Argonne National Laboratory

ENGINEERING PROPERTIES OF DIPHENYL

By

Kermit Anderson
FOREWORD

The main body of the physical data on pure diphenyl is the property of the Monsanto Chemical Company and has been published by them in various technical reports and sales literature.

Data on vapor pressure, enthalpy and densities of liquid diphenyl and its saturated vapor were made available by members of the Monsanto Chemical Company research staff at Anniston, Alabama. This was also the source of information on the viscosity of diphenyl as a function of temperature, the Mollier diagram and the temperature entropy diagram.

The data on the thermal conductivity of Dowtherm A was furnished by the Dow Chemical Company.

The phase-rule diagrams for diphenyl and the diphenyl benzenes and for mixtures of diphenyl and its pyrolysis products along with viscosities of three mixtures were determined at Argonne.
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ENGINEERING PROPERTIES OF DIPHENYL

by

Kermit Anderson

ABSTRACT

Data collected from the literature on the vapor pressure, enthalpy, liquid density, and vapor density of pure diphenyl are presented. A Mollier diagram, a temperature entropy diagram, and data on the viscosity of diphenyl as a function of temperature are also presented.

Data on the melting points of several binary systems containing diphenyl and for complex mixtures of diphenyl and its pyrolysis products are presented graphically. Graphs of viscosity versus composition at 130°C for the systems are also presented.

I. PHYSICAL PROPERTIES OF DIPHENYL

These data were obtained by the research staff of the Monsanto Chemical Company and of the Dow Chemical Company. No discussion of the methods used in obtaining the data presented herewith will be given. Original sources can be consulted for the methods used in obtaining the data.

1. Miscellaneous Physical Data on Diphenyl

Table I consists of a collection of miscellaneous data on diphenyl. Part of these items were furnished by the Dow Chemical Company of Midland, Michigan, the remainder being taken from standard chemical handbooks.

2. Thermodynamic Properties of Diphenyl

The thermal properties of diphenyl are quoted in Table II from data compiled by the technical staff of the Monsanto Chemical Company.¹

¹The following is quoted from the acknowledgement in the Monsanto Chemical Company’s technical files at Anniston, Alabama.

"In collecting this data several different sources have been consulted, and we wish especially to acknowledge the work done by the following:

Professor J. M. Cork and Mr. D. A. Wilbur of the University of
Table I

MISCELLANEOUS PROPERTIES OF DIPHENYL

| Property                                                | Value  
|----------------------------------------------------------|--------
| Molecular Weight, gms/gm mol                             | 154.2  
| Melting point, °C                                        | 69.4   
| Specific gravity at 75.4°C, gms/cc                       | 0.991  
| Lbs/gal at 75°C                                         | 8.27   
| Flash point (Cleveland Open Cup), °C                     | 106    
| Fire Point (Cleveland Open Cup), °C                      | 124    
| Specific heat at boiling point, Btu/(lb)(F)              | 0.60   
| Latent heat of vaporization at boiling point, Btu/lb     | 136.5  
| Heat of Fusion, Btu/lb                                   | 177.8  
| Solubility at 25°C, gms/100 gms solvent                  |        
| Acetone                                                  | 95     
| Benzene                                                  | 95     
| Carbon Tetrachloride                                     | 143    
| Ether                                                    | 63     
| N-Leptane                                                | 19     
| Methanol                                                 | 7      
| Water                                                    | 0.1    

Michigan for work done on vapor pressure, latent heat, and densities of both the vapor and liquid diphenyl.

Laboratory of Applied Chemistry, Massachusetts Institute of Technology, for work done on specific heat of the liquid which work was done by Messrs. L. W. Cummings, F. W. Stones, M. A. Volante, under the direction of Messrs. H. O. Forrest and Elmer W. Brugmann.

Mr. R. O. Fowler of the University of Michigan, for work on specific heat of the liquid at temperatures below the boiling point.

Messrs. John Chipman and S. R. Peltier, Georgia School of Technology, for their article appearing in Industrial and Engineering Chemistry, Volume 21, page 1106, (1929) relating to vapor pressures.

Dr. W. L. McCabe, University of Michigan, and associates for work done in collecting these data and preparing them for publication.

Professor W. L. Badger, Swenson Evaporator Company, for his cooperation in the preparation of these tables and for the timely and helpful suggestions which he has offered."
Table II

THERMAL PROPERTIES OF DIPHENYL

(Courtesy Monsanto Chemical Company)

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### Table II (Continued)

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3. **Mollier Diagram**

The Mollier Diagram of the diphenyl system is shown in Figure 1.

4. **Temperature-Entropy Diagram for Diphenyl**

The temperature-entropy diagram is shown in Figure 2. A temperature-entropy diagram for water is also included for comparison.

5. **Viscosity Data**

The viscosity of diphenyl as a function of temperature is shown in Table III. Data were obtained using Ostwald type viscometers by standard techniques.

<table>
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<th>Temp, F.</th>
<th>Viscosity, Centipoises</th>
<th>Temp, F.</th>
<th>Viscosity, Centipoises</th>
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6. **Thermal Conductivity**

Data on the thermal conductivity of diphenyl are not available. It is felt, however, that due to the high diphenyl content and basic similarity
of Dowtherm A to diphenyl, data for the thermal conductivity of Dowtherm A would lead to no serious errors. Figure 3 shows a plot of these data as well as data for Dowtherm E as a function of temperature.²

7. Coefficients of Heat Transfer

Data are lacking on this property. Figure 4 graphically presents the liquid film coefficient for Dowtherm A inside pipes. In this figure \( G' \) = mass velocity in \( \text{lb/(sec)(ft}^2) \), \( h \) = film coefficient of heat transfer in \( \text{Btu/(hr)(ft}^2)(\text{F}) \), and \( D' \) = inside diameter of pipe in in.²

II. DATA ON MIXTURES OF DIPHENYL WITH OTHER MATERIAL

Since chemical reactions of diphenyl occur under conditions which would be encountered in heat transfer systems, it is of interest to consider the results of mixing some of the more common reaction products of diphenyl with the pure material. In general, the more probable compounds would be the isomeric terphenyls and tetraphenyls, and several alkyl benzenes.

The most significant physical properties of such systems might be their melting points, vapor pressures, and viscosities. Thermal properties are also important, but these would probably not differ greatly from the same properties for diphenyl if variation in composition of the system is restricted to those ranges where melting points and viscosities are not too greatly changed.

No data are available on the physical properties of mixtures of diphenyl with the various pure alkyl benzenes which might be formed by ring scission in the diphenyl molecule. Neither are data available on the properties of the binary systems consisting of diphenyl and the isomeric tetraphenyls. Preliminary work at Argonne has yielded the data presented below on binary systems of diphenyl and the three isomeric terphenyls and on mixtures of diphenyl with still bottoms from the diphenyl purification stills at the Anniston, Alabama, plant of the Monsanto Chemical Company. The latter tar-like material is considered to be probably quite representative of the complex systems which might result from the pyrolysis or radiolysis of diphenyl.

Melting points of all of these mixtures were determined by conventional methods, mostly by observation of cooling curves run on large samples of originally molten material. Viscosities were determined at 130°C using Ostwald pipettes.

²“Dowtherm for Accurate High Temperature, Low Pressure Heat,” The Dow Chemical Company, Midland, Michigan
1. **Mixtures of Diphenyl with o-Diphenylbenzene**

   Figure 5 shows data on the melting points of the system diphenyl-o-diphenylbenzene. Viscosities for the same system determined at 130°C are plotted as functions of composition in Figure 6.

2. **Mixtures of Diphenyl with m-Diphenylbenzene**

   Data on melting points for this system are plotted in Figure 7, while the kinematic viscosities at 130°C are plotted against composition in Figure 8.

3. **Mixtures of Diphenyl with p-Diphenylbenzene**

   Data on melting points for this system are shown in Figure 9. Figure 10 gives data on kinematic viscosities for these mixtures only up to a composition of 20 per cent p-diphenylbenzene. The melting points for compositions much above this temperature were too high to be liquid at 130°C, and since this was a practical limit for both the equipment used and for some of the other systems studied it was concluded that comparable data for all systems would be preferable. These data indicate that systems containing p-diphenylbenzene might be expected to give deposits of solid material first when operated at lower temperatures.

   Plotted on the graph of Figure 9 are several points taken from data published in the literature. These were added in order to give a comparison with the Argonne data.

4. **Mixtures of Diphenyl with its Pyrolysis Products**

   The pyrolytic still bottoms mentioned above have the analysis shown in Table IV.

   Figure 11 shows melting points for this system, and Figure 12 gives the kinematic viscosity in centistokes for the system as a function of composition at 130°C.

---

"The Solubility of p-Terphenyl in o- and m-Terphenyls and in Diphenyl,"  
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<td>tetraphenyls and higher</td>
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FIG. 2
TEMPERATURE
ENTROPY DIAGRAM
FIG. 3
CALCULATED THERMAL CONDUCTIVITY OF DOWTHERM A
$D^t = \text{Diameter - in.}$

$G^t = \text{Mass Velocity - lb/(sec)(ft}^2\text{)}$

$h = \text{Film Coefficient = Btu/(hr)(ft}^2\text{)(F)}$

**FIG. 4**

**LIQUID FILM COEFFICIENT FOR DOWTHERM INSIDE PIPES**

*COURTESY DOW CHEMICAL CO.*
FIG. 5
MELTING POINTS
FOR THE SYSTEM
DIPHENYL --- O-DIPHENYL BENZENE
FIG. 6
KINEMATIC VISCOSITY OF MIXTURES OF DIPHENYL WITH O-DIPHENYLBENZENE AT 130°C
FIG. 7
MELTING POINTS
FOR THE SYSTEM
DIPHENYL --- M-DIPHENYLBENZENE
FIG. 8
KINEMATIC VISCOSITY OF MIXTURES OF DIPHENYL WITH M-DIPHENYL BENZENE AT 130 °C
FIG. 9
MELTING POINTS FOR THE SYSTEM DIPHENYL --- p-DIPHENYLBENZENE
FIG. 10
KINEMATIC VISCOSITY OF MIXTURES OF DIPHENYL WITH p-DIPHENYLBENZENE AT 130 C
FIG. 11
MELTING POINTS FOR THE SYSTEM DIPHENYL-TAR
FIG. 12
KINEMATIC VISCOSITY OF MIXTURES OF DIPHENYL WITH PYROLYTIC TARS AT 130 C