Densities and Viscosities of 2-Bromobiphenyl and 2-Iodobiphenyl

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Densities and viscosities of liquid 2-bromobiphenyl and 2-iodobiphenyl have been measured over the temperature range 253.15–333.15 K. A quadratic formula is reported which reproduces the density data to 0.02%. The viscosity data are fitted to an equation of the form log $\eta = A/(T - T_0) + B$ with an error of 0.5%.

Introduction

During a recent study of dielectric properties of polar liquids, it became necessary to know the densities and viscosities of several semirigid polar molecules as a function of temperature. Among those selected whose properties were not well documented in the literature were 2-bromobiphenyl and 2-iodobiphenyl. In this paper, the densities and the viscosities of these liquids are reported over the temperature range 253–333 K. Equations relating viscosity and density with temperature are reported.

Experimental Section

The 2-iodobiphenyl was purchased from K & K Laboratories and vacuum distilled at 8 torr. Purity was determined with a Beckman GC5 gas chromatograph using matched columns of SE 30 on Chromosorb G and a thermal conductivity detector. Estimated purity was 99+%.

The 2-bromobiphenyl was synthesized by a Meerwein reaction using a method similar to that published by Kochi (*1*). Practical-grade 3-aminobiphenyl (Eastman Kodak) was recrystallized from 60–110 °C petroleum ether. Acetone (750 mL) and concentrated hydrogen bromide solution (200 mL) were added to the aminobiphenyl (100 g) and chilled to 8–10 °C. While the solution was stirred, 8 M sodium nitrite (160 mL) and cuprous bromide (0.5 g) were added, and the reaction was allowed to continue overnight. The acetone was then boiled off and the organic layer was washed with dilute sodium hydroxide solution and water. The product was vacuum distilled twice at 8 torr, boiling range 131–135 °C. Purity was determined as above and found to be greater than 99%.

Densities were determined with a Sprengel-Ostwald pycnometer (10 mL), calibrated with deionized water and methanol over a temperature range of −45 to 60 °C (228–338 K). Densities are reported relative to the density of water at 4 °C. Precision of results was within 0.02%.

Kinematic viscosities were determined with capillary viscometers of the Ubbelohde type (Cannon Instrument Co.), sizes 1, 1C, 2, 3, and 4. Calibration constants were supplied by the manufacturer. A minimum of five measurements at each temperature achieved a precision of 0.03–0.2%. Efflux times always exceeded 200 s; thus, any corrections due to kinetic energy were unnecessary.

Temperature control was maintained with a Lauda Ultrakryomat to about ±0.05 °C, and the temperature measured with several precision thermometers calibrated against NBS reference liquids to at least 0.1 °C. The experimental density and kinematic viscosity values are reported for 2-bromobiphenyl and 2-iodobiphenyl in Tables I and II, respectively. Included are the few literature values available for comparison.

Table I. Density and Kinematic Viscosity of 2-Bromobiphenyl

temp, K	density, g/cm³	kinematic viscosity, cSt
333.15 ± 0.05	1.3561 ± 0.0002	2.615 ± 0.002
323.15	1.3667	3.338 ± 0.002
313.15	1.3771	4.471 ± 0.002
303.15	1.3875	6.354 ± 0.013
293.15	1.3973	9.836 ± 0.003
282.95	1.4081	16.87 ± 0.01
273.15	1.4192	35.30 ± 0.01
268.15	1.4250	55.75 ± 0.02
263.15	1.4310	99.31 ± 0.09
256.95	1.4381	224.0 ± 0.2
253.15	1.4428	462.4 ± 0.6
293.15	1.3522 (*2*)	
293.15	1.2175 (*3*)	

Table II. Density and Kinematic Viscosity of 2-Iodobiphenyl

temp, K	density, g/cm³	kinematic viscosity, cSt
333.15 ± 0.05	1.5658 ± 0.0002	3.282 ± 0.004
323.15	1.5770	4.402 ± 0.009
313.15	1.5882	6.270 ± 0.002
303.15	1.6004	9.733 ± 0.009
298.15	1.6064	12.715 ± 0.003
293.15	1.6125	17.40 ± 0.02
283.15	1.6245	36.18 ± 0.04
273.15	1.6373	103.60 ± 0.03
263.15	1.6466	495.6 ± 0.3
253.15	1.6640	5179 ± 5
293.15	1.5511 (*2*)	
293.15	1.6038 (*4*)	

Table III. Refractive Index Data (n^{25}_D) Data

2-bromobiphenyl	2-iodobiphenyl
1.626	1.6588
1.62616 (*5*)	1.65878 (*5*)
1.6248 (*2*)	1.6548 (*2*)

Results and Discussion

Literature values are not many and do not agree well with each other or with our data. There is somewhat better agreement among the refractive index data presented in Table III.

Using a standard least-squares technique, we fitted the density (ρ) data with the aid of an IBM-1620 computer to a quadratic equation of the following form:

$$\rho = AT^2 + BT + C \quad (1)$$

The values for A, B, C are given in Table IV, and the equations reproduce the experimental data to within 0.02%. The kinematic viscosities (μ) were converted to "absolute" viscosity coefficients (η) by multiplying each by its corresponding density:

$$\eta = \mu\rho \quad (2)$$

A modified least-squares program was used to fit the resulting viscosity data to the Williams–Landel–Ferry–Doolittle (WLFD) equation (*9*):

$$\log \eta = a/(T - T_0) + b \quad (3)$$

The values for a, b, and T_0 are given in Table IV, and the

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Table IV. Coefficients for Eq 1 and 3

	eq 1			eq 3		
	10^6A	10^3B	C	a	b	T_0
2-bromobiphenyl	1.258 85	−1.811 45	1.820 39	140.7	−0.604	212
2-iodobiphenyl	1.263 61	−1.947 11	2.074 32	151.9	−0.631	220

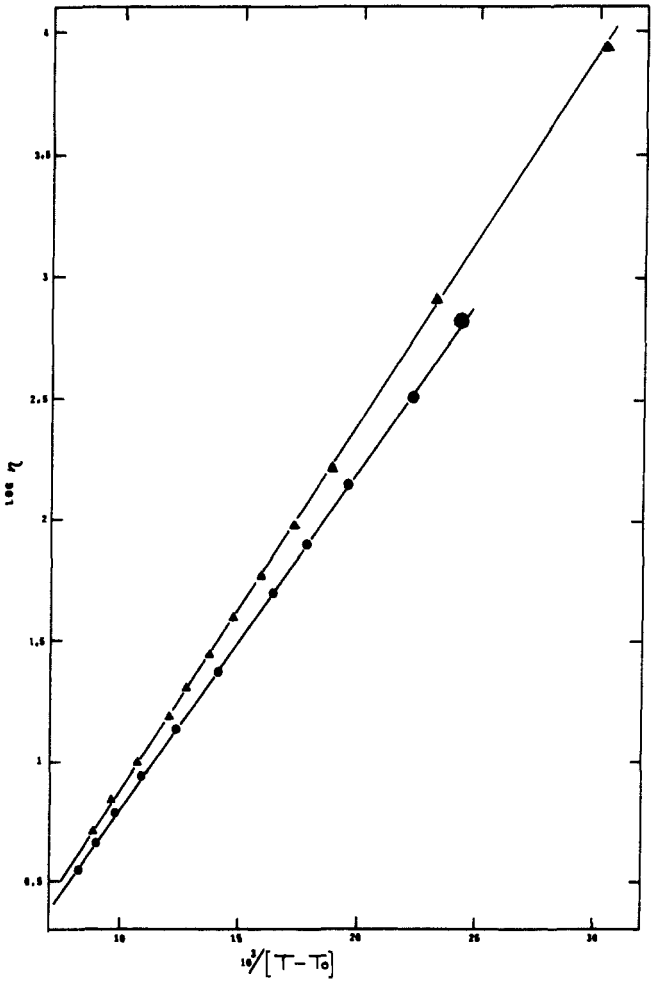

Figure 1. Logarithm of the viscosity of 2-iodobiphenyl (▲) and 2-bromobiphenyl (●) plotted as a function of $(T - T_0)^{-1}$. Values for T_0, obtained by least-squares analysis, are listed in Table IV.

equations reproduce the experimental viscosities (in units of centipoises) to within 0.5%.

It is clear from Figure 1 that the viscosity data are linear for this function over a wide temperature range. In contrast, attempts to fit the viscosity of these liquids as well as chlorinated biphenyls (*7*) to functions such as the Arrhenius equation

$$\eta = A \exp(B/T) \quad (4)$$

$$\log (\log \eta) = K + C/T \quad (5)$$

have not met with much success.

Brunet and Marrony (*7*) attempted to explain this apparently anomalous behavior by invoking molecular association. But molecular association in the sense of specific dipole–dipole interactions or dimer formation seems unlikely. Both of these liquids readily supercool, which is consistent with their asymmetric nonplanar geometry (*8*). The non-Arrhenius behavior, characterized by a dramatic increase in viscosity at lower temperatures, may suggest the onset of a glassy state. If so, then eq 3 not only is an excellent fit of the data but may provide a model for low-temperature behavior as well. The fundamental parameter, T_0, is defined as the temperature below which the viscosity becomes essentially infinite, and, with the WLFD theory, defines the temperatures below which free volume is no longer available for viscous flow.

Glossary

A, B	coefficients in eq 1 and 4
a, b	coefficients in eq 3
C	coefficient in eq 1 and 5
K	constant in eq 5
n	refractive index
T	temperature
cP	centipoise
cSt	centistoke
T_0	temperature parameter in eq 3

Greek Symbols

η	viscosity in cP
μ	kinematic viscosity in cSt
ρ	density in g/cm^3

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