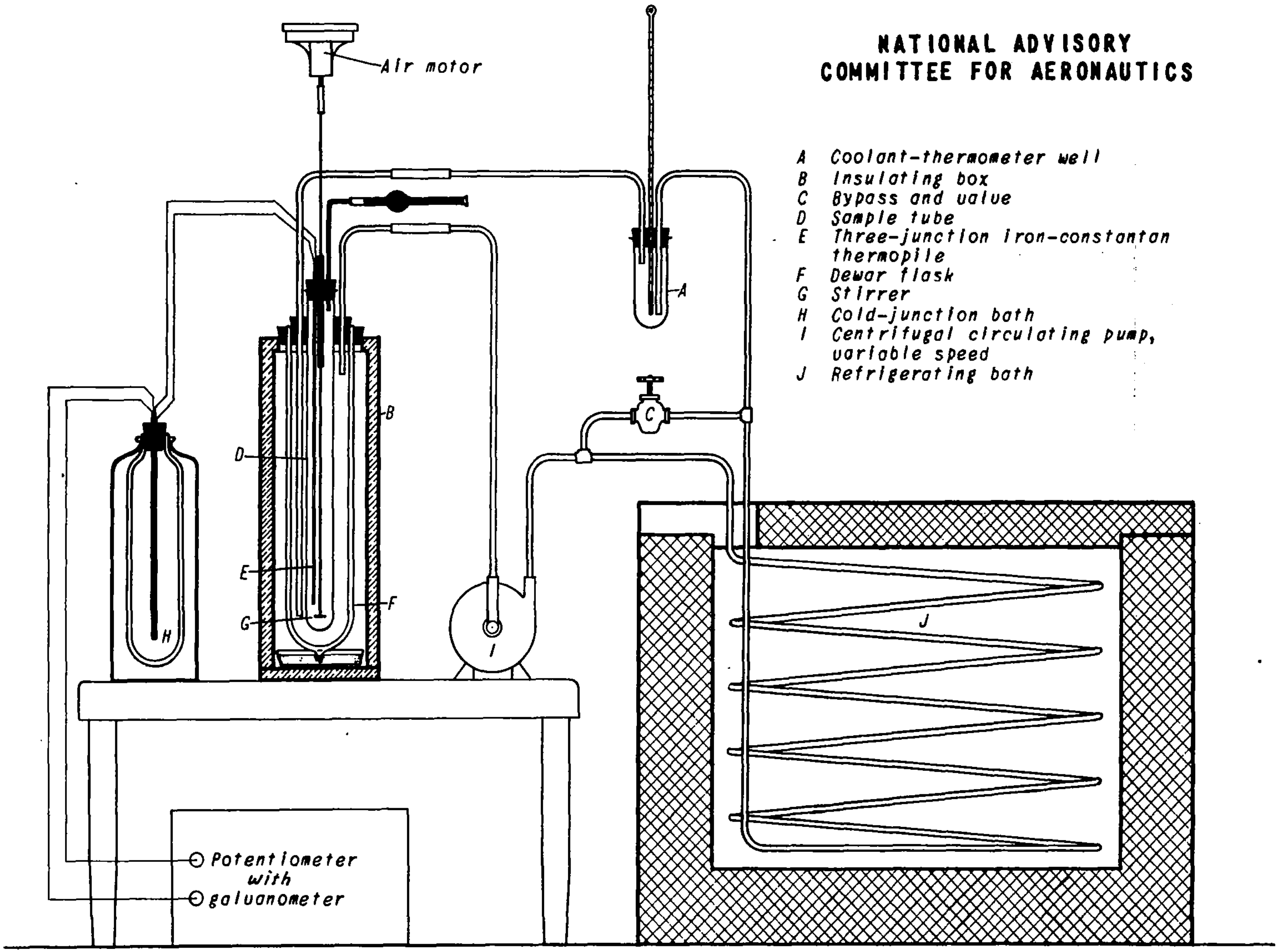

Figure 1. - Cloud-point apparatus.

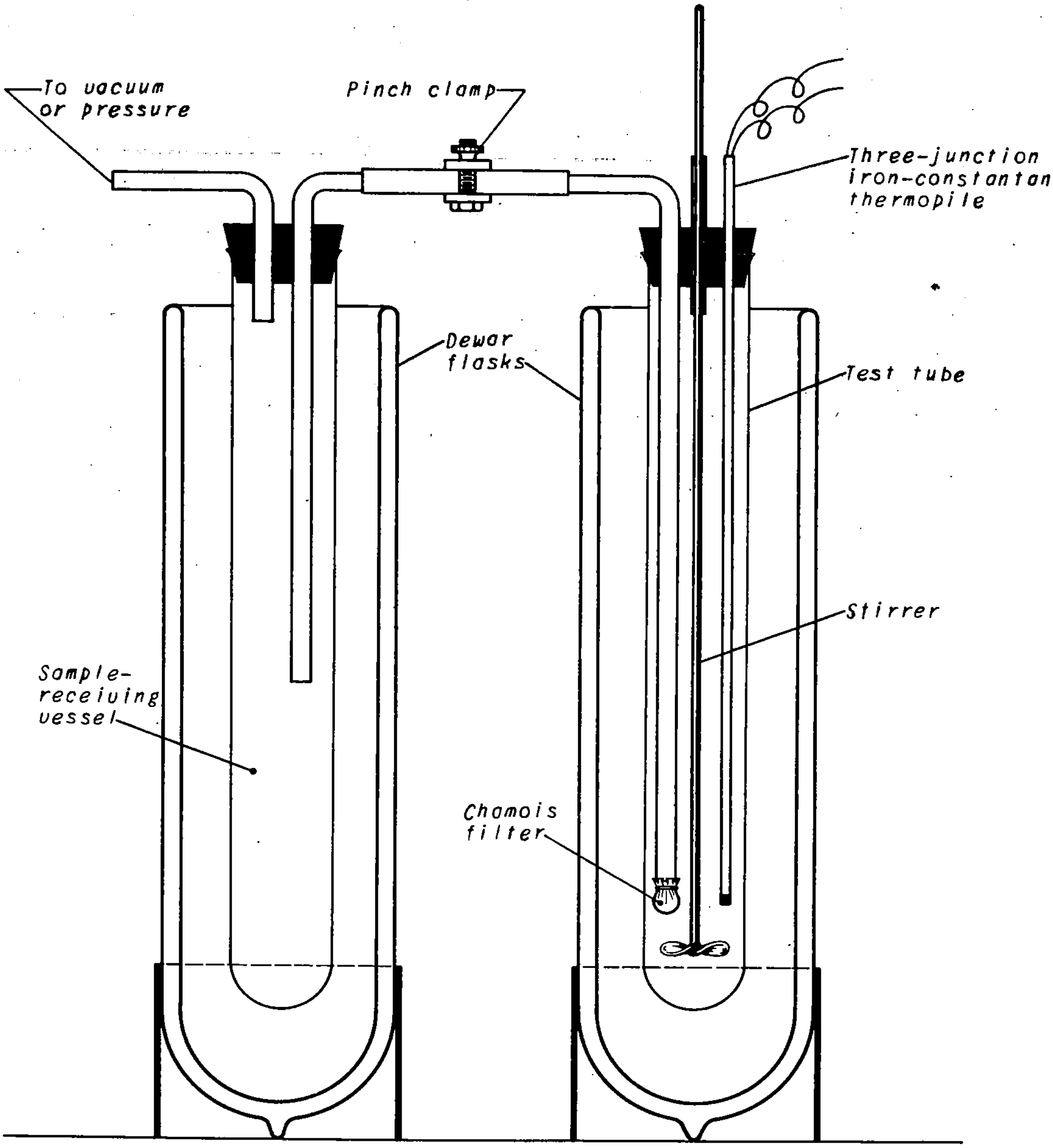

Figure 2. - Apparatus for obtaining saturated samples.

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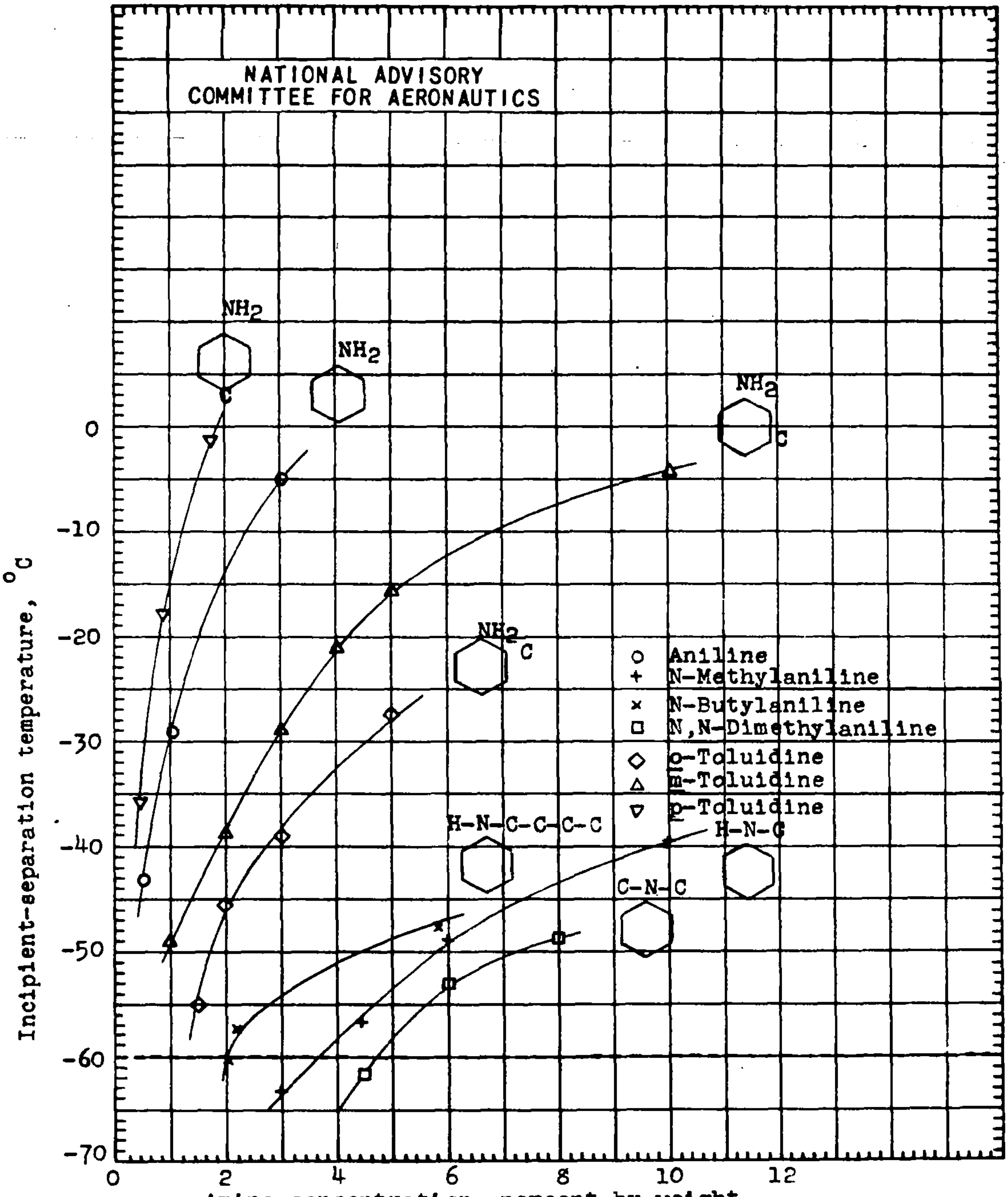

Figure 3. - Solubility of aromatic amines in grade 65 base stock with the aromatic hydrocarbons extracted.

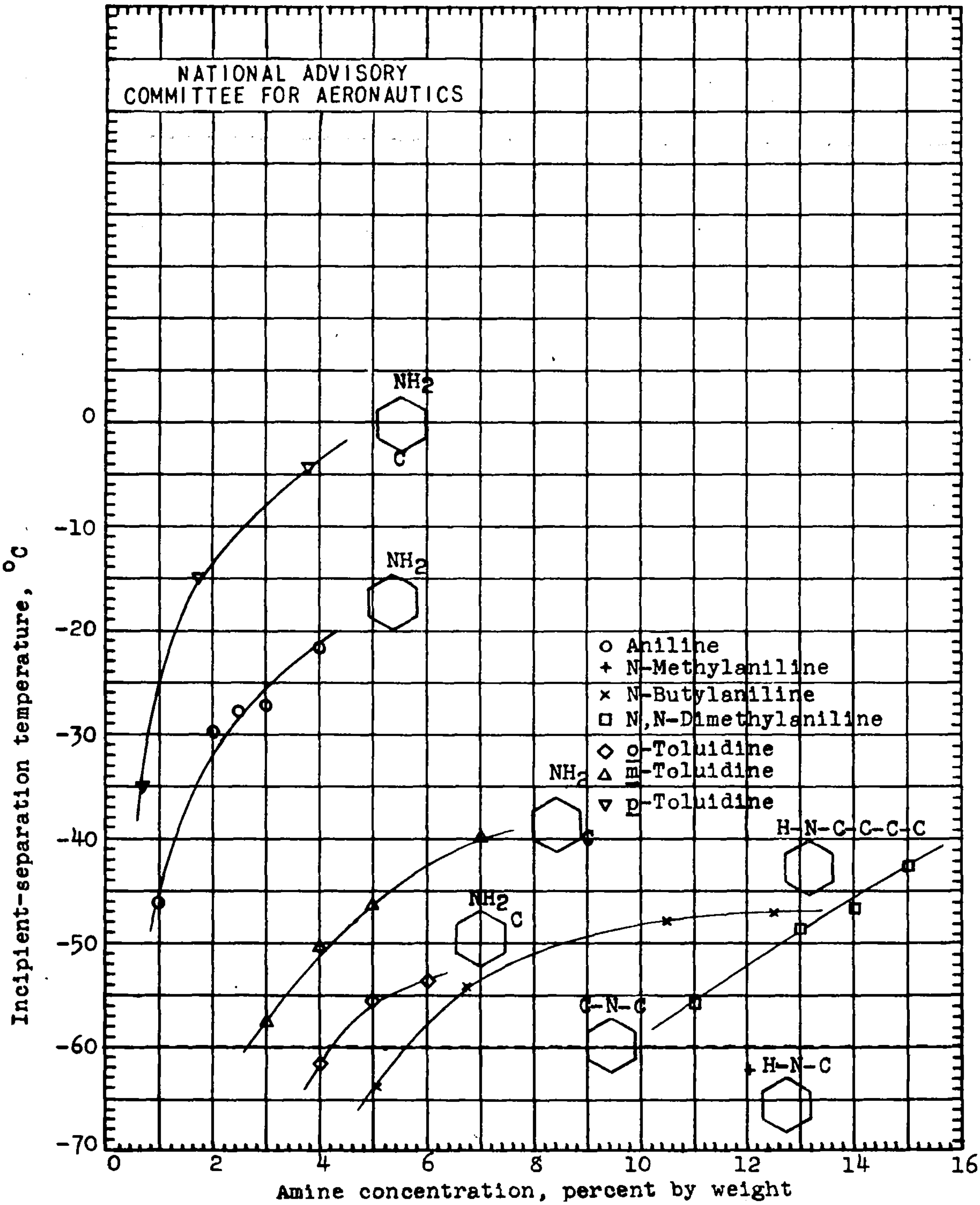

Figure 4. - Solubility of aromatic amines in a blend of 85 percent extracted grade 65 base stock and 15 percent by volume of an aromatic mixture consisting of 15 parts xylene, 2 parts cumene, and 1 part toluene.

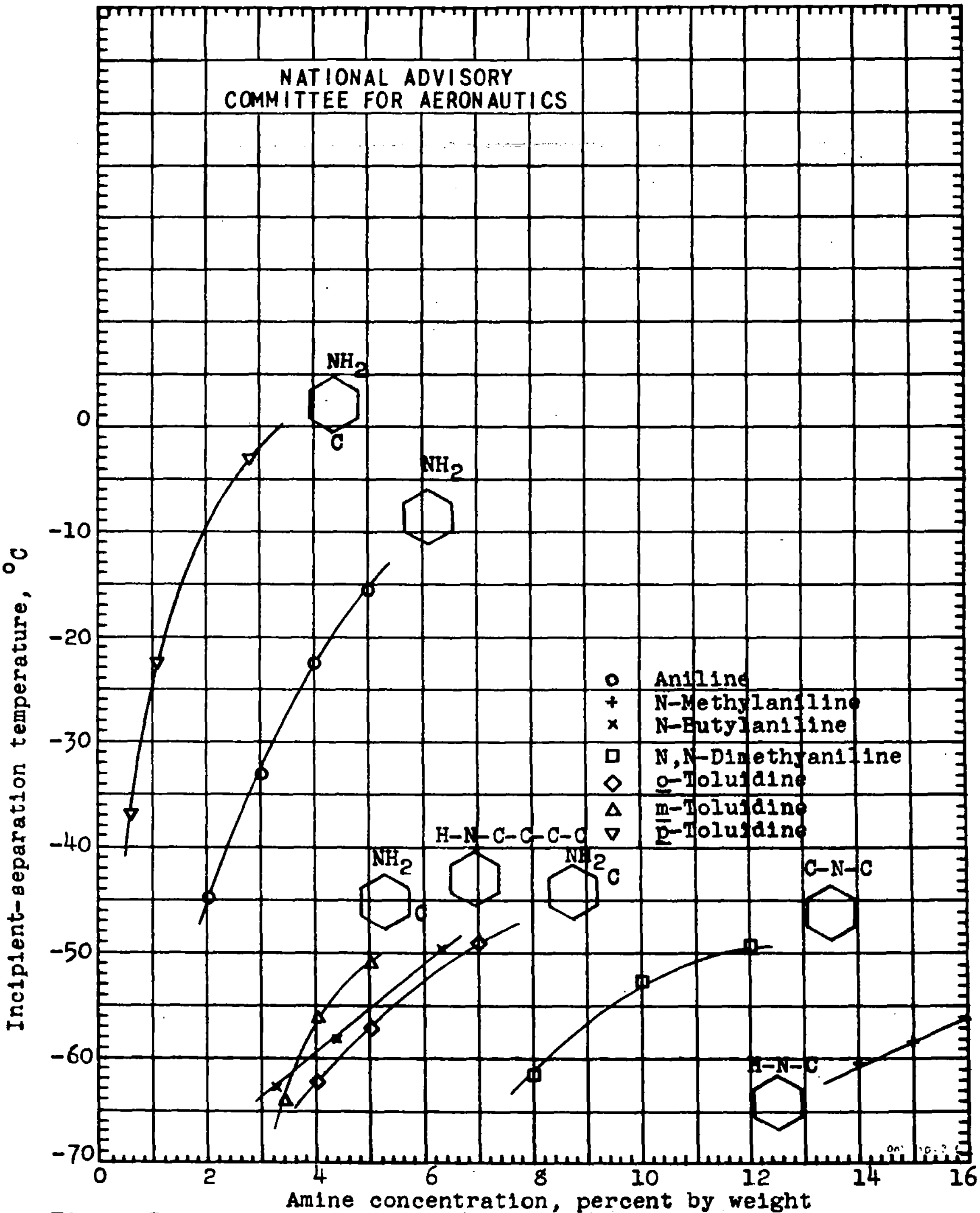

Figure 5. - Solubility of aromatic amines in grade 130 aviation gasoline.