Phase Diagram of the Solid-Liquid System 1-Methylnaphthalene--2-Methylnaphthalene

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PHASE DIAGRAM OF THE SOLID-LIQUID SYSTEM
1-METHYLNAPHTHALENE--2-METHYLNAPHTHALENE

by

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A thesis presented to the Department of Chemistry of Union College
in partial fulfillment of the requirements for the degree of Bachelor of
Science with a Major in Chemistry.

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 Approved by

May 1961
INTRODUCTION

The subject of this paper is the freezing point-composition diagram of the system 1-methylnaphthalene--2-methylnaphthalene. The reason for writing this paper was that it was felt the resulting phase diagram might be of use in the separation of mixtures of the two components, since they frequently occur together in petroleum, and the preparation of 2-methylnaphthalene by Friedel-Crafts alkylation also results in the formation of some 1-methylnaphthalene. Also, it was felt that it would be of interest to determine the phase diagram for a system of two compounds as similar as these.

HISTORICAL

The phase rule was first derived by Gibbs in 1875 as part of his famous paper, "On the Equilibrium of Heterogeneous Substances." However, it was not until 1887 that Rooseboom perceived the true importance of this generalization, and used it as the basis of classification of the cases of chemical equilibrium thus known. Since then, phase rule chemistry has become a very important branch of physical chemistry and is treated thoroughly in every elementary course in physical chemistry.

The only investigation of the system 1-methylnaphthalene--2-methylnaphthalene described in the literature is that of Morgan and Coulson (5). They found that the system forms a continuous series of solid solutions, with a minimum at -45-46°C. and 81% 2-methylnaphthalene.
A. Purification:

The first problem to be solved was that of the purification of the two components. The purification of the 2-methylnaphthalene was quite simple. Eastman Kodak No. 2416 2-methylnaphthalene was recrystallized from methanol to give a product melting in the range 55-56°C (8,9).

The purification of the 1-methylnaphthalene proved to be a much more difficult problem. The starting material used was Eastman Kodak No. P-2415 1-methylnaphthalene. When received, this was a clear yellow liquid which changed on standing to an opaque brown liquid. An attempt was made to determine the freezing-point of this material by plotting a cooling curve with a Beckmann freezing-point apparatus. When the thermometer became so frosted over that it was impossible to read it, the temperature was below -40°C and there was still some liquid present. Since the several values given in the literature for the freezing-point of pure 1-methylnaphthalene are all between -19°C and -30.8°C (10,9,8,1,2), it was decided that the material needed further purification.

An attempt at purification of this mixture by distillation through a six-foot column packed with iron helices gave a product which was still a clear yellow liquid freezing below -40°C. Since the main contaminant was believed to be 2-methylnaphthalene, a literature search was made in an effort to find methods of separating these two isomers. Some methods of purification considered were fractional freezing (rejected because, while the 2-isomer can be isolated by this method, the 1-isomer cannot) (4), recrystallization of the picrate complexes (rejected because this does not give good
separation) (5), recrystallization of urea or thiourea complexes (rejected because aromatic compounds will not complex with urea and thiourea) (7), and recrystallization of the sulfonic acids (9). This last was the method used. One hundred grams of the mixture were sulfonated with 200 grams of concentrated sulfuric acid at a temperature just below 40°C, 130 grams of water were added, and the mixture was allowed to cool. The mixture was then treated with 200 ml. 50% sulfuric acid to dissolve the more soluble 2-methylnaphthalene sulfonic acids, and the residual 1-methylnaphthalene sulfonic acids were desulfonated by steam distillation of a solution of them in 70% sulfuric acid held at 150°C in a paraffin bath. The product of this operation was a liquid which was much improved in appearance but which still melted below -40°C. At this point, due to lack of time, it was necessary to suspend efforts to purify the 1-methylnaphthalene and use the remaining time to obtain as good results as possible on the rather impure material already on hand. Since some quite pure 2-methylnaphthalene was already on hand, it was decided to begin plotting the diagram from the 2-methylnaphthalene end.

B. Theory and Procedure of the Determination of the Phase Diagram:

1. Theory.

The phase diagram of the system was determined by thermal analysis. The "thaw-point, melting point" method of Rheinboldt (15) and the bulb method of Collet and Johnston (3) were considered and rejected because it was felt that, for systems involving melting points below room temperature, these methods would present great experimental difficulties, due mainly to difficulty in controlling temperature and fogging over of thermometer scales. The microscopic method of Kofler (14), which would have given only qualitative
results anyway, was not attempted due to lack of equipment. Also, the low
temperature would probably have caused the microscope lenses to fog over.

The theory of thermal analysis (6,14) is as follows: When a pure
sample of material is heated or cooled in such a way that the temperature
of the surroundings changes at a constant rate, the temperature of the
sample will also change at a constant rate until the melting point of the
material is reached, at which point the temperature of the sample will
remain constant until the sample has stopped melting and become completely
liquid. At this point the temperature change of the sample will regain the
same rate as that of the surroundings. If, however, the sample is not pure,
but is a mixture of two or more components, the compositions of the two
phases will be constantly changing as the sample melts; and since each com-
position has its own melting point, the temperature of the sample will not
remain constant as the sample melts but will change slowly, at a slower rate
of change than the surroundings. For samples of mixtures, the changes in
slope at the beginning and end of the melting may be so gradual as to make
it impossible to determine the exact point at which the phase transition
begins and ends, but if there is a reasonably long straight portion during
the transition range, it is possible to extrapolate this portion and the
portions of the curve just adjacent to the transition. It can be shown
that the point of intersection of the two extrapolated straight lines gives
the exact location of the beginning or end of the phase transitions (13).
The above considerations apply both to heating and cooling curves, and to
all kinds of phase changes. The above method can also distinguish simple
eutectic systems from systems forming mixed crystals since, in the eutectic
system, the first liquid will appear on heating and the last liquid will
disappear on cooling at the same temperature (the eutectic temperature).
For a system forming solid solutions, however, the phase change will begin
or end at a different temperature for each composition.

2. Procedure.

The first apparatus considered for the time-temperature curves was
the Beckmann apparatus. However, this was rejected because, at tempera-
tures below room temperature, it can give rise to errors due to condensa-
tion of water vapor into the melt and solubility of air in the melt (14).
Therefore, the Beckmann apparatus was not used to determine the phase diagram
of this system.

The apparatus finally decided upon (Figure 1) was similar to that of
Skau and Saxon (12). A is the sample. B is a 4-inch test tube containing
the sample. C is a 6-inch test tube; D is a shield of Wood's metal prepared
by centering the 6-inch test tube in a 150-ml. electrolytic beaker, surround-
ing it with granulated Wood's metal and melting the Wood's metal, adding
enough additional Wood's metal to completely fill the electrolytic beaker
with Wood's metal. On cooling, the Wood's metal expanded, cracking the
beaker, which was then broken away completely. E is a three-foot-long heating
coil of No. 24 nichrome wire, which was used to obtain a uniform rate of
heating for the surroundings. Power for the heating coil was drawn from the
line through a constant-voltage transformer attached to a variac. F is two
layers of asbestos paper, one placed between the heating wire and the Wood's
metal to insulate the wire from the Wood's metal, and one wrapped around the
outside of the heating wire to keep the wire in place. G is a copper-
constantan thermocouple connected to a Weston recording potentiometer and
used to measure the temperature of the sample; H is another copper-constantan
thermocouple connected to a Varian Associates recording potentiometer used to record the temperature of the surroundings. The Weston recorder was calibrated at the freezing point of water (0°C), the boiling point of water (100°C), and the temperature of dry ice (-78.7°C). The Varian recorder was not calibrated at all, since its only function was to insure that the temperature of the surroundings (the Wood's metal shield) changed at a uniform rate. This apparatus had the advantage that, since the sample was enclosed, errors due to solubility of air in the melt and condensation of water vapor into the melt were avoided. These factors can cause considerable error (14).

Heating curves were used to determine the phase diagram. The reasons for this were: (1) When working below room temperature it seemed much neater and more convenient to control the rate of heating of a pre-cooled sample than to control the rate of cooling of a warm sample, and (2) Considerable extra effort and error due to super-cooling were avoided.

To determine the heating curves, the samples were first made up by weight into the test tube B. The ones that were not liquid at room temperature were warmed until they were liquid and then shaken to make them assume uniform composition. The test tube was then set in place in the Wood's metal jacket, which was then placed in a water-proof plastic bag and cooled to 0°C. The purpose of this was to obtain better results by causing equilibrium to be attained at 0°C, since, in a system which forms a continuous series of solid solutions, heating or cooling curves will produce exact results only when the sample is cooled slowly enough to be in equilibrium during the cooling. The metal jacket, asbestos paper and heating wire were then immersed in a beaker of acetone and dry ice was added to bring the
temperature down as far as possible. Before the temperature was down as far as it could go, the ends of the heating wire were connected to the power source, which was then turned on. The purpose of this was to eliminate any discontinuity in the heating curve of the sample due to turning on the heat source after the heating curve was started. When the sample was cool enough, the Wood's metal jacket was removed from the cooling bath, placed in the one-quart Dewar flask, and surrounded with expanded vermiculite insulation material. The sample was then allowed to heat up, recording the rate of heating of the sample and surroundings on the two recorders, and gradually increasing the current in the heating coil so as to attain a uniform rate of heating for the jacket. At the beginning of each experiment, the variac used to control the current in the heating coil was set at 40-50 volts, and at the end of each experiment it was up to 110 volts. By the use of this apparatus, heating rates of less than 1°C per minute were easily obtained.
### EXPERIMENTAL RESULTS

#### A. Data:

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>Error (+ or -)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. 2-methylnaphthalene (g.)</td>
<td>0.8916</td>
<td>0.8011</td>
<td>0.7101</td>
<td>0.0002</td>
</tr>
<tr>
<td>Wt. 1-methylnaphthalene (g.)</td>
<td>0.1121</td>
<td>0.2137</td>
<td>0.2948</td>
<td>0.0002</td>
</tr>
<tr>
<td>Mole %2-methylnaphthalene</td>
<td>38.81</td>
<td>78.95</td>
<td>70.71</td>
<td>0.9%</td>
</tr>
<tr>
<td>Mole %1-methylnaphthalene</td>
<td>11.19</td>
<td>21.07</td>
<td>29.29</td>
<td>0.9%</td>
</tr>
<tr>
<td>Liquidus (scale divisions)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trial 1</td>
<td>5.15</td>
<td>4.95</td>
<td>4.75</td>
<td>0.02</td>
</tr>
<tr>
<td>trial 2</td>
<td>5.23</td>
<td>4.90</td>
<td>4.75</td>
<td>0.02</td>
</tr>
<tr>
<td>Liquidus (degrees C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trial 1</td>
<td>28.6</td>
<td>23.5</td>
<td>18.7°C</td>
<td>1°C</td>
</tr>
<tr>
<td>trial 2</td>
<td>29.8</td>
<td>22.9°C</td>
<td>18.7°C</td>
<td>1°C</td>
</tr>
<tr>
<td>Solidus (scale divisions)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trial 1</td>
<td>4.70</td>
<td>4.51</td>
<td>4.20</td>
<td>0.02</td>
</tr>
<tr>
<td>trial 2</td>
<td>4.70</td>
<td>4.45</td>
<td>4.10</td>
<td>0.02</td>
</tr>
<tr>
<td>Solidus (degrees C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trial 1</td>
<td>18.7°C</td>
<td>13.0°C</td>
<td>5.1°C</td>
<td>2°C</td>
</tr>
<tr>
<td>trial 2</td>
<td>18.7°C</td>
<td>13.5°C</td>
<td>3.0°C</td>
<td>2°C</td>
</tr>
</tbody>
</table>
Calibration Curve

Temperature vs. Scale Deflection on Weston Recorder

FIGURE 2
Figure 3. Calibration points on the Weston recorder, and heating curves for the two trials on sample A.
Figure 4. Heating curves for the two trials on sample B.
Figure 5. Heating curves for the two trials on sample C.
E. Calculations:

1. A calibration curve of temperature versus scale deflection on
the Weston recorder was plotted, using average values of all trials for
the steam, ice and dry ice points (Figure 2).

2. At the liquidus and solidus regions of the recorded curves,
straight portions of the curve on either side of the curved portions were
extrapolated back. The point of intersection of the two extrapolated lines
was considered to be the liquidus or solidus, as the case may be.

3. The temperature in degrees centigrade of the point sought was
determined by interpolation on the calibration curve.

4. From the known weights of the components in the samples, the
percent compositions of the samples were calculated.

5. The phase diagram was plotted.

C. Discussion of Errors:

On each sample, two trials were run. The highest value obtained was
used for the temperature of the solidus point, since any error due to
failure to maintain equilibrium in cooling would tend to lower the value
obtained for the solidus point. For the liquidus point, the average value
of all trials was used.

The errors in mole percentages were calculated as follows:

\[
\Delta = \text{mole \% 2-methylnaphthalene} \left[ \frac{\Delta W_2}{W_2} + \frac{\Delta(W_2 + W_1)}{(W_2 + W_1)} \right]
\]

\[
= 88.81\% \left[ \frac{0.0002}{0.8916} + \frac{0.0004}{1.004} \right]
\]

\[
= 0.05\% \text{ (negligible, on the scale used for my graph)}
\]

The liquidus points were determined with a reproducibility of
1°C, the solidus points within about 2°C.
SUBJECT

From the results of this experiment, it can be seen that my results (Figure 6) do not agree exactly with those of Morgan and Coulson (5). This could be due to impurities in my impure 1-methyl-naphthalene, or it could be due to errors either in my method or in that used by Morgan and Coulson (5). If there are any errors in one of the methods, it would seem that they would be in that of Morgan and Coulson, since the points on their solidus are much more uneven than those on my solidus, and because their solidus is much lower than mine. Although their paper does not state the exact method used by them to determine the phase diagram, it seems probable that the method used was only approximate, since the phase diagram was not the primary objective of their paper. If they used the Beckmann apparatus or some similar method involving the use of heating or cooling curves, the solidus would probably be low - if the melt was not cooled slowly enough to be in complete equilibrium during the cooling.

It can be seen that there are breaks near -50°C in the heating curves of the samples containing 70 per cent 2-methylnaphthalene. Some of the other heating curves also show slight breaks in this region, as well as some of the cooling curves. This could be due to impurities in the sample forming a eutectic with one of the components. For example, it is known that naphthalene and 2-methylnaphthalene form a eutectic mixture (15), and if naphthalene were present as an impurity in the 1-methylnaphthalene used for this experiment, this could explain the breaks. It is impossible to check the temperature of this eutectic,
since the abstract in CHEMICAL ABSTRACTS does not give any temperature. Another possibility is some kind of solid phase transition in the sample, or perhaps the phase diagram of Morgan and Coulson is in error and the actual diagram includes a region in which the two components are immiscible in the solid state. This last possibility, however, does not seem very probable for this particular system.
Figure 6

Phase Diagram of the System
1-Methylnaphthalene-2-Methylnaphthalene

Data of this paper

oo Data of Morgan and Coulson

Temp. (Centigrade Degrees)
REFERENCES

(2) Ibid., Vol. 5, 2nd supp., p. 460.
(4) Coscia, Petroleum Z., 32, No. 17, 4-7 (1938).